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EPA

Evaluation of Lead Service Line Lining and Coating Technologies

Project #4351

Evaluation of Lead Service Line Lining and Coating Technologies

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WRF's mission is to advance the science of water to improve the quality of life. To achieve this mission, WRF sponsors studies on all aspects of drinking water, including resources, treatment, and distribution. Nearly 1,000 water utilities, consulting firms, and manufacturers in North America and abroad contribute subscription payments to support WRF's work. Additional funding comes from collaborative partnerships with other national and international organizations and the U.S. federal government, allowing for resources to be leveraged, expertise to be shared, and broad-based knowledge to be developed and disseminated.

From its headquarters in Denver, Colorado, WRF's staff directs and supports the efforts of more than 800 volunteers who serve on the board of trustees and various committees. These volunteers represent many facets of the water industry, and contribute their expertise to select and monitor research studies that benefit the entire drinking water community.

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Evaluation of Lead Service Line Lining and Coating Technologies

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FOREWORD

The Water Research Foundation (WRF) is a nonprofit corporation dedicated to the development and implementation of scientifically sound research designed to help drinking water utilities respond to regulatory requirements and address high-priority concerns. WRF’s research agenda is developed through a process of consultation with WRF subscribers and other drinking water professionals. WRF’s Board of Directors and other professional volunteers help prioritize and select research projects for funding based upon current and future industry needs, applicability, and past work. WRF sponsors research projects through the Focus Area, Emerging Opportunities, and Tailored Collaboration programs, as well as various joint research efforts with organizations such as the U.S. Environmental Protection Agency and the U.S. Bureau of Reclamation.

This publication is a result of a research project fully funded or funded in part by WRF subscribers. WRF’s subscription program provides a cost-effective and collaborative method for funding research in the public interest. The research investment that underpins this report will intrinsically increase in value as the findings are applied in communities throughout the world. WRF research projects are managed closely from their inception to the final report by the staff and a large cadre of volunteers who willingly contribute their time and expertise. WRF provides planning, management, and technical oversight and awards contracts to other institutions such as water utilities, universities, and engineering firms to conduct the research.

A broad spectrum of water supply issues is addressed by WRF's research agenda, including resources, treatment and operations, distribution and storage, water quality and analysis, toxicology, economics, and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide a reliable supply of safe and affordable drinking water to consumers. The true benefits of WRF’s research are realized when the results are implemented at the utility level. WRF's staff and Board of Directors are pleased to offer this publication as a contribution toward that end.

Charles M. Murray
Chair, Board of Directors
Water Research Foundation

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Chief Executive Officer
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The investigators' affiliations on the title page were those in effect for the first years of the project. At the present time, Craig D. Adams is Oliver Parks Chair and Professor, Department of Civil Engineering, Saint Louis University (St. Louis, MO); J. Alan Roberson is Executive Director

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EXECUTIVE SUMMARY

OBJECTIVES

The primary objectives of this research project were: (1) to evaluate lead service line (LSL) lining and coating technologies as alternatives to full or partial LSL replacement, and as a means of protecting and repairing copper service lines (CSLs); and (2) to provide information and recommendations to water utilities, engineering consultants, consumers, property owners, state and provincial regulators, and other stakeholders to assist them in making informed decisions regarding lining and coating of both lead and copper service lines. To accomplish these primary objectives, the investigators sought, as a secondary objective, to obtain and evaluate information on many different aspects of linings and coatings, including the following:

- Effectiveness in preventing lead release from LSLs and reducing tap-water lead levels
- Advantages and disadvantages for full versus partial LSL replacement
- Commercial availability, suitability for use in small-diameter pipes, and utilization of materials certified for use in contact with potable water
- Potential, upon installation and after aging, to leach organic and inorganic chemicals of concern with respect to water quality
- Long-term effectiveness and durability
- Ability to control internal water-service-line corrosion, prevent metal release from both service lines and the scales inside them, and repair service-line leaks
- Costs to both utilities and property owners, especially relative to the cost of LSL replacement
- Engineering feasibility, commercial availability, certification, and property access issues

BACKGROUND

Water service lines are the pipes extending from water mains to residential dwellings or commercial buildings. Generally, the portion of pipe from the water main to the property line is the responsibility of the public water system, while the section of pipe from the property line to the building is generally the responsibility of the property owner. However, there are exceptions. For example, customers served by Denver Water own the entire service line, and the Lansing (MI) Board of Water and Light owns their service lines from the main to the water meter inside the house. Water service lines made from lead or copper are referred to as lead service lines (LSLs) and copper service lines (CSLs), respectively; and, as they corrode, they can release lead or copper into the water supply, potentially in excess of allowable concentrations.

In the United States, the Lead and Copper Rule (LCR), promulgated by EPA under the Safe Drinking Water Act (SDWA), established an action limit (AL) of 15 µg/L for lead and an AL of 1.3 mg/L for copper. These ALs are based on the 90th percentile of first-draw tap-water samples collected, after a stagnation period of at least 6 hours, from homes with higher risk of lead exposure due to the presence of an LSL or relatively new lead solder. Public water systems exceeding the AL must take corrective action, which may include corrosion control treatment, public education, and/or lead service line replacement (LSLR). The maximum acceptable concentration (MAC) of lead in drinking water under Canadian guidelines is currently 10 µg/L, which is intended to apply to the average concentration in distributed water, typically based on samples collected after the faucet is flushed and prior to the water being taken for analysis or consumption. However, a new guideline of 5 µg/L has been proposed that would include sampling the water using a random daytime or a 30-minute stagnation sampling approach.

Older cities in some regions of the United States and Canada still have many LSLs in place. Cornwell et al. (2016) estimate there were 10.2 million LSLs in service when the LCR was promulgated in 1991, with approximately 6.1 million remaining in service and about 30% of community water systems having at least some LSLs in their system. The LCR does not require public water systems in the United States to replace the customer-owned portion of an LSL, and many public water systems are prohibited from performing work on private property at city or utility expense. Many utilities performing LSLRs, whether on a mandatory or voluntary basis, offer property owners an opportunity to sign an agreement to pay to replace their portion of the LSL at the same time, which reduces the cost. However, most property owners choose not to replace their LSLs, so the overwhelming majority of LSLRs in most cities to date has been partial LSLRs.

In recent years, it became increasingly clear that LSLs can contribute significantly to tap-water lead levels, that partial LSLRs can temporarily increase tap-water lead levels, and that lead may pose greater health risks than previously believed. For these and other reasons, a recent report by the LCR Working Group of the National Drinking Water Advisory Committee (NDWAC) in the United States recommended full replacement of LSLs, to the building wall, over a 30-year front-loaded timeframe (EPA 2015a and 2015b). This group also concluded that "[minimizing] exposure to lead in drinking water is a shared responsibility; public water systems, consumers, building owners, public health officials and others each have important roles to play."

The NDWAC report did not address linings and coatings, nor is it clear whether they will be addressed in future LCR revisions or, if they are addressed, what the relevant provisions will be. However, developing an LSLR program that ultimately replaces all LSLs all the way to the building wall, which necessarily includes LSLs on private property, will pose challenges for every public water system in the United States that has LSLs in its service area. This project provides information and recommendations intended to help all stakeholders evaluate the advantages and disadvantages of lining and coating technologies and to determine if such technologies would be helpful in planning or revising an LSLR program to meet the challenges facing their communities.

APPROACH

To accomplish the project objectives stated above, the investigators:

- Gathered, reviewed, and critically evaluated published and unpublished articles and reports regarding lining and coating of water service lines and the technologies and materials used
- Sought and obtained information from water utility personnel (e.g., utility and distribution system superintendents); consulting engineers; technical experts having specialized knowledge in relevant subdisciplines; state regulatory agencies and regulatory agencies outside the United States; NSF International (NSF) and other organizations involved in product certification; and manufacturers of lining and coating technologies and their representatives

- Identified issues stakeholders should consider before lining or coating LSLs, and developed a list of criteria for evaluating lining and coating technologies
- Identified lining and coating technologies potentially suitable for controlling lead release from LSLs and evaluated them with respect to their availability, effectiveness, cost, ease of installation, suitability for use in contact with potable water, estimated and warranted service life, potential impacts on water quality, and other advantages and disadvantages
- Identified three promising technologies and conducted laboratory studies on two of them – epoxy coating and polyethylene terephthalate (PET) lining – focusing primarily on their effectiveness in controlling lead and copper release and their potential to leach chemical constituents that might be of concern with respect to health or water quality (the third technology is relatively new and samples of the material used could not be obtained.)
- Based on the results of the above efforts, developed general recommendations for all stakeholders, and more specific recommendations for water utilities and their consultants, consumers and property owners, state and provincial regulators, and manufacturers and contractors.

RESULTS AND CONCLUSIONS

Three currently available lining or coating technologies can effectively reduce or eliminate release of lead from LSLs, are expected to have a long service life, and can potentially result in significant cost savings and other benefits relative to LSL replacement, depending on site-specific conditions. Other possible benefits include fewer and shorter disruptions of vehicular and pedestrian traffic; reduced damage to landscaping, trees, sidewalks, and driveways; less potential for damage to other utility lines (gas, electric, phone, cable, sewers); and facilitating delay of LSL replacements until they can be more efficiently and more cost-effectively performed in concert with future main rehabilitation or replacement projects. Thus, lining and coating technologies are potentially useful tools for reducing public exposure to lead in drinking water. Public water systems and property owners should be encouraged to evaluate their use, to the extent permitted by applicable regulations, in situations where significant cost savings and/or other benefits can be realized; and, where applicable, to incorporate their use into well organized, system-wide LSLR programs to help minimize costs and maximize benefits.

Three technologies are deemed to be especially promising and are therefore recommended for consideration by both public water systems and property owners: PET lining, epoxy coating, and polyurea/polyurethane coating. Each can effectively reduce or eliminate lead release, is commercially available, and is, or has been, certified for use in contact with potable water in the United States, Canada, and/or the UK. Each of these technologies involves materials that could potentially affect water quality by leaching certain constituents into the water; but that is true of every material that is used, or could conceivably be used, in water service lines. This issue has been effectively addressed for many years by requiring any material that may come into contact with potable water in a public water system to be certified as meeting NSF/ANSI Standard 61 (NSF 2016a).

Laboratory Experiments on Epoxy-Coated LSL and CSL Sections

The effectiveness of an epoxy coating in limiting lead release from LSLs was demonstrated in fill-and-dump experiments on 4-foor (ft.) lengths of LSLs. Lead in samples from a heavily disturbed, uncoated control LSL section ranged from 1,200 to 25,000 µg/L, whereas lead was non-detectable (≤0.5 µg/L) in 16 of 27 samples drawn from the epoxy-coated LSL sections. Only one sample (from the first extraction of one pipe section) had a lead concentration exceeding the AL, and when the same pipe section was extracted twice more, neither sample contained a detectable amount of lead. Epoxy coating also effectively limited release of copper from epoxy-coated CSL sections.

Freshly applied epoxy coatings exposed to chlorinated extraction water exerted a strong demand for free chlorine, with most of the chlorine being consumed in 6 hours (h). Similar results were observed for combined chlorine, for pipe sections stored wet or dry for 7 months, and for pipe sections repeatedly exposed to high concentrations of free chlorine. A significant chlorine demand associated with a lining or coating could potentially influence biofilm growth, disinfection byproduct formation, or other water quality parameters in a service line or downstream interior plumbing. The chlorine demand of the uncoated control pipe sections in the initial fill-and-dump experiments was similar to that observed in the epoxy-coated pipe sections, suggesting that, at least in some cases, the chlorine demand associated with an epoxy coating may have little or no net impact on water quality.

Freshly applied epoxy coatings leached an average of 0.58 mg/L of total organic carbon (TOC) into two extraction waters prepared using reagent water, but there was no significant change in average TOC concentration in dechlorinated pH 8 tap water. TOC leaching from epoxy coatings into water is expected to decrease to negligible levels over time.

Low concentrations of bisphenol A diglycidyl ether (BADGE) and two BADGE hydrolysis products were found to leach from freshly applied coatings of a BADGE-based epoxy. Two epoxy-coated pipe sections were stored wet for 7 months, with the water replaced with fresh reagent water every 7 days. When these pipe sections were again extracted, BADGE and one hydrolysis product were not detected in any of the samples, and the second BADGE hydrolysis product was detected in only a single sample, at a concentration slightly above the detection limit.

Leaching of BADGE is already addressed in NSF/ANSI Standard 61 (NSF 2016a), but additional experiments were conducted to examine: (1) how fast BADGE and bisphenol-F diglycidyl ether (BFDGE, another common epoxy ingredient) were hydrolyzing, which would affect human exposure to these compounds and their hydrolysis products; (2) whether these compounds were reacting with free or combined chlorine to form byproducts; and (3) whether bisphenol A (BPA) was hydrolyzing or reacting with chlorine and therefore going undetected.

BADGE hydrolysis was studied as a function of pH (2–12) and temperature (15–40 °C). BADGE hydrolyzed to BADGE-H_2O and then to BADGE-$2H_2O$, the major end product under these conditions. Experimentally measured BADGE hydrolysis rates agreed well with modeled rates; thus, the model can be used to estimate BADGE concentrations remaining in water over time, facilitating exposure assessments. The half-lives of BADGE at pH 7 and 15, 25, 35, and 40 °C were found to be 11, 4.6, 2.0, and 1.4 days, respectively. At 25 °C and pH 2–12, BFDGE hydrolyzed at a rate very similar to that of BADGE, with a half-life of 5 days at pH 7 and 25 °C. No hydrolysis or decay of BPA was observed for reaction times up to 30 days for pH values of 2–12 at 25–40 °C.

Chlorination of bisphenols and BADGE was investigated using free chlorine and combined chlorine. BADGE was unreactive with free or combined chlorine at pH values of 7.6–9.0 at 25 °C, but the bisphenols reacted relatively rapidly with free chlorine at pH values of 3–12 at 10–25 °C. Estimated BPA half-lives for a free chlorine residual of 1 mg/L as Cl_2 ranged from 3–35 minutes at pH values of 6–11 over the temperature range of 10–25 °C, but half-lives of 1–10 days were estimated for a monochloramine residual of 3.5 mg/L as Cl_2 under similar conditions. These results, and a model based on them, can be used to characterize the concentrations of bisphenols and BADGE in drinking water distribution systems after leaching from epoxy coatings, thereby facilitating future risk assessments.

Laboratory Experiments on PET-Lined LSL and CSL Sections

In fill-and-dump experiments on PET-lined LSL and CSL pipe sections, very high lead and copper concentrations were found in samples drawn from the unlined (control) sections; lead increased by 1,400–21,000 µg/L, and copper by 310–910 µg/L, respectively. Only trace amounts of lead were found in the samples from PET-lined pipe sections. In one experiment, the average lead concentration in samples from PET-lined LSLs was 1.2 µg/L, and the average in samples from PET-lined CSLs was 1.3 µg/L. In a second experiment, the average lead concentration found in samples from PET-lined LSLs was 1.9 µg/L, and the average in samples from PET-lined CSLs was 1.0 µg/L. The lead levels found in both experiments were only slightly above the method detection limit (0.5 µg/L) and about an order of magnitude lower than the AL for Pb (15 µg/L). The investigators believe the traces of lead found in these samples came from the fittings used on the ends of the pipe sections (any effects of which would have been accentuated on relatively short LSL sections) and from inadvertent contamination during sample collection and handling, and not from lead permeating through the PET lining, which would not be expected to occur.

Samples from one experiment on PET-lined pipe sections were also analyzed for antimony (Sb), a common PET ingredient. Sb was detected in all but two samples, but the concentrations were very low. The average increase in Sb using dechlorinated pH 8 tap water as the extraction water was only 0.09 µg/L; the increases using chlorinated pH 8 and low pH (6.5) extraction waters were 0.09 and 0.29 µg/L, respectively; and the median increase for both LSLs and CSLs was 0.13 µg/L. The antimony concentrations in all of the samples were not only well below the MCL (6 µg/L) but also below the concentrations found in samples from the unlined LSL control section (0.42–3.94 µg/L). Thus, PET liners can actually reduce exposure to Sb if there is Sb present in the pipe being lined, as was the case in this study. PET liners and epoxy coatings can also serve as effective barriers against numerous other traces constituents found in pipe deposits.

There was no significant increase in TOC associated with the PET liners. None of the 10 phthalate esters determined using GC-MS, and none of the 3 phthalic acids determined using LC-MS/MS, were detected in any of the extraction water samples, nor were these compounds detected in solvent extracts of an unexpanded section of PET liner. The PET liners exhibited very little chlorine demand in the first set of fill-and-dump tests; only about half of the initial free chlorine residual of 2 mg/L as Cl_2 was consumed after 96 hours. In subsequent tests, the chlorine demand dropped to less than 0.1 mg/L in 24 hours.

Experiences in the United States, Canada, and Elsewhere

When evaluating new technologies, or when developing or revising a program to address a complex and important challenge, it is often helpful to consider the experiences of others – what they have tried, what worked well and what did not, what could be done differently or better in the future, and what aspects or program elements are most applicable to the local situation being addressed. For this reason, brief case studies were prepared to describe the challenges faced by eight utilities in the United States and Canada in dealing with their LSLs, and to describe practices and experiences in other countries in lining, coating, and replacing lead and copper water service lines.

Over the past two decades there have been demonstration trials of PET lining and epoxy coating installations in LSLs in a number of locations in the United States, Canada, and elsewhere around the globe. More recently, a new polyurea/polyurethane coating designed for use in LSLs has been successfully demonstrated and approved for use in the UK. In the United States and Canada, few lining or coating installations in LSLs have been left in place, since most were done solely for demonstration purposes. In other locations, outside North America, larger trials have been conducted, and greater numbers of linings or coatings have been installed in LSLs that remain in service. One manufacturer reports having installed more than 100,000 PET liners in LSLs in France, and manufacturers of two different coating technologies (one using an epoxy product and the other a polyurea/polyurethane product) are reported to have recently signed contracts for tens of thousands of installations in the UK.

What is clear from these trials and installations, based on lead levels measured before and after the linings or coatings were installed, is that linings and coatings can and do effectively reduce lead leaching from LSLs. What is less clear is how many linings and coatings installed in LSLs remain in service, how long they have remained in service, and how well they have performed over time with respect to both effectiveness in controlling leads levels and physical durability. Attempts to obtain such information from utilities, manufacturers, and the literature were largely unsuccessful, apparently because retrospective studies on linings and coatings installed in LSLs are rare. However, the limited information available from studies of lined or coated LSLs, and from other studies involving related applications (e.g., epoxy coating of water mains), indicates that PET liners and epoxy coatings are durable and can be expected to remain effective for very long periods of time. These technologies are old enough that some installations have now been in place for more than 30 years, and manufacturers report that they are holding up well, although those contacted by the investigators said they were not aware of any retrospective studies on older installations of their products. The investigators have identified this as a research need that could potentially be addressed by well-designed surveys.

APPLICATIONS/RECOMMENDATIONS

General Recommendations to All Stakeholders

It is now widely believed that no safe level of lead in drinking water can be established, that the public health goal for lead should therefore be zero, and that the health risks of lead exposure are greatest for those least able to protect themselves (i.e., those still in the womb, infants, toddlers, and young children). NDWAC (EPA 2015a) recommended removal of all lead services lines, all the way to the building wall, over a 30-year timeframe, and concluded that "[minimizing] exposure to lead in drinking water is a shared responsibility; public water systems, consumers, building owners, public health officials and others each have important roles to play." The authors agree with this assessment, recommend that all stakeholders give it careful consideration, and also recommend that manufacturers of LSL lining and coating systems be counted among the "others [having] important roles to play."

Linings and coatings can effectively reduce exposure to lead, on either a short-term or long-term basis, and should be considered by all stakeholders as viable tools that can be used for that purpose, where appropriate, taking their pros and cons into consideration on a site-specific basis. Any system-wide lead control or LSLR program is going to be full of challenges, and linings and coatings can potentially play an important role in meeting some of those challenges in a timely and cost-effective manner. Besides reducing exposure to lead, linings and coatings may also provide other water-related benefits, including:

- Corrosion control
- Leak repair
- Improved hydraulics (flow and pressure)
- Elimination of metal leaching from scale deposits
- Less favorable conditions for biological growth
- Improved aesthetic quality of water (taste and odor, clarity, color)

Other potential advantages of linings and coatings include:

- Fewer and shorter disruptions of vehicular and pedestrian traffic
- Reduced damage to landscaping, trees, sidewalks, and driveways
- Less potential for damage to other utility lines (gas, electric, phone, cable, sewers)
- Increased property value (relative to leaving an LSL in service)
- Cost savings relative to LSL replacement, especially where service lines are buried deep in the ground to avoid freezing, where the soil or subsoil is rocky, or where other factors render less expensive replacement methods impractical
- Facilitating delay of LSL replacements until they can be more efficiently and more cost-effectively performed in concert with water main rehabilitation and replacement projects

Potential disadvantages of linings and coatings include:

- Resurfacing of a lead problem in the future, if the lining or coating deteriorates, even if that happens many decades later, since the LSL remains in place
- Uncertainty regarding their service life, which though expected to be very long is likely to be known with less certainty than that of a new copper service line (though perhaps with no less certainty than the service life of alternative water service line materials, such as plastic pipe, being used or considered for use because of the high cost of copper)
- Any monitoring that may be required to verify continued performance
- Disparities between anticipated service life and warranty period
- Failure to meet future regulatory requirements
- Leaching of traces of various constituents into the water

Linings and coatings could potentially leach chemical constituents into the water, or fail to meet future regulatory requirements, but that is true of every material that is used, or potentially could be used, in water mains, service lines and interior household plumbing. The leaching concern is currently and effectively addressed by requiring materials in contact with drinking water, including plumbing materials and linings and coatings, to be certified as meeting NSF/ANSI Standard 61. The known health risks of lead exposure far exceed those associated with traces of other constituents that may leach from other plumbing materials, including linings and coatings. Thus, concerns about leaching of trace chemicals should not be used as an excuse to avoid lining or coating an LSL to reduce exposure to lead. Nevertheless, reasonable caution is recommended in selecting materials for applications involving materials that are difficult and expensive to replace, such as water service lines and household plumbing, in contrast to materials used above ground, such as exposed process piping and water treatment chemicals, which can be more readily replaced if the need arises.

Public water systems should recognize that the cost of replacing the privately-owned portion of an LSL will be very significant to most homeowners, especially those in less affluent neighborhoods. At the same time, public water systems need to recognize, and help property owners recognize, that the cost of replacing an LSL is typically modest compared to other costs of property ownership such as painting a house or building; putting new shingles on a roof; or replacing a major component of an aging heating, ventilating, and air conditioning system. Public water systems can help mitigate the impacts of LSLR expenses on property owners using creative financing arrangements, such as adding a small monthly charge to their water bill.

To minimize the cost of a full LSLR program, all stakeholders should work cooperatively to plan and implement a proactive system-wide approach, taking advantage of economies of scale and maximizing the productivity of the various work crews involved in scheduling, site preparation, traffic control, installation, and road and sidewalk repair. The approaches used by public water systems in Madison (WI), Lansing (MI), and Saskatoon (SK) are excellent examples of how to plan and implement a system-wide approach.

In planning a system-wide LSLR program, all stakeholders should evaluate using lining and coating technologies, if permitted under all applicable regulations, in locations where they have potential to generate significant cost savings or to provide other benefits. Examples include:

- Congested urban areas, where construction activities and traffic disruptions need to be minimized
- Locations where installing a new service line poses a safety risk, e.g., puncturing a gas line, cutting into an underground electrical wire, or damaging a communications cable serving a large office building
- LSLs connected to a water main, perhaps one in a congested urban area, that is not scheduled to be replaced for another 30-50 years
- Homes for which LSLR would pose a significant risk of damage to landscaping, other utility lines, or structures

Recommendations to Water Utilities and Their Consultants

Public water systems with LSLs should take the lead in working with all stakeholders to cooperatively plan and implement a proactive, system-wide LSLR program. The managers and employees of a public water system usually have a wealth of knowledge about their system and are already in communication with most, if not all, of the other stakeholders, who will be looking to the public water system to provide leadership. They will also bear primary responsibility for paying for the LSLR program and fairly allocating the costs among the rate payers.

Public outreach will be an extremely important means of informing consumers and property owners about their "shared responsibility," including financial responsibility for replacing privately owned portions of LSLs. Public water systems should provide information for consumers and property owners that emphasizes the importance of shared responsibility for minimizing exposure to lead, engages them in the planning process for the service area, clearly informs them about plans and progress to date, recommends actions they can or should take, and starts a dialog about possible financing options. Public water systems should recommend full LSLR, where reasonably possible, to consumers and building owners.

Public water systems developing (or revising) an LSLR program should involve regulatory stakeholders from the beginning of the planning process and maintain their involvement into the implementation phase. In the United States, the applicable regulations associated with the LCR are in flux, so all stakeholders, most especially public water systems with LSLs, would be well advised to keep abreast of proposed or newly promulgated regulations. Until the regulatory picture is clear, public water systems should approach with caution their use of any lining or coating system as part of their compliance strategy.

Public water systems are responsible not only for meeting the requirements of the LCR, but also for meeting state and local regulations, including building codes, that apply to their LSLR programs. State primacy agencies in the United States, and provincial regulatory agencies in Canada, may adopt policies or regulations that differ from those established or recommended at the federal level. As always, public water systems are strongly encouraged to ensure that any materials in their system, including linings and coatings, are certified to NSF/ANSI Standard 61 by an accredited certification body, and in most states and provinces this is legally required. Public water systems should also require post-installation testing of LSL linings and coatings for tap-water lead levels, adequate flow, and integrity (e.g., visual inspection using a high resolution mini-camera).

Public water systems should also engage manufacturers (or vendors) of lining and coating systems in the planning process, as well as contractors – if they plan to hire contractors to perform some or all of the work instead of doing all the work in-house using their own crews. The potential cost savings and other benefits associated with lining and coating technologies can be more effectively realized if they are evaluated ahead of time and incorporated into the program in an organized fashion, rather than considering them on a case-by-case basis, as individual situations are encountered where they might be advantageous. Both manufacturers and contractors are likely to have some excellent suggestions as to how a public water system can maximize the cost savings associated with lining and coating technologies.

For specific situations where full LSLR does not appear to be technically feasible, or economically or socially acceptable, lining or coating the customer-owned portion of the LSL should be considered as an option, if allowed under applicable regulations. During the planning process, public water systems should identify potential needs and/or opportunities for use of linings and coatings to reduce short-term and/or long-term exposure to lead, such as avoiding:

- Disturbances of historic sites or structures
- Environmental damage (e.g., to mature trees)
- Traffic disruption

- Interference with, or damage to, other utilities (gas, phone, cable, sewer, electric)

If such needs and/or opportunities exist for using linings or coatings, public water systems should take the lead in exploring them with all other stakeholders. As part of the exploration process, public water systems should assess their customers' attitudes on the following issues:

- Importance of (and willingness to pay for) minimizing exposure to lead
- Expected length of service interruptions for LSL replacements, linings, and coatings
- Disruptions to yards, trees, driveways, sidewalks, etc.
- Potential cost savings associated with linings or coatings
- Expected service life of new service lines versus lined or coated service lines
- Concerns about materials used in service lines

Epoxy coatings have been used in building plumbing systems for many years, in many countries, including the United States. However, the purpose of such coatings usually has little to do with lead. Coatings have primarily been used in building plumbing systems to control corrosion, repair leaks (especially pin-hole leaks in copper pipe), and improve the aesthetic quality of the water. Due to the growing recognition that lead can be released from interior plumbing, especially from corroded galvanized pipes, use of epoxy coatings primarily for lead control in buildings is likely to become more common in the future. While interior plumbing in buildings is not the responsibility of public water systems, building owners, public health officials, building inspectors, and others are likely to look to water utilities for information and guidance on lead control, use of epoxy coatings, potential impacts of materials on water quality, and related topics. Public water systems should strive to become more familiar with such matters to better serve their customers, and as a sign of their commitment to provide their communities with safe drinking water.

Recommendations to Consumers and Property Owners

The overwhelming majority of stakeholders are consumers and/or property owners, which could be collectively referred to as the water system's customers or the public; and they have a lot at stake. Consumers' health may be adversely affected by elevated lead levels, and property owners are usually financially responsible for replacing, lining, or coating the privately-owned portions of their LSLs. Consumers include not only bill-paying customers, but also children, tenants whose water bills are included in their rent, school teachers and students, occupants of office buildings (who may live outside the service area), visitors, and other members of the general public. The first thing consumers (especially bill-paying customers) and property owners should do is develop a general knowledge of drinking water in their communities, including lead levels in residences, schools, and office buildings. In most cases, this can be accomplished by reviewing the water system's annual Consumer Confidence Report (CCR) and other information posted on the system's website. Many water systems in communities with LSLs have posted at least some information about lead control on their websites; if not, consumers and property owners should request that they do so.

Home and building owners should determine whether or not they have LSLs. Materials developed to assist public water systems in developing LSLR programs also provide guidance for property owners to assist them in determining whether a home or other building has an LSL (AWWA 2014a). In many cases, this information will be available on the public water system's website if there are LSLs in their service area; if not, property owners should request that this information be made readily available. Property owners who have LSLs should consider full LSLR. Even though full LSLR is not currently mandated, it is a wise thing to do to protect themselves and their families, or their tenants or other occupants, as well as guests and future residents or occupants, from unnecessary exposure to lead. Property owners should recognize that although replacing their portion of an LSL is expensive, the cost is typically modest compared to other costs of home or building ownership. Full LSLR might also improve the value of the property in the long run. It would not be surprising to see, in the near future, information about LSLs included on disclosure forms for real estate transactions or included as part of property inspections. If full LSLR is not technically feasible, or economically or socially acceptable, property owners should investigate the possibility of lining or coating their portion of the LSL.

Many public water systems have already reached out to consumers and property owners, by means of billing inserts or website postings, to inform them about lead in their community, lead monitoring results, the presence or absence of LSLs in their service area, corrosion control practices, the status of any system-wide plans for lead control, any financial incentives or financing arrangements that are available to property owners wanting to replace their portion of an LSL, and recommendations for limiting exposure to lead, especially inside homes and buildings. Consumers and property owners whose water systems have not provided this information should request it, if LSLs are known to be present within the service area. Property owners with LSLs should consider taking advantage of any financial incentives their water systems offer to help property owners pay to replace their portion of an LSL.

Disturbing an LSL and/or the plumbing connected downstream from it is likely to cause temporarily increased lead levels that may persist for a month or two and perhaps as long as a year. Possible causes of disturbances include full or partial LSLR, lining or coating an LSL or a portion of it, and various other construction activities in the vicinity of an LSL, such as landscaping, foundation repair, or sprinkler installation. In the event of such a disturbance, consumers or property owners with LSLs should monitor their tap water for lead and/or filter their water (specifically the water used for drinking, cooking, and preparing beverages) using a filter designed (and certified to NSF/ANSI Standard 53 [NSF 2016b] for lead removal) to remove both particulate and dissolved lead, until the lead level is consistently within the recommended limits. Consult the public water system’s website (or contact them directly if necessary) for information about lead monitoring (which they may be able to assist with, especially if they were involved in the disturbance, e.g., an LSLR) and for recommendations regarding filtration. All interior water lines should be thoroughly flushed any time a service line (whether or not it is an LSL) or other component of a plumbing system in a home or building is worked on by a plumber or contractor.

In homes and buildings having interior water lines heavily encrusted with lead-bearing deposits, especially interior plumbing made of galvanized iron pipe, the deposits may be releasing more lead into the water than an LSL, even if the LSL is the source of the lead that slowly built up inside the pipes over many years. Consumers and property owners who encounter such situations should either replace their interior plumbing with lead-free materials, coat their interior water lines to prevent lead leaching, or purchase NSF 53 certified water filters and carefully follow the operating and maintenance instructions.

Recommendations to State and Provincial Regulators

State and provincial regulators should assist public water systems in developing LSLR programs and other lead control strategies that minimize public exposure to lead in drinking water, meet all applicable regulations, and effectively utilize available tools that can contribute to this effort at a reasonable cost. Consistent with the NDWAC recommendations (EPA 2015a, b), full LSLR should be the preferred option for controlling lead associated with LSLs.

When replacing an LSL does not appear to be technically feasible, or economically or socially acceptable, lining or coating LSLs should be considered as an option, if allowed under applicable regulations. State and provincial regulators should help make both current and proposed regulations, including the aspects listed below, clear to other stakeholders with respect to both utility-owned and privately-owned segments of LSLs:

- Are linings and coatings allowed and, if so, under what conditions, and how are lined or coated LSLs treated with respect to compliance requirements?
- If full LSLR is mandated, will exceptions or exemptions be granted permitting the use of linings and coatings in situations where exposure to lead can be more rapidly controlled; where significant savings can be realized; or where damage to historic sites, landscaping, structures, or other utility lines can be avoided?
- If public water systems and/or property owners can apply for exception or exemptions, will they be permanent or temporary, and what criteria will be used to decide whether to approve exceptions or exemptions?
- What monitoring requirements apply to lined or coated LSLs?

Recommendations to Manufacturers and Contractors

Manufacturers of lining and coating technologies, and their representatives, including local contractors licensed to install their products, should familiarize other stakeholders with their technologies, the potential benefits they can provide, and the situations in which they are most likely to provide significant cost savings or other benefits. As manufacturers know, and should be prepared to help public water systems and other stakeholders recognize, LSL lining and coating costs depend heavily on the number of LSLs to be lined or coated, where they are located, and how they are scheduled. In other words, there are significant economies of scale involved, and much greater cost savings can be realized if the LSLs can be lined or coated as part of a well-organized, system-wide program that most likely will also include full and/or partial LSLRs.

To promote their products while also helping communities minimize exposure to lead in drinking water, manufacturers of linings and coatings and their representatives are encouraged to:

- Recognize that a disparity between the expected service life of a product and the warranty period can be a stumbling block for other stakeholders
- Document and publicize supporting information regarding product service life
- Consider increasing warranty periods, when appropriate, and finding creative ways to share real or perceived financial risks in partnership with other stakeholders
- Continue to develop new or improved products and faster, better, and less disruptive installation methods

- Encourage public water systems to adopt a proactive system-wide approach for controlling lead release from LSLs, and to take advantage of the potential cost savings and other benefits of lining and coating technologies
- Consider installing sampling taps at selected locations to facilitate performance monitoring of lined or coated LSLs, since tap-water samples may be contaminated with lead from sources other than the LSLs, making it difficult to document the true effectiveness of linings or coatings
- Place a permanent tag on a lined or coated water service line to alert water utility crews, residents, and plumbers to the need to properly handle it when making repairs to the service line or other pipes, fittings, or devices connected to it

CHAPTER 1
INTRODUCTION

OBJECTIVES

The primary objectives of this research project were: 1) to evaluate lead service line (LSL) lining and coating technologies as alternatives to full or partial LSL replacement, and as a means of protecting and repairing copper service lines (CSLs); and 2) to provide information and recommendations to water utilities, engineering consultants, consumers, property owners, state and provincial regulators, and other stakeholders to assist them in making informed decisions regarding lining and coating of both lead and copper service lines. To accomplish these primary objectives, the investigators sought, as a secondary objective, to obtain and evaluate information on many different aspects of linings and coatings, including the following:

- Their effectiveness in preventing lead release from LSLs and reducing tap-water lead levels, upon installation and after aging
- Advantages and disadvantages of linings and coatings versus full or partial LSL replacement
- Commercially available lining and coating processes and materials suitable for use in small diameter pipes and in contact with potable water
- The durability of linings and coatings and their potential, upon installation and after aging, to leach organic and inorganic chemicals of concern with respect to water quality
- The use of linings and coatings to reduce internal water-service-line corrosion, to prevent metal release from service lines and the scales inside them, and to repair service-line leaks
- Costs to both utilities and property owners, especially relative to the cost of LSL replacement
- Engineering feasibility, commercial availability, certification, and property access issues

Another project objective was to contribute to the broader research effort addressing two priority areas of EPA's STAR-F1 program (Advancing Public Health Protection through Water Infrastructure Sustainability). These areas were:

- Designs, technologies, tools, approaches, and supporting data for preventing, predicting, assessing, responding, and managing public health and economic risks associated with breaches or failures of water infrastructure systems
- Innovative and practicable approaches to manage water infrastructure that serve to prevent introduction, retention, accumulation, and mobilization of waterborne pathogens and chemical contaminants under various system conditions and metrics to evaluate the overall effectiveness of these approaches

APPROACH

To accomplish the objectives of the research project, a research plan was developed consisting of the following seven tasks:

Task 1: Gather and Evaluate Existing Information and Identify Issues
Task 2: Acquire and Evaluate Monitoring Data
Task 3: Conduct Laboratory Studies
Task 4: Design and Conduct Demonstration Experiments
Task 5: Build New Case Studies
Task 6: Evaluate Available Lining and Coating Technologies
Task 7: Develop Recommendations for Stakeholders

These tasks are briefly described below, including changes made during the course of the project as challenges arose and the investigators sought, in consultation with the Project Advisory Committee (PAC), to take advantage of the best opportunities available to further the progress of the research. Although Task 1 was a logical first step and developing recommendations in Task 7 relied on the first six tasks, work on all of the tasks was on-going throughout the project, with more effort being devoted to one task than another at any given time, but work on each task was always used to inform and shape work on other tasks.

Task 1: Gather and Evaluate Existing Information and Identify Issues

The first order of business was to begin gathering, organizing, analyzing, and critically evaluating existing information. This facilitated the research team's work on all subsequent tasks and helped the team to avoid duplicating prior work and to identify significant issues not yet adequately addressed by others. Work on this task continued through the duration of the project. Sources of information included:

- Published and unpublished article and reports
- Water utility personnel, especially utility and distribution system superintendents
- Consulting engineers
- Technical experts having specialized knowledge in relevant subdisciplines
- State regulatory agencies
- Regulatory agencies outside the United States
- NSF International and other organizations involved in product certification
- Manufacturers of lining and coating technologies and their representatives

Surveys were not allowed under the terms of the grant supporting this research. Therefore, information was solicited in an informal manner from individuals and organizations as they were encountered during the course of the project (e.g., at conferences), recommended by others, or identified in publications or on websites. A number of individuals reached out to the project team and voluntarily provided information upon learning about the project.

Task 2: Acquire and Evaluate Monitoring Data

Data collected from existing pilot and field installations of commercially available LSL linings and coatings were specifically sought as part of Task 2. As such data were obtained they were evaluated to determine what they indicated (or did not indicate) about the effectiveness of linings and coatings, both initially and over time. This effort was not limited in scope to lead and LSLs, but also included use of linings and coatings in CSLs and information regarding organic or inorganic chemicals that could potentially leach from linings and coatings. This information was particularly helpful in designing the laboratory studies conducted as part of Task 3.

Task 3: Conduct Laboratory Studies

The laboratory studies, described in Chapters 3 and 4, gave members of the research team hands-on experience with two commercially available lining and coating technologies: epoxy coating and PET lining. These technologies were deemed, based on preliminary evaluation (Task 6) of information obtained in the early stages of Tasks 1 and 2, to have strong potential for successful performance in subsequent pilot and demonstration tests (Task 4) and to be the most promising technologies available for use in controlling lead release from LSLs. Subsequent laboratory experiments focused on leaching of constituents of potential concern with respect to health or other water quality issues. Efforts to obtain the materials needed to test a third technology were unsuccessful.

Task 4: Design and Conduct Demonstration Experiments

Initial plans included in the project proposal submitted in 2009 called for pilot- or field-scale demonstration testing of at least three lining or coating technologies. Preference was to be given to technologies able to effectively reduce lead levels without increasing exposure to other chemical contaminants, and with estimated life-cycle costs that would make them attractive to water utilities and/or their customers. These tests were to be conducted by utility partners in cooperation with manufacturers of the selected lining and coating technologies. The investigators were to develop detailed testing plans in collaboration with utilities and the PAC, and it was envisioned that the analytical work would be divided between utility and university laboratories.

When this project finally got underway, in 2011, circumstances had changed considerably from those in 2009, especially economic circumstances. By 2011 it was clear that the economic downturn that began in 2008 was not just a short-term problem from which the U.S. (and the world) would quickly recover, but the start of a full-blown recession. Water sales were down, many properties were in foreclosure, and a growing number of customers were filing for bankruptcy. Thus, revenues were down for many drinking water utilities, which were also under growing pressure not to raise rates and put additional financial stress on their communities. To keep expenditures in balance with revenues, many drinking water utilities began postponing projects, not only 'big-ticket' capital improvement projects but also smaller projects, including research projects, that could be delayed without compromising their basic mission of providing safe drinking water. Some delayed hiring new staff members to fill open positions, leaving less staff time available for supplemental projects such as those initially envisioned as part of this task.

Efforts to recruit utilities to participate in Task 4 were unsuccessful, with one exception (described in Chapter 5), even though some had previously expressed interest. This was due in large part to difficult economic times, but other factors also played a role. Some utilities were unwilling to participate in demonstration tests of lining and coating technologies that under current interpretations of the LCR would not count toward replacement quotas. Other utilities, thinking that proposed changes to the Lead and Copper Rule (LCR) were imminent, decided that wanted to wait until the revisions were proposed before spending money, time, and effort to explore their lead control options so that they could focus their resources on solutions that would meet any revised compliance requirements. There was a personnel change in one utility that had earlier expressed interest in participating in demonstration testing, and the new head of water distribution was not interested in getting involved, perhaps for some of the aforementioned reasons.

While efforts were still underway to recruit utilities to participate in demonstration tests, the investigators began to have doubts about the value of demonstration tests. Demonstration tests involving a limited number of service lines had already been conducted in several locations in the U.S. and Canada, and larger numbers of linings or coatings reportedly had been or were being installed in a number of locations outside North America. It was clear based on the results of Task 3 and reports by others that the linings and coatings could effectively control lead release, though in most cases some lead was still present at the tap due to release from interior water lines and plumbing fixtures. Thus, additional demonstrations of the effectiveness of these linings and coatings, especially in short-term tests involving short holding times, appeared to be of little value.

As the results became available from experiments (conducted as part of Task 3) involving freshly applied linings or coatings and very long holding times, it was clear that some constituents being monitored were present in only trace amounts or were non-detectable and would therefore not be found in significant amounts in samples from demonstration tests involving shorter holding times and/or linings and coatings that were being regularly flushed while in use. Some of these constituents were already being effectively controlled in potable water systems through product certification requirements. Other constituents found in some samples in Task 3 needed additional study that could be much better accomplished in controlled laboratory experiments than in field demonstration tests.

All of these issues were discussed at length among the investigators and, in consultation with both the PAC and the Project Officer at the Water Research Foundation (WRF), the research team decided to redirect the time and effort that would have been devoted to demonstration tests to: 1) seeking detailed information (from utilities, manufacturers, regulators, and others) regarding the use of linings and coatings, whether for demonstration purposes or on a permanent basis, not only in the U.S. and Canada, but also in countries outside North America, where much more lining and coating activity was reportedly occurring than in the U.S.; and 2) conducting additional laboratory tests to examine specific issues that could be better explored in a controlled laboratory setting. Thus, in essence, the effort planned for Task 5 was integrated back into Tasks 1, 2, and 3.

Task 5: Build New Case Studies

Anticipating that any case studies in the U.S. identified as part of Task 1 would involve pilot- or field-scale demonstration tests that were limited in scope and focused almost exclusively on tap-water lead levels, the research team initially proposed to build new case studies that were more comprehensive in nature. These case studies were to evaluate: 1) potential system-wide benefits (including cost savings) to utilities if the most promising lining and coating technologies were to be approved for use as alternatives to LSL replacement, and for other purposes such as leak repair; and 2) the potential long-term health and economic benefits of these technologies to consumers. Since lining and coating technologies have been rarely used to date on LSLs in the U.S. and Canada, these case studies were expected to be partly hypothetical in nature, but the intent was to base them on actual utilities having LSLs in their service area – the same utilities hosting the demonstration tests to be conducted in Task 4.

For the same reasons noted for Task 4, efforts to collaborate with utilities in developing comprehensive new case studies were unsuccessful. Also, it became clear from discussions with both public water systems and manufacturers that costs are highly site specific and strongly influenced by many different factors. Thus, even cost estimates that are reasonably accurate for one location under a specific set of conditions are not readily transferable to other locations, as previously noted by Mesman et al. (1995). Therefore, in consultation with the PAC and WRF, the research team decided to change the focus of this task and to instead develop a series of short case studies describing situations encountered by various utilities; their reasons for considering (or actually using) linings or coatings (i.e., potential benefits); their experiences, if they participated in any demonstration tests or field trials; and their concerns or reservations about the use of linings or coatings, either in their own water services lines or those of their customers.

Task 6: Evaluate Available Lining and Coating Technologies

The objective of this task was to compile and analyze the information obtained in Tasks 1–5 and to use it to comprehensively assess the effectiveness, durability, costs, benefits, limitations, and implementation requirements of available lining and coating technologies suitable for use in water service lines. This task was on-going throughout the course of the project, with the results providing feedback to the investigators and the PAC and ultimately serving as the basis for developing recommendations for stakeholders (Task 7). The last major element of this task was preparation of the final project report.

Task 7: Develop Recommendations for Stakeholders

The last task was to develop recommendations for stakeholders – general recommendations for all stakeholders and more narrowly tailored recommendations for specific groups of shareholders, including utilities (public water systems) and their consultants; consumers and property owners; state and provincial regulators; and manufacturers and contractors. Readers should note that since this project was funded by EPA, the investigators are not permitted to provide advice to EPA regarding policy or regulatory matters as part of this project. Comments and recommendation here or elsewhere in this report regarding regulatory matters are either factual or are directed to state, provincial, and other non-federal regulators, and not to EPA.

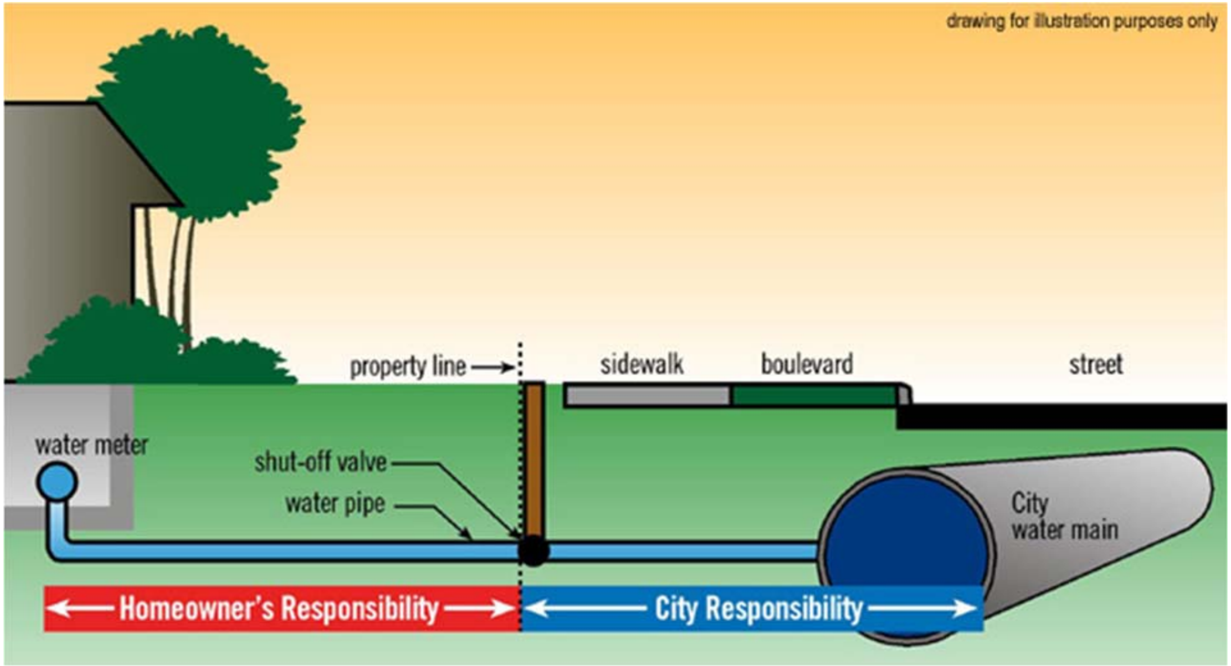
BACKGROUND

Water Service Lines

Drinking water service lines are the pipes that extend from the water main to a residential dwelling or commercial building. Generally, as illustrated in Figure 1.1, the portion of the pipe from the water main to the property line (or stop valve or water meter) is the responsibility of the public water system, while the section of pipe from the property line to the building is generally the responsibility of the property owner; but there are exceptions. For example, customers (i.e., property owners) served by Denver Water are responsible for their water services lines all the way from the main (corporation stop) to the house; and the Lansing (MI) Board of Water and Light owns their service lines from the main to the water meter inside the house (Roost 2016). Some cities, e.g., Saskatoon, SK, have passed ordinances modifying the responsibilities of property owners with respect to their water service lines.

Water service lines made from lead or copper are referred to as lead service lines (LSLs) and copper service lines (CSLs), respectively; and, as they corrode, they can release lead or copper into the water supply, potentially in excess of allowable concentrations. In 1991, EPA promulgated the Lead and Copper Rule (LCR) to guard against unsafe levels of these metals in drinking water. This rule established an action limit (AL) of 15 μg/L for lead and an AL of 1.3 mg/L for copper. Public water systems in the U.S. are required to monitor lead and copper levels at the tap, and if an AL is exceeded in 10% of the water samples, to take action to achieve lower levels. A public water system, as defined under the Safe Drinking Water Act (SDWA), is an entity that provides drinking water to at least 15 connections or regularly serves at least 25 people. A public water system may be either publicly or privately owned. The maximum acceptable concentration of lead in drinking water under current Canadian guidelines (Health Canada 2014) is 0.010 mg/L (or 10 μg/L), but this criterion is intended to apply to the average concentration in distributed water, and compliance samples are collected accordingly (Health Canada 1992). The LCR and the Canadian guidelines are described in greater detail in subsequent sections of this chapter.

The 1986 amendments to the SDWA prohibit the use of lead pipe (LSLs) and lead-containing solder or flux in drinking water distribution system; but the SDWA does not mandate removal of LSLs, except as noted below (see The Lead and Copper Rule). Older cities in some regions of the U.S. and Canada still have many LSLs in place. Cornwell et al. (2016) estimate that there were 10.2 million LSLs in service when the LCR was promulgated in 1991, and that number has been reduced to approximately 6.1 million. Copper service lines (CSLs) have been used for many decades due to their ease of installation, low cost, and corrosion resistance (AWWA 2011). In 1994 approximately 80% of residential water pipes were CSLs (Lewis 1999).



Source: City of Winnipeg 2016.

Figure 1.1 Typical financial responsibility for a water service line extending from a water main to a home or building

Lead Service Line History and Usage

Although lead water pipes were a public concern as early as the 1850s (Kirkwood 1859), large scale installation of LSLs began in the late 1800s in the more populous U.S. cities (Rabin 2008). Being more corrosion resistant and malleable than readily available cast iron, LSLs lasted longer and allowed installers to easily bend pipes around obstacles. Installation of LSLs began to diminish in the 1920s due to increasing public concern, but remained significant through the 1950s. LSLs were not banned outright until the Safe Drinking Water Act Amendments of 1986 (Rabin 2008). The actual number of LSLs remaining in service in the U.S. is not precisely known, since records are incomplete and sometimes in error. Also, some service lines are not LSLs but have lead-bearing components, such as soldered connections or lead goosenecks. The 51 utilities that responded to a 2007 survey had an estimated 1.1 million lead service lines still in service, representing 12% of their service lines (Sandvig et al. 2008); but in the same survey 31 utilities reported another 368,000 lead connections, including goosenecks. Cornwell et al. (2016) estimated the number of LSLs remaining in service in the U.S. to be between 5.5 and 7.1 million, with the best estimate being 6.1 million. They also noted that about 30% of community water systems reported having at least some LSLs in their system.

Health Issues Associated with Lead

Exposure to lead has been widely studied and is believed to cause, or to have the potential to cause, significant adverse health effects, especially in children. Blood lead levels (BLLs) of 15 to 30 micrograms per deciliter (μg/dL) can cause neurological damage such as diminished psychomotor performance, reaction time, and intelligence quotient (IQ); and encephalopathy (brain disease) or even death can occur in children with a BLL of 80 to 100 µg/dL (EPA 2006). Renewed calls for lowering the allowable BLL have cited recent research that indicates neurological damage at BLLs below 10 µg/dL, including a decrease of one IQ point at a BLL as low as 0.1–1.0 µg/dL (Budtz-Jergensen et al. 2013). For these and other reason, the reference level used in the U.S. to identify children with an elevated BLL was lowered to 5 µg/dL from the previous guideline of 10 µg/dL (CDC 2017). Although the median BLL in U.S. children 1-5 years old has dropped from 15 to 1 µg/dL over the past 40 years, further action to reduce the number of children with elevated BLLs, and to reduce exposure for other vulnerable groups and for the general population, is recommended (EPA 2016b).

If the health effects from lead poisoning are largely irreversible, as is widely believed, exposed individuals have to live with the inflicted damage for the rest of their lives. From a public health perspective, if the damage cannot be treated, then it must be prevented. Lead in drinking water can be a significant source of exposure, especially for young children, and its potential health effects are the driving force behind recent proposals for further action to reduce exposure to lead in drinking water (EPA 2015a and 2016b; Health Canada 2017). Replacing, lining or coating LSLs is an important means of achieving that goal.

The Lead and Copper Rule (LCR)

On June 7, 1991, the U.S. Environmental Protection Agency (EPA) published the final Lead and Copper Rule (LCR; 40 CFR 141.86; EPA 1991, 2007a, and 2013). The LCR established an action level (AL) of 0.015 mg/L for lead and an AL of 1.3 mg/L for copper based on the 90th-percentile concentrations of lead or copper in first-draw one-liter tap-water samples collected in home with higher risk of lead exposure due to having an LSL or relatively new lead solder. Samples are drawn from a fixture from which water is consumed, typically the kitchen sink, after a stagnation period of at least 6 hours. An AL exceedance is not in itself a violation, but triggers other regulatory requirements that can include water quality parameter monitoring, corrosion control treatment (CCT), source water monitoring and source water treatment (SOWT), public education, and lead service line replacement (LSLR).

Immediately after the LCR was finalized in 1991, water systems and state primacy agencies were challenged with LCR implementation. One challenge was identifying the appropriate customers that met the regulatory requirements for the sampling pool (homes or buildings that were are higher risk due to having lead service lines or relatively new lead solder), securing their commitment to participate in the sampling, and training them on how to take a first-draw sample after the appropriate stagnation period. Over the long-term, maintaining the interest of these customers in remaining in the sample pool proved to be another significant challenge.

One of the most challenging LCR components for some systems is the LSLR requirement. Water systems are required to annually replace 7% of their lead service lines (LSLs) if they continue to exceed the AL after installing CCT and/or SOWT. Replacement of LSLs can be discontinued when ALs are not exceeded for 2 consecutive 6-month monitoring periods, but must be re-continued if the AL is exceeded again. Utilities can count an LSL as "replaced through testing" if all samples collected from the LSL are below the AL. However, the status of these LSLs must be reconsidered if later sampling results exceed the AL. For the purpose of determining if an individual LSL requires replacement, sample collection is designed to obtain water allowed to stagnate in the LSL for at least 6 hours. Instead of collecting the first draw, the calculated volume of water between the tap and LSL is flushed prior to sample collection. The sample collector can also flush until a significant change in water temperature is observed or tap into the LSL itself to collect a sample, with the latter being a much less common practice.

An important aspect of water service lines is that in most cases the water utility owns only the portion that extends from the water main to the curb stop, water meter, or property line, and the rest of the water service line is privately owned and located on private property. The LCR does not require public water systems in the U.S. to replace the customer-owned portion of an LSL, and many public water systems are prohibited from performing work on private property at city or utility expense. Many utilities performing LSLRs, whether on a mandatory or voluntary basis, offer property owners an opportunity to sign an agreement to pay to replace their portion of the LSL at the same time, taking advantage of the cost savings that can be realized by having the crew or contractor already on site perform the additional work. However, most property owners do not see the need to replace their portion of the LSL, not deeming the benefits sufficient to justify the cost, which can exceed $2,000 per line. Therefore, the overwhelming majority of LSLRs performed by public water systems are partial LSLRs, in which only the utility-owned portion of the LSL is replaced.

For partial LSLRs, the LCR requires water system to notify customers at least 45 days prior to replacement about the potential for increased lead levels (due to disturbance of the LSL). The LCR also requires water systems to collect samples within 72 hours of an LSLR, to determine the lead levels in the samples, and to provide the results to the property owner within 3 days after the monitoring results are received. In 1991, the drinking water community generally thought that partial LSLRs would significantly reduce lead exposure over the long-term and would therefore be preferable to leaving the entire LSL in place.

In early 2004, the EPA began a wide-ranging review of LCR implementation to determine if the rule needed to be revised or strengthened, and/or if additional issues needed to be addressed by additional regulations. As part of its review, EPA analyzed lead monitoring data and other information, carried out a review of state implementation, held four expert workshops to discuss elements of the regulations (including a national meeting to discuss challenges and needs), and worked to understand the scope and variety of state and local efforts to monitor for lead in drinking water in schools. In March 2005, EPA released a Drinking Water Lead Reduction Plan (DWLRP) that outlined both short-term and long-term goals for improving LCR implementation (EPA 2005).

In 2007, EPA published the Short-Term Revisions to the LCR that were identified in the 2005 DWLRP (72 CFR 57781; EPA 2007a). These additional requirements were intended to address regulatory gaps that could be addressed through minor revisions. More substantive revisions were delayed until additional detailed information could be collected to inform a more thorough regulatory development process. These revisions enhanced the implementation of the LCR in the areas of monitoring, treatment, LSLR, public education, and customer awareness. The short-term revisions were intended to better ensure that drinking water consumers receive timely and useful information needed to help them limit their exposure to lead in drinking water.

After the Short-Term Revisions to the LCR were published in 2007, the EPA continued to work on more substantive LCR revisions. However, as knowledge about lead in drinking water continued to evolve, EPA determined that any proposed revisions were going to be challenging due to the complexity of the LCR itself, as well as the results of more recent research that found that partial LSLRs led to increased lead levels for some period of time after replacement. These temporary increases in lead levels are an unintended consequence of partial LSLRs and need to be addressed as part of more substantive LCR revisions. Recent developments and anticipated changes to the LCR, and possible implications for the use of linings and coatings are discussed below. One particular issue arises from the common practice of partial LSR replacement with copper pipe, which can create galvanic corrosion cells that accelerate corrosion of the remaining lead pipe sections (Triantafyllidou and Edwards 2011, Cartier et al. 2012, Welter et al. 2013). This is addressed in more detail below (see LSL Contributions to Lead in Tap Water).

Canadian Guidelines for Lead in Drinking Water

The Guidelines for Canadian Drinking Water Quality are established by the Federal-Provincial-Territorial Committee on Drinking Water (CDW) and published by Health Canada. The Committee is comprised of members from each province and meets on regular basis to determine if a new guideline for a specific contaminant is needed (or not), or if an existing guideline needs to be revised based on new research. The CDW establishes guidelines specifically for contaminants that meet the three following criteria:

- Exposure to the contaminant could lead to adverse health effects in humans
- The contaminant is frequently detected or could be expected to be found in a significant number of Canadian drinking water supplies
- The contaminant is detected, or could be expected to be detected, in drinking water at a level that is of possible human health significance

The development of each guideline is based on current, published research on health effects, aesthetic issues, and treatment. Health-based guidelines are based on a comprehensive review of the known health effects associated with each contaminant, on exposure levels and on the availability of treatment and analytical technologies. Aesthetic effects (primarily taste and odor) are considered when these play a role in determining whether consumers will consider the water drinkable. Treatment is considered when the presence of a specific contaminant may interfere with a specific treatment process or technology (e.g., turbidity interfering with chlorination or UV disinfection) or adversely affect drinking water infrastructure (e.g., corrosion of pipes).

After the Committee establishes a specific guideline, each province makes its own decision on whether to adopt that guideline as an enforceable standard for that province. In general, the provincial standards follow the guidelines established by Health Canada.

Under the current Guidelines for Canadian Drinking Water Quality (Health Canada 2014) the maximum acceptable concentration (MAC) of lead in drinking water is 10 µg/L, which is intended to apply to the average concentration in distributed water, typically based on samples collected after the faucet is flushed and prior to the water being taken for analysis or consumption Health Canada 1992). However, a new guideline of 5 µg/L is being proposed (Health Canada 2017) that would include sampling the water using a random daytime or a 30-minute stagnation sampling approach. Limiting exposure to lead in drinking water is but one component of Health Canada's risk management strategy for lead (Health Canada 2013).

Anticipated LCR Revisions and Implications for LSL Linings and Coatings

The current LCR does not explicitly address linings or coatings, but it is possible they will be addressed in revisions to the LCR that EPA is expected to propose in 2017. This section of the report describes recent developments in this regard, and discusses the possible implications of anticipated changes on the use of linings and coatings in LSLs. Readers should note that since this project was funded by EPA, the investigators are not permitted to provide advice to EPA, as part of this project, regarding policy or regulatory matters. Comments and recommendation here or elsewhere in this report regarding regulatory matters are either factual or are directed to state, provincial, and other non-federal regulators, and not to EPA.

Anticipated LCR Revisions

In 2013, EPA realized that any substantive revisions to this complicated rule would be complex and would need input from a variety of stakeholders. From EPA's perspective, a facilitated stakeholder process would be the best approach for providing recommendations for these more substantive revisions. In early 2014, the agency established an LCR Working Group (LCRWG) under the National Drinking Water Advisory Council (NDWAC). The goal of the LCRWG was to develop recommendations that would serve as the foundation for proposed Long-Term LCR (LT-LCR) revisions.

The LCRWG held seven meetings and one webinar from March 2014 through June 2015 (EPA 2016a). After lengthy deliberations and discussions, the LCRWG report was finalized in August 2015 (EPA 2015a). The LCRWG's recommendations were approved by the full NDWAC in December 2015 (EPA 2015b), and were endorsed by AWWA in 2017 (AWWA 2017). EPA is carefully evaluating the NDWAC report as it prepares to propose the LT-LCR revisions sometime in 2017 (EPA 2016b). A large number of public comments are anticipated, given recent events in Flint, Michigan and other locales. After EPA analyzes and responds to the public comments from the proposal and the final rule goes through another round of governmental review and approvals, the final Long-Term LCR Revisions will likely be finalized approximately two years after the proposal, likely sometime in 2019.

The recent events in Flint, MI, and other locales in 2014 and 2015 have somewhat changed the context for the LT-LCR Revisions in that the public, media, and Congressional scrutiny has substantially increased. EPA has been pressured to speed up the schedule for the proposed revisions, but pressure does not necessarily translate into an accelerated regulatory schedule due to the regulatory development requirements in the Safe Drinking Water Act (SDWA). Translating the narrative language in the NDWAC recommendations to *Federal Register* preamble and regulatory language takes substantial time, and the NDWAC recommendations also left many details for EPA to resolve as part of its regulatory development process. Both the proposed rule and the final rule require several layers of review and approval before either is actually signed by the EPA Administrator and ultimately published in the *Federal Register.*

An important aspect of the NDWAC recommendations is that they are just that – recommendations, which EPA may accept, revise, or reject in favor of other options as the agency proposes and ultimately finalizes the LT-LCR. On some issues, such as the Household Action Level (HAL), which is different than the water system AL trigger, the LCRWG left the decision-making to EPA – noting that the LCRWG recommended that EPA propose the HAL as part of the LT-LCR and also recommended that the local health department be notified if a sample is above the HAL. On other issues, EPA is likely to propose multiple options, accept public comments on the different options, and then come to a final decision for the final LT-LCR.

The NDWAC recommendations cover a broad range of LCR issues ranging from LSLR to more robust public education requirements to tighter corrosion control requirements. One of the more challenging requirements for water systems is the development of a proactive LSL program that would result in all LSLs being replaced to the building wall over a 30-year timeframe. Replacing the LSLs all the way to the building wall will require replacement in public right-of-ways, as well as on private property.

It should also be noted that one of the NDWAC recommendations is to revise the definition of LSLs to include any service line where any portion, including a lead pigtail, gooseneck, or other fitting, is made of lead. If incorporated into the final rule, this would be a significant revision as many water systems have limited records of where a lead pigtail or gooseneck might have been used, as opposed to a full lead service line.

Developing a LSLR program that ultimately replaces all LSLs all the way to the building wall will be a challenge for each and every water system that has LSLs. The American Water Works Association (AWWA) has developed guidance materials to assist water systems in developing such programs (AWWA 2014a). Under the LT-LCR, water systems will potentially be required to develop targeted outreach programs so that customers understand their "shared responsibility" (including financial responsibility) for replacing their portion of the LSL. Water systems will potentially be required to provide both rate-based and non-rate-based financial incentives for property owners to pay for their portion of the LSL. Based on the recommendations in the NDWAC Report, these incentives could potentially include rate design considerations such as low rates for low-volume customers and household-size-based rates. Non-rate-based financial incentives could include:

- Budget billing
- Fixture retrofits and plumbing assistance by the water system
- LSL replacement and insurance programs not provided by the water system
- Direct assistance and/or emergency bill payment relationships
- Fixture retrofits and plumbing assistance by non-governmental organizations (NGO) providing affordable housing
- Subsidies including LSL and/or connection replacement costs associated with street, sidewalk, and other repairs not related to drinking water infrastructure
- On-bill financing provided by the water system

Additionally, the NDWAC report recommends that the LSLR requirements be "front-loaded," with 60% of the LSLs being replaced in the first 15-year half of the 30-year replacement window. The intent of this provision is to recognize that progress may be more difficult to achieve in later years with those LSLs that still remain in service at that time. There will likely be some property owners who fail to reply to the water system's invitation to participate in full LSLR and/or may refuse to participate in full LSLR no matter what financial incentives the water system offers.

Implications for LSL Linings and Coatings

The NDWAC LCRWG report (EPA 2015a) did not address linings and coatings, nor is clear whether they will be addressed in the LT-LCR or, if they are addressed, what the relevant provisions will be. The focus of the NDWAC report was on full LSLR, but system-wide LSLR programs are going to encounter many challenges, including: significant financial costs; disruptions of vehicular and pedestrian traffic; and damage to structures, historic sites, landscaping, and other utility lines (gas, electric, sewer, and telecommunications). It remains to be seen:

- Whether the LT-LCR will allow the use of linings and coatings to help address these challenges and, if so, whether their use will be permitted for both utility-owned and privately-owned LSLs, whether they will be permitted on an interim or permanent basis, and what monitoring requirements or other conditions will apply
- Whether an LSL that has already been lined or coated, perhaps as an emergency measure to protect public health, will have to be replaced if the anticipated new Household Action Limit is being met
- Whether state agencies and officials responsible for local building codes will approve the use of linings and coatings in lead or copper water service lines to the extent permitted by the LT-LCR, or whether they will adopt more stringent regulations
- Whether the courts will uphold a requirement to replace LSLs on private property (if such a provision is included in the LT-LCR), since such a provision would most likely be highly controversial, especially given the very low participation rate in current LSLR programs

Regardless of what provisions are ultimately incorporated into the final LT-LCR, it is clear that they are likely to have a very significant impact on interest in the use of linings and coatings in LSLs in the U.S. The same is true for the proposed lowering of the Canadian MAC for lead in drinking water, from 0.010 to 0.005 mg/L. This change, if adopted by the provinces, would likely necessitate action on the part of both water utilities and property owners to replace, line, or coat LSLs.

NSF International (NSF) and Other Product Certification Standards

NSF International (NSF) is an independent non-governmental organization that sets standards intended for voluntary use by government organizations, utilities, manufacturers, and others. Some NSF standards are also adopted by the American National Standards Institute (ANSI). Of particular relevance to this project is NSF/ANSI Standard 61-2016, *Drinking Water System Components – Health Effects* (NSF 2016a), hereinafter referred to as NSF 61. NSF 61 establishes certification requirements for products, product components, and materials with respect to chemicals that may leach into drinking water and cause adverse health effects. The chemicals include those for which limits have been set by EPA or Health Canada; and products include pipes, pipe fittings, barrier materials (including linings and coatings), and various non-metallic materials (including many plastics). Water utilities, designers, state and provincial regulators, and other entities commonly require any product or material used in a public water system to be certified as meeting NSF 61 if it will come into contact with potable water.

NSF has also developed other standards relevant to drinking water treatment and distribution systems. NSF 60 establishes minimum standards for the purity of chemicals used in drinking water treatment, to protect public health. NSF SE 9857 defines requirements for epoxy coatings applied to the interior surfaces of metallic potable water pipes by mechanical means. NSF/ANSI Standard 372 establishes limits on the lead content of drinking water system components. NSF/ANSI Standard 53 (NSF 2016b) establishes minimum certification requirements for the performance of residential water filters in removing health-related contaminants such as lead, and is widely used to verify manufacturers' claims.

Other standards setting organizations have also adopted standards relevant to water service line linings and coatings. For example, the International Association of Plumbing and Mechanical Officials (IAPMO) has adopted IAPMO Guide Criteria IGC 189 for Internal Pipe Epoxy Barrier Coating Material for Application in Pressurized (Closed) Water Piping Systems; and ASTM International (American Society for Testing and Materials International) has a standard (D4541) specifying the method used to measure the pull-off strength of coatings using portable adhesion testers and another standard (D5162) specifying standard practice for measuring discontinuities (holidays) in nonconductive protective coating on metallic substrates.

Other countries have adopted standards similar to those used in the U.S. and Canada, but specific requirements and approval procedures vary from one country to another. For example, in England and Wales, products used in public water supplies must be included on a list of products approved for use by the Drinking Water Inspectorate (DWI) under Regulation 31 of the Water Supply (Water Quality) Regulations. The approval process includes certification to British Standard BS 6920 (British Standards Institution 2014), which is similar to NSF 61 but also includes a test to determine whether the product stimulates the growth of aquatic microorganisms. Scotland and Northern Ireland use similar procedures, but publish their own lists of approved products. Products used after the water passes to consumers in the UK are regulated by not by DWI but under the Water Regulations Advisory Scheme (WRAS) used to ensure conformity with the Water Supply (Water Fullings) Regulations. Australia and New Zealand Standard AS/NZS 4020, modelled after BS 6920, is also similar to NSF 61, as are standards adopted by Germany, France, and various other countries.

LSL Contributions to Lead in Tap Water

Sandvig et al. (2008) used both historical data and data from their own sequentially collected tap water samples to estimate contributions from faucets, premise plumbing, LSLs, and water meters to lead concentrations in tap water. They concluded that 50–75% of the lead found at the tap had come from LSLs. These results and others suggest that tap-water monitoring results based on first-flush compliance samples from a home or office building may greatly underestimate the risk of elevated lead levels in a home or building, and especially the contributions from LSLs. This is because first-flush compliance samples typically contain mostly dissolved lead from in or near a faucet. During the 6-h (minimum) stagnation period used when collecting first-flush compliance samples, any particulate lead might settle out and fail to be collected, and any lead released into the water from an LSL during this time will be missed entirely. See Health Canada (2017) for an excellent review of sampling methods emphasizing the need to match the sampling method to the monitoring objective.

In a study of lead in samples collected for LCR compliance in Washington, D.C., particulate lead comprised only about 10% of the total lead (EPA 2007b), whereas much higher percentages of particulate lead have been observed in other types of samples, such as those collected using profile sampling or following high-rate flushing. Cartier et al. (2013) noted that increased particulate lead levels can result from higher flow rates that destabilize accumulated lead scale layers or suspend heavier solids. The importance of particulate lead, its role in lead transport and exposure, the many factors contributing to its variability, and the difficulties encountered in attempting to quantify its occurrence in tap water in homes and buildings have been emphasized in a number of studies (e.g., McNeill and Edwards 2004, Schock and Lemieux 2010, Deshommes et al. 2010, Cartier et al. 2011, Del Toral et al. 2013, Doré et al. 2013, Clark et al. 2014, and Deshommes et al. 2016). A closely related issue is the relative bioavailability of the various forms of lead present in drinking water, which is critical to linking lead exposure to blood lead levels and potential health effects (Deshommes et al. 2012).

Lead concentrations in tap water can also be underestimated as a result of other sampling and analytical artifacts. Inspection of faucet aerator screens taken from the apartment building of a lead poisoned child in North Carolina revealed trapped particles of lead solder. Small pieces of lead solder may be more commonly present in tap water than is generally recognized. Lead solder was used for many decades (until its use in potable water systems was banned in 1986) to seal the sweat fittings on copper water lines. It would not be unusual for small pieces of solder, especially excess solder protruding beyond the end of a fitting, to gradually corrode and fall off over an extended period of time. Not only would small particles of solder likely be under-sampled when collecting first-flush LCR compliance samples, for the reasons noted above, but solder, lead particles, and particles containing lead (IV) oxide may not dissolve completely in some cases when using current EPA-approved analytical methods (Triantafyllidou et al. 2007), such that reported levels would be lower than those actually present in the sample.

As noted above (see The Lead and Copper Rule) and below (see LSL Replacements by Public Water Systems), most LSLRs to date in the U.S. and Canada have been partial LSLRs, in which only the utility-owned portion of the LSL has been replaced. Partial LSLRs have been found in a number of studies to cause significant short-term increases in tap-water lead concentrations (e.g., EPA 2011, Commons 2011, Camara et al. 2013, Cartier et al. 2013, Trueman et al. 2016, St. Clair et al. 2016). These increases appear to be caused by disturbance of the portion of the LSL that is not replaced (usually the privately-owned portion), and perhaps also, to some extent, disturbance of lead-bearing deposits in the interior plumbing when a portion of the LSL is removed and water lines are drained and later refilled and flushed. Other disturbances besides partial LSLR can also cause short-term increases in lead levels (Lewis et al. 2017). Some investigators have seen spikes above 1000 µg Pb/L, or 67 times the AL, immediately after partial LSLR, due mostly to particulate lead (Boyd et al. 2004, Sandvig et al. 2008). Such spikes can last a month or two, as was typical for many of the homes studied by Lewis et al. (2017); but they can also persist for longer periods of time, as noted in an extensive review of partial LSLR (PLSLR) by EPA's Science Advisory Board (EPA 2011), which concluded that:

> "… PLSLR is frequently associated with short-term elevated drinking water lead levels for some period of time after replacement, suggesting the potential for harm, rather than benefit during that time period. Available data suggest that the elevated tap water lead levels tend to then gradually stabilize over time following PLSLR, sometimes at levels below and sometimes at levels similar to those observed prior to PLSLR."

The amount of lead reaching the tap from an LSL also depends on other factors, including the length of the LSL, the extent to which dissolved lead is adsorbed by deposits in the interior plumbing, the corrosivity and redox potential of the water, and galvanic corrosion associated with the connection of dissimilar metals. Rust deposits have been found to strongly adsorb lead (Sandvig et al. 2008, McFadden et al. 2011, Camara et al. 2013, Trueman and Gagnon 2016a and 2016b); and heavy rust deposits are commonly found inside corroded galvanized pipes, which were widely was used in some communities in homes with LSLs, and were even used for service lines in some cases (e.g., in Rochester, NY; see the case study in Chapter 5). Lead adsorbed to rust can later be released back into the water, in either dissolved or particulate form, for a number of reasons, such as changes in water quality or physical disturbance of the deposits. Manganese deposits also strongly adsorb lead and can significantly influence tap-water lead concentrations (Schock et al. 2014).

The water in an LSL will typically have only a moderately strong redox potential, due to the presence of combined chlorine or a relatively low free chlorine residual. However, in some locations in systems employing higher levels of free chlorine, the redox potential can be high enough to oxidize lead to Pb(IV), a more insoluble form of lead than the more common Pb(II) (Schock 2001, Schock and Giani 2004, Lytle and Schock 2005, Vasquez et al. 2006, Schock and Lytle 2011), which can result in lower tap-water lead levels (Triantafyllidou et al. 2015). However, if the redox potential later drops, the Pb(IV) can be reduced, causing elevated lead levels for a period of time. Manganese can inhibit formation of a PbO_2 scale layer (Schock et al. 2014).

The impact of galvanic corrosion due to partial lead service line replacement with copper pipes has been investigated in a number of studies over the past decade, e.g., EPA 2011, Triantafyllidou and Edwards 2011, Cartier et al. 2012, Welter et al. 2013, Clark et al. 2015, St. Clair et al. 2016, Trueman et al. 2016). An assessment of previous Water Research Foundation reports on this topic is contained in Welter et al. (2013), while St. Clair et al. (2016) provide a current summary of the existing literature. Current research indicates that there is substantial potential for galvanic corrosion to occur in cases of partial LSR replacement with copper pipe. This corrosion can result in increased lead release after partial LSRL for a period of time – possibly 4 to 6 months (Welter et al. 2013), or possibly a year or longer (St. Clair et al. 2016), depending on sampling and flow conditions. These reactions may even produce conditions where partial LSR replacement leads to long-term (>6 month) lead concentrations greater than those before replacement (Trueman et al. 2016). EPA (2011) noted that "Insertion of a lead-free dielectric eliminates galvanic corrosion at the new pipe junction … [and] will likely reduce lead levels in tap water …." However, since water service lines in older homes may still be in use for electrical grounding, public water systems installing or recommending use of dielectrics should warn residents, plumbers, and electricians in their service area to maintain proper electrical grounding.

LSLs contribute to tap-water lead concentrations in various ways that can be difficult to control and to properly monitor, and partial LSLR has been found to cause short-term increases in tap-water lead levels. For these reasons, public water systems and other are increasing leaning toward or actively promoting full LSLR. The high cost of full LSLR and the associated disruptions and potential damage to other utilities and property have resulted in an upsurge of interest in lining and coating technologies that may be able to reduce the cost of lead control while also avoiding some of the disruptions and damage associated with full LSLR.

LSL Replacements by Public Water Systems

Only a small number of public water systems in the U.S. have been on mandatory LSLR programs in recent years, no Canadian providence mandates LSLRs, and only a few cities in the U.S. and Canada have mandated replacement of private-side LSLs. Many public water systems voluntarily replace LSLs as they are encountered in the normal course of their operations, e.g., when repairing leaks or replacing mains, a process some utilities expect to continue for decades into the future. The end result is that the majority of LSLRs, in both the U.S. and Canada, are voluntary; and, since most property owners choose not to replace their portion of an LSL, most LSLRs are also partial. Some utilities have already replaced many or most of their LSLs. Others have replaced only a small fraction of their LSLs, perhaps because they have not exceeded the action level or because they were quickly able to reduce their lead levels below the AL and avoid or discontinue mandatory replacements. Overall, the number of LSLs in service is gradually declining, but an estimated 6.1 million remain in service (Cornwell et al. 2016).

A public water system might voluntarily replace utility-owned LSLs: 1) to minimize the contributions of their LSLs to lead in drinking water, thereby providing public health benefits to consumers; 2) to avoid future exceedances of the AL that could potentially occur due to water quality or regulatory changes; and 3) to minimize the long-term cost of LSL replacement, by replacing them gradually, in the normal course of operations, over a period of many years, perhaps anticipating that replacement will be required in the future. However, many public water systems with LSL programs also have concerns that may include the following: 1) some are concerned about the lack of customer buy-in, especially in light of the growing recognition in recent years of the limitations of partial LSLRs, and are seeking ways to encourage more property owners to replace their LSLs; 2) some, especially those with a goal of eventually replacing all of their LSLs, are concerned about the costs involved and are seeking ways to reduce costs; and 3) some are encountering situations where replacement of utility-owned LSLs would be complicated, hence more expensive. For these and other reasons, many utilities with LSLs in their service area are especially interested in better and less expensive ways to deal with them.

One factor significantly influencing the cost of LSL replacement, lining, or coating, as well as the associated disruptions and potential damages, is the location of the water main relative to the customer's property. A water main typically runs down one side of the street or the other, though some run through alleys or other right-of-ways. If the main is located on the same side of the street as the property, the LSL is typically relatively short. For "short-side" replacements, trenching (excavation) is often the preferred replacement method, and in some cases the LSL is short enough that digging the access pits required for trenchless replacement methods (or lining or coating) would expose most or all of the LSL, in which case trenchless methods offer little or no advantage – unless the portion of the LSL on private property is also being replaced.

Although an old LSL can be pulled from the ground without excavating, a new trench is often required for its replacement, especially in situations where a pipe could potentially damage nearby utility lines or structures if pulled. Trenching represents a significant portion of service line installation costs due to the machinery and labor involved; and trenching, especially if required for a long-side replacement, may also necessitate traffic control and pavement repair. Furthermore, if a newly located trench is required, conflicts with other utilities can arise.

In the 2007 survey performed by the EPA, 80% of the responding utilities said that customers were responsible for all aspects of replacing their portion of the LSL (Sandvig et al. 2008). Despite the health risks, relatively few homeowners opt to replace their portion of the LSL. Cost is clearly a major factor in homeowners' decision making. A 2006 survey conducted of utilities lists the cost of replacing the utility owned portion of a LSL at $250–$3,000 and the homeowner's portion at $600–$4,000 (Sandvig et al. 2008). A survey conducted by Boyd et al. (2000a) lists the cost to utilities for open trench replacement of LSL at $240–$3,600, whereas PET lining may cost $450–$700 and epoxy coating $900–$1,100. A significant portion of the cost savings associated with lining or coating comes from avoiding trenching. Instead, a pit is typically dug at each end of the pipe in order to connect the installation equipment. The lack of trenching can also help minimize traffic delays and disruption of the land surface which, combined with the cost savings, could help entice property owners to take action to eliminate lead release from their LSLs.

For "long-side" replacements, the LSL runs underneath the street, so excavation (trenching) damages the pavement and disrupts traffic. This makes trenchless replacement methods, such as pulling the LSL out with a cable and dragging in a new copper service line behind it, much more attractive. However, trenchless water service line replacement methods are not always feasible, e.g., due to tight bends, excessive length, soil conditions, or proximity to other utilities or to structures. In such cases, alternative replacement methods are usually considerably more expensive and disruptive, sharply driving up costs (monetary and otherwise) and making lining or coating all the more attractive. Other factors influencing costs, particularly the costs associated with lining or coating, are discussed in more detail in Chapter 2.

Linings and Coatings as Alternatives to LSL Replacements

Kirmeyer et al. (2000) and Boyd et al. (2001) examined linings and coatings as alternatives to LSL replacement. Lining involves slip-lining an LSL with a smaller diameter pipe (usually one made of plastic) that may be expanded and pressed or sealed against the wall of the LSL. Coatings (usually epoxy-based, though polyurethane is now being used in the UK) are cured in place after application by one of several methods. Typically, pits are excavated to reach the ends of the LSL, which are usually located at the main and curb stop (or water meter) for the utility-owned portion and at the curb stop (or water meter) and foundation wall for the customer-owned portion. The ends of the LSL are cut, the LSL is cleaned, the lining or coating is applied, and the ends are then reconnected using standard or special fittings. Sometimes these technologies cannot be used (e.g., for LSLs with sharp bends, hidden damage, or heavy deposits); but they offer advantages in some situations, most notably lower installation costs and less disruption to above-ground property (e.g., roads, sidewalks, trees, and lawns) and activities (e.g., pedestrian and vehicular traffic).

Although Kirmeyer et al. (2000) and other investigators have considered lining and coating technologies primarily from a utility perspective, both consumer (property owner) and regulatory viewpoints also merit consideration. Property owners may find these technologies attractive for the same reasons utilities are interested in them, i.e., reduced property disruption and potential for significant cost savings. These technologies may be especially cost-effective for property owners if they require only one pit (i.e., if the customer-owned LSL can be accessed from the meter) or none at all (i.e., if the customer-owned portion of the LSL is lined or coated at the same time as the utility-owned portion). Additionally, if these technologies were widely recommended by trusted authorities, or if replacement, lining, or coating of LSLs were required, installation costs would be expected to decrease significantly as manufacturers, plumbers, and contractors competed for a share of the market. The time needed to cure epoxy coatings (16-24 hours) may concern some homeowners, but this problem can be circumvented using temporary bypass connections, and several technologies are now available that promise to deliver same-day return to service.

State and provincial regulators are interested in lining and coating technologies because: 1) approaches more effective than partial LSLR are needed, since some studies (e.g., Sandvig et al. 2008, Welter et al. 2013, Trueman et al. 2016) have found that partial LSLRs may increase tap-water lead levels over extended periods (up to 6 months or more), or fail to reduce lead concentrations below the desired level; 2) linings and coatings can significantly reduce exposure to lead in drinking water, potentially providing significant health benefits to a large number of people at reduced cos and inconvenience; and 3) state and provincial regulators sometimes receive inquiries (official or unofficial) from water utilities or other stakeholders regarding the regulatory status of linings and coatings.

Since linings and coatings are not explicitly addressed in the current regulations in the U.S. (i.e., by the LCR), the response from state and provincial regulators is typically rather speculative. There is currently no prohibition against using a lining or coating, provided it is certified as meeting NSF/ANSI Standard 61. In the U.S., a lined or coated LSL is not counted as replaced for systems in mandatory LSLR programs (which is a disincentive for such systems to use linings or coatings); however, if an LSL scheduled for replacement is lined or coated, it can "test out," i.e., be sampled to show that the lead concentration is under the AL and then be exempted from replacement. Furthermore, public water system and property owners can voluntarily line or coat LSLs to lower lead levels in tap water before the 90th percentile exceeds the action limit, thereby avoiding mandatory replacement requirements. It is not clear whether linings and coating will be addressed in the long-anticipated revisions to the LCR or, if so, what the requirements might be. Recent developments in this regard, and possible implications for the use of linings and coatings, are discussed above (see Anticipated LCR Revisions and Implications for LSL Linings and Coatings).

In addition to reducing lead release from LSLs, lining and coating technologies may offer other important benefits to utilities, consumers, and property owners. They have the potential to reduce corrosion of copper service lines (CSLs), which are very widely used but susceptible to pin-hole corrosion, to repair leaks in both LSLs and CSLs, and to reduce the release of other metals (besides lead) from pipe surfaces and scale deposits (Schock et al. 2008). Some lining technologies may save time when making emergency repairs, or may reduce the cost of repairing services lines that develop leaks, which most commonly occur in the same places where an access pit is needed for slip lining, i.e., at the main, the curb stop, or the meter (Le Gouellec and Cornwell 2007). For partial LSLRs, linings and coatings can be used to protect both a newly installed CSL and a customer-owned LSL that is left in place, including the connections between the two pipes. By removing the direct connection between the pipe materials and the water, linings and coatings could neutralize the impact of galvanic corrosion cells that could otherwise occur at these connections. For these reasons, use of linings and coatings in CSLs was included, as a secondary matter, in this project, even though exceedances of the AL for copper are relatively rare and, when they do occur, CSLs are rarely the major source of copper.

One obstacle to wider use of lining and coating technologies in the U.S. and Canada is lack of certainty among public water systems, consumers, property owners, and regulators regarding their long-term performance. This concern is accentuated by the lack of long-term installations in the U.S. in Canada, and by the disparity between estimated service life and warranty period for commercially available lining and coating technologies. Kirmeyer et al. (2000) recommended long-term field trials. Several utilities in the U.S. and Canada have participated in field trials, but if any follow-up studies have been done to monitor the long-term performance of the linings and coatings involved in these trials, it does not appear that the information has been widely circulated.

In summary, lining and coating technologies can potentially reduce costs and provide other benefits to both utilities and property owners, and therefore merit consideration as alternatives to LSL replacement. Key stakeholders (public water systems and their consultants, consumers and property owners, and state and provincial regulators) could better evaluate linings and coatings as alternatives to LSL replacement if they had more information about their technical feasibility, long-term performance, cost effectiveness, and water quality impacts.

CHAPTER 2
IDENTIFICATION AND EVALUATION OF LINING AND COATING TECHNOLOGIES

CLASSIFICATION OF LININGS AND COATINGS, AND IDENTIFICATION OF OPTIONS FOR LSLS

Linings and coatings can be classified based on their structural properties, as described in Appendix A of AWWA's *Manual of Water Supply Practices M28 – Rehabilitation of Water Mains* (AWWA 2014b). All linings and coatings suitable for use in water service lines fall into the same class (Class I, non-structural linings). A relatively thick epoxy coating could provide enough structural strength to qualify as a Class II liner, but using a thicker coating in a water service line would provide no additional water quality benefits and would simply hinder flow. If a water service line needs structural strengthening, e.g., due to corrosion, it would be better to replace it than to install a structural lining, with rare exceptions.

Word usage pertaining to linings and coatings varies among authors and organizations. AWWA (2014b) refers to epoxy coatings as epoxy resin linings, and collectively refers to all linings and coatings as linings. Other authors make a distinction between the two, but definitions vary. In this report, the word 'coating' refers to any protective barrier initially applied as a liquid (like paint), which then dries (cures) to form a solid barrier that might reasonably be referred to as a liner, and many prefer this terminology.

ASCE (2016) groups pipeline renewal methods, according to their method of installation, into six categories: cured-in-place pipe (involving materials saturated with a thermoset resin); cement mortar linings; spray-in-place polymer linings (including epoxy, polyurea, and polyurethane coatings); sliplining; close-fit pipe; and fiber-reinforced polymer linings. Of these categories, only spray-in-place polymer linings, sliplining, and close-fit pipe could conceivably be used to line or coat water service lines using existing technologies.

In their landmark study of LSL rehabilitation and replacement techniques, Kirmeyer et al. (2000) reviewed and evaluated a number of lining and coating technologies. Their report and its predecessor by Tarbet et al. (1999) are highly recommended for those seeking additional information about LSL replacement techniques and the history, advantages, and disadvantages of LSL rehabilitation methods. Kirmeyer et al. (2000) made specific mention of two technologies not explicitly identified by ASCE (2016); these were expandable PET liners (a close-fit pipe technology that the manufacture does not consider to be a form of slip-lining), and sliplining with thin, inflatable PE liners. They also mentioned a cured-in-place pipe lining technology (Paltem^{TM}) in which a polyester hose coated with polyethylene on one side and epoxy on the other is inverted into a pipe and heat is then applied to cure the epoxy. This method is reportedly applicable only to pipes three inches or larger in diameter, offers no obvious advantages over epoxy coatings for LSLs, and does not appear to have ever been used to line LSLs. Therefore, it was not considered further in the present study described herein.

Kirmeyer et al. (2000) addressed epoxy coatings, but made no mention of polyurea or polyurethane coatings, which were being used for other applications at the time of their report, but not for coating water service lines. They also mentioned a calcite deposition technology that was then under development; but this technology would not be suitable for LSLs exposed to an aggressive water, i.e., those most likely to cause an exceedance of the AL for lead. This technique may appear attractive to some, since depositing a thin layer of calcite on pipe surfaces is often described as a goal of drinking water stabilization practices; but such deposits are rarely well formed in practice, are often porous, and should not be relied on to control human exposure to lead in drinking water.

Based on Kirmeyer et al. (2000), ASCE (2016), and information obtained from other reports (published and unpublished), utility personnel, manufacturers, engineers, technical experts, and others, as outlined in more detail in Chapter 1, the investigators developed the following list of candidate technologies for further evaluation:

- Epoxy coatings
- Polyurea (PUA) coatings
- Polyurethane (PUR) coatings
- Sliplined polyethylene terephthalate (PET) liners
- Sliplined loose-fit high-density polyethylene (HDPE) liners
- Sliplined close-fit HDPE liners

Each of these technologies has either been proven to be or would be expected to be effective in preventing lead release into drinking water, and implementable at reasonable cost under circumstances that might be advantageous to a public water system or property owner. Any technology not meeting these basic criteria (i.e., availability, effectiveness, and affordability), which is the case for other technologies mentioned above that were not included in this list, does not merit further consideration until circumstances (e.g., product features or customer needs) change and these criteria are met.

EVALUATION CRITERIA FOR CANDIDATE TECHNOLOGIES

In addition to availability, effectiveness, and affordability, other criteria are important to both public water systems and property owners considering lining or coating LSLs as an alternative to replacement. These include:

- Cost savings in comparison to LSL replacement
- History of success in relevant applications
- Suitability for use in aged pipes, especially if corroded or scale encrusted
- Ability to bridge gaps, repair leaks, and control corrosion
- Surface preparation requirements, e.g., scraping, sandblasting, drying
- Ease of installation, including size and number of access pits
- Ability to negotiate tight bends, elbows, and tees
- Time required for installation and to return to service
- Impacts on water flowrate and pressure
- Potential to minimize disruptions to vehicular and pedestrian traffic
- Potential to minimize damage to historic sites, landscaping, driveways, sidewalks, etc.
- Potential to minimize damage to other utility lines
- Service life
- Warranty period
- Potential to leach constituents into water that might after health or water quality
- Certification to NSF/ANSI Standard 61

- Potential to support biofilm growths

Based on many discussions with stakeholders, and especially water utility personnel and property owners, who are usually financially responsible for their LSLs, cost is usually the first criterion that comes up in a conversation about alternatives to LSL replacement. Cost is not necessarily the most important concern, but in logically thinking through alternatives, people want to establish the rationale for considering them. If there are no cost savings involved, the next logical step is to inquire about the added benefits that would justify an alternative course of action. Even if there are cost savings, many will ask if there are other benefits besides cost savings; but the second most commonly mentioned criterion after cost is whether linings and coatings will leach contaminants into the water that may affect health. Both cost savings and health concerns are discussed in more detail below (in the next section of this chapter). Since cost savings are closely related to many other criteria listed above, discussion of cost savings per se is the last criterion discussed at the end of the next section of this report, after the other criteria are considered. Health and water quality concerns associated with chemical constituents leached from linings and coatings are also addressed as the primary focus of Chapters 3 and 4.

EVALUATION OF CANDIDATE TECHNOLOGIES

History of Success in Relevant Applications

None of the candidate technologies has been extensively used on LSLs in the U.S. or Canada; but each has a history of success in LSL applications elsewhere around the globe, albeit a relatively limited history in the case of PUA/PUR coatings, since the only product certified for use in LSLs has been on the market for only a few years. Epoxy coatings have long been used to rehabilitate interior plumbing; and both epoxy and PUA/PUR coatings have a history of success in related applications, such as coating water mains, drains, and sewers. Moreover, PET is extensively used to make beverage containers, and epoxies and polyurethanes are widely used in a variety of consumer products. Therefore, both public water system personnel and their customers are inclined to feel familiar and comfortable with these technologies and to view them favorably in terms of both performance and reliability, even if they have no direct knowledge of their use in LSLs. Nevertheless, when a public water system considers lining or coating a large number of LSLs, or when a customer considers lining or coating the LSL connected to their home, the cost is significant enough that the buyer can be expected to seek additional information and assurances that a particular technology can and will be successfully applied if a contract is signed.

For public water systems, a common approach in such circumstances is to invite the manufacturer or a representative to demonstrate their technology. For LSLs, this typically involves lining or coating a limited number of LSLs in the field in what is usually referred to as a trial, a demonstration, or a pilot test. A demonstration can be very helpful in promoting understanding of a particular technology and reassuring potential buyers. A demonstration also gives the manufacturer and opportunity to become familiar with local conditions, which strongly influence costs and the likelihood of successful installations.

There is a tendency to equate the results of a demonstration test of a particular technology with its history of success, at least on a local level; but it is important to recognize that the success rate for a given technology is likely to be lower during demonstration tests than for a full-scale program involving numerous installations. Possible reasons for this include the following:

- Only a fraction of LSLs in a given service area, perhaps 50 to 75 percent by some manufacturers' estimates, are suitable candidates for lining or coating; and, in a full-scale program, some unsuitable sites would be screened out ahead of time and others would be identified in the early stages of installation and the LSL might be replaced instead of being lined or coated
- During a demonstration, the installation crew may feel compelled to complete the installation at a designated site, even when problems such as sharp bends or other obstructions are encountered that would, under other circumstances, suggest a different course of action
- The installation crew, if brought in from outside the area, may be unfamiliar with local conditions, and they may also not bring along all of the tools and equipment they would ordinarily have on hand when performing installations on a routine basis
- Demonstrations typically involve a very small number of installations, in which case any conclusions about installation success rates based on the results of the demonstration will be inherently unreliable due to the small sample size involved

These issues are evident in some of the water utility case studies described in Chapter 5. Prospective users of these technologies should recognize that a manufacturer will factor their estimated installation success rate into their pricing and, if the potential cost savings associated with lining or coating are substantial relative to replacement costs are significant, then a certain installation failure rate can be tolerated. In a well-organized system-wide program, the installer will be prepared to replace an LSL that cannot be successfully lined or coated.

Suitability for Use in Aged Pipes

All of the candidate technologies are well suited for use in aged pipes and can effectively bridge gaps, repair leaks, and control corrosion. In fact, several of the candidate technologies were developed for, and/or have been used for, these purposes in larger water lines (mains). There are, of course, both physical and economic limits to the use of linings and coatings in heavily corroded or heavily encrusted water service lines. If a water line is near failure due to corrosion, it makes little sense to line or repair it, especially with a non-structural or semi-structural lining or coating. HDPE pipes could withstand the pressure in a water service line compromised by corrosion, but this option is not attractive for water service lines for other reasons noted below.

When used in aged-pipes, all of the candidate technologies require at least some surface preparation prior to installation, typically scraping or pigging to remove deposits. If the deposits are heavy and/or difficult to remove, this may preclude lining or coating as a matter of practicality and/or cost. As noted by Kirmeyer et al. (2000), the ability to pass a small pig through an LSL and its condition when recovered are simple, useful indicators of the likelihood of that an LSL can be successfully lined or coated. PET liners do not actually adhere to the surface of an LSL, so require less surface preparation than coatings. Epoxy coatings require sandblasting to pit the surface well enough to support a good bond between the epoxy and the pipe wall. Sandblasting will also remove scale deposits. For PUA and PUR coatings, the surface must be both clean and dry, so special cleaning and drying processes are employed.

Ease of Installation and Ability to Negotiate Bends

All of these technologies are trenchless technologies and use the existing water service line as a conduit, so trenching is avoided and there is no moling, guided drilling, or cable pulling involved, all of which make lining or coating advantageous relative to common LSL replacement methods. In most cases, pits must be dug to provide access to each end of the LSL to be lined or coated, but in some cases, only one pit is needed, e.g., if one end can be accessed in a meter pit, through a shut-off valve, or in the basement of the home or building served by the LSL. One end may already be exposed when a water main is being replaced; but in such cases, many water utilities would take advantage of the opportunity to completely remove their portion of the LSL, unless local conditions are such that lining or coating the LSL would be advantageous. For example, if for some reason an LSL running underneath a street (a long-side LSL) cannot be pulled, lining or coating the LSL might be an especially attractive alternative to replacement using the trenching method (i.e., digging up the street).

Not all installations go smoothly, especially when working underground on a pipe that cannot actually be seen. There may be obstructions that interfere with the lining or coating process; joints where the LSL is enlarged, constricted, or offset; sharp protrusions able to tear a liner; or bends too sharp to accommodate insertion of a PET liner or sliplining with an HDPE pipe. In some cases, it is possible to work around the problem; in other cases, it may be necessary to abandon the effort to line or coat an LSL and to simply replace it. The risk of failure factors into cost estimates, and can be better defined in service areas where distribution system personnel have experience with LSL replacements and know what types of problems are likely to be encountered.

Tight bends are a problem for all of the technologies involving pipe insertion or sliplining, since the ability to pass the pipe through a bend will be limited by its bend radius. This is more of a problem in some locations than others, depending on the extent to which the original LSL was bent during installation, perhaps to circumvent obstructions, or if it was cut long and then coiled up to take up the excess. In the latter case, the coiled length can simply be cut out and discarded if it happens to be exposed when the access pit is dug, or if a probe indicates it is close by. PET lining or sliplining must normally be terminated at each elbow or tee, then continued on the other side, with a new elbow or tee used to reconnect the lines segments. Tight bends are especially problematic for HDPE liners, since they are relatively stiff and relatively large compared to the ID of the pipe being lined, even if they were to be folded to facilitate insertion, a feature not available for pipes of this size.

Bends, elbows, and tees are not a problem for epoxy, PUA, and PUR coatings, since they are applied as liquids. They need to be applied properly, of course, to avoid pooling at the bottom of vertical bends or coils, and to adequately coat both branches connected to a tee.

Installation Time and Return-to-Service Time

Each candidate lining and coating can be installed very quickly once the access pits are dug, provided no problems are encountered, but some require additional time before the service line is returned to service. Some epoxy coatings require relatively long curing times, 12-16 hours according to AWWA (2014b). ASCE (2016) notes that a 16-h return-to-service time is common when epoxy coating water mains. Some manufacturers have developed epoxies that cure more rapidly, resulting in return-to-service times of 2 to 4 hours. PUA and PUR coatings dry very rapidly, so rapidly in the case of PUA that some manufacturers actually attempt to slow the reaction so the coating has time to fully wet the pipe surface and form a better bond (Dunn 2014). Additional curing time may be required by a regulatory authority, or as part of an approved procedure (instructions for use) related to product certification, to minimize leaching of certain constituents in the water. PET liners and sliplined pipes are factory cured and do not need to be cured in the field. PET liners are expanded using pressurized hot water for a relatively short period of time. Regardless of the lining or coating process employed, additional time is needed to dig access pits, to disconnect the service line, to install a bypass line if water service is to be maintained during the lining or coating process, and to flush the lines after installation is complete.

Impacts on Water Flowrate and Pressure

Any lining or coating has a finite thickness and will reduce the cross-sectional area of the host pipe. Under other circumstances, one might assume that this would constrict the flow and create a higher pressure drop. However, when a service line is cleaned its cross-sectional area may be significantly enlarged, and linings and coatings tend to have much smoother surfaces than aged pipes, so lining or coating a pipe often results in a higher flowrate (and lower pressure drop). However, if a thick coating is applied or a thick-walled liner is inserted, the water flowrate may indeed decrease.

Effects on water flowrate can be a significant concern for public water systems. Some often receive complaints about low flow and/or pressure from their customers, especially those in older parts of the service area where LSLs are typically located, and where smaller-diameter pipes were commonly used in the past. Many LSLs have an inner diameter (ID) of only about 1/2 to 5/8 in., whereas modern water services made of copper or various plastics typically have an ID of at least 3/4 in. Some utilities are reluctant to approve any work on their distribution system that is not consistent with their current standards and practices. One distribution system superintendent the investigators spoke with (in confidence) indicated that to reduce low-flow complaints his utility was considering requiring replacement, rather than rehabilitation or repair, of any water service line that needed to be worked on if it had an ID smaller than specified by the current city code.

Potential to Minimize Disruptions and Damage

All of the candidate technologies offer significant advantages over conventional trenching methods with respect to potential to cause both disruptions and damage; and this is also true, albeit to a lesser extent, relative to trenchless technologies used to install a new water service line along a new route, or even cable pulling to remove an LSL and pull in a new water service line behind it. Each of the candidate technologies requires relatively small access pits relative to those required for LSL replacement, and aside from the access pits and connecting bypass lines, if used, little else is disturbed because application of the lining or coating takes place inside the existing LSL.

Service Life and Warranty Period

The estimated service life of each candidate lining or coating is many decades long. Although most such estimates are made by the manufacturer, the materials used in each of the candidate technologies have been used in similar applications for a very long time, so there is generally a good basis for manufacturer's estimates, and they typically do not differ much from independent estimates. The durability (service life) and performance of selected linings and coatings are discussed in more detail later in this chapter. An important point to note is that some stakeholders do not consider lining or coating an LSL to be a permanent solution, since many LSLs have already been in service for 90 or more years and might last another century or two – their durability being one of the major reasons they were used in the past. However, although a lining or coating may not outlast an LSL, it might very well outlast a copper or plastic water service line used to replace an LSL. When a lining or coating is economically evaluated as an alternative to LSLR, its service life should be compared to the service life of the piping material that would otherwise be used to replace the LSL, not to the service life of the LSL.

One issue that can concern both public water systems and property owners is a discrepancy between the warranty period and the estimated service life of a lining or coating. This can lead a buyer to wonder whether a manufacturer trusts the estimated service life of their product. However, in some cases the warranty is provided by a contractor licensed to install the lining or coating, and the terms of the warranty are established or negotiated as a business decision on the part of the contractor. Also, some manufacturers and many contractors are relatively small corporations that may be limited in their ability or willingness to accept a large long-term liability even though they strongly believe in the quality of their product. Another very important consideration is that manufacturers recognize that the actual service life of any lining or coating will depend heavily on how well the surface was prepared and whether the installer followed the directions carefully enough to ensure that the lining or coating was properly installed. One manufacturer of epoxy coatings (not used in LSLs) cited household paint as an example. The paint might be expected to last 10 to 20 years, but might start peeling off in less than 5 years if applied to a poorly prepared surface or one in need of repair due to its poor condition; but the buyer is likely to blame the paint. Significant discrepancies between service life and warranty period are common for many products, and should be evaluated using due diligence.

Potential to Leach Contaminants into Water

After cost, potential leaching of constituents into the water and their possible effects on human health and water quality was typically the second issue raised in conversations with public water system personnel, consumers, and regulators; and some individuals were clearly more concerned about this issue than with costs. Known leachates that may affect health, including a number of emerging contaminants, are already controlled, or indirectly regulated, by requiring products and materials used in contact with potable water to be certified as meeting NSF/ANSI Standard 61 (NSF 2016a). However, many utilities and individuals are concerned that a new contaminant will be identified in a lining or coating in the future, and they will once again be faced with the need to replace their water service lines. This is a valid and logical concern, and there is no guarantee that such a situation will not arise. An appropriate response might include the following points:

- Use of water service lines cannot be avoided without a major change in current utility practices and consumer habits, and they must be made out of some material
- Any material potentially useful for making water service lines might someday be found to be leaching a constituent into the water that raises concern or is found to cause adverse health effects, but this will always be true of any material used and is not a valid reason to delay taking action to address known problems

- The known and suspected health risks associated with lead are far greater than those associated with trace constituents leached from other plumbing materials, including linings and coatings
- The materials used in linings and coatings are widely used in numerous other applications consumers are familiar with (e.g., beverage containers in the case of PET), so any future problems of this sort will not be limited to water service lines and will need to be addressed by society as a whole, not just water utilities and property owners

Water utilities and property owners should use products and materials certified as meeting NSF/ANSI Standard 61 whether replacing, lining, or coating an LSL. All of the candidate technologies are either certified as meeting NSF 61 (or equivalent, if used in countries outside North America, such as those in the UK), have previously been certified, or employ materials that have been certified. As suggested by the wording of the previous sentence, certification is relatively fluid for some lining and coating technologies, especially those serving relatively small markets in multiple countries. Very few LSLs have actually been lined or coating in the U.S. and Canada, whereas lining and coating of water mains is relatively common. In recent years, new or improved technologies have become certified for use in LSLs; some products are no longer certified, not necessarily because they failed a certification test but perhaps because they were replaced by the manufacturer with better products or materials or because the manufacturer did not have any active projects in a country requiring a particular certification; some products and materials are not currently certified but would be expected to meet certification requirements; and some products are certified for use in the U.S. and Canada, but not in the UK, and vice versa.

Potential to Support Biofilm Growths

Organic chemicals leaching from a lining or coating material, if biodegradable, could stimulate the growth of microorganisms growing in a biofilm attached to the surface of the lining or coating or attached to downstream surfaces such as interior water lines and plumbing fixtures. Such growths could potentially affect water quality (taste, odor, turbidity), influence corrosion rates and disinfection byproduct formation, or support the growth of opportunistic pathogens. In the UK and Australia, products used in contact with drinking water must, as part of the approval process, be certified as meeting standard BS 6920 or AS/NZS 4020, respectively, each of which includes a test to determine whether the product stimulates the growth of aquatic microorganisms. See van der Kooij and van der Wielen (2014) for an excellent collection of papers addressing in detail various aspects of microbial growth in drinking-water supplies and why it is important. The following paragraphs summarize information specific to linings and coatings potentially suitable for use in water service lines.

The high-molecular weight polymeric materials used in liners and plastic pipes are generally resistant to biological deterioration, but smaller molecular weight additives (plasticizers and other fillers) also present have greater potential to leach out and provide a nutrient source for microbial growth (Morton and Surman 1994). This leaching process can create a diffusion gradient in the bulk material and cause the material to become more brittle over time, a process known as biodeterioration (Flemming 2010). Biofilm growth could thus affect both drinking water quality and the long-term durability of the lining material, as brittle plastics have decreased structural integrity and may allow for increased penetration of water and ions.

Mesman et al. (1995) studied the biofilm formation potential of PET, measured as the average concentration per cm^2 after 8, 12, and 16 weeks, and compared it to that of glass, Teflon®, rigid PVC, and soft PVC. The concluded that the biofilm formation potential of PET was similar to that of Teflon® and rigid PVC and considerably less than that of soft PV, and that it was suitable for use in contact with drinking water. Other studies of biofilm growth on PET found in a search of the literature focused primarily on PET beverage containers. The growth of mold spores in PET bottles was identified as being associated with leaching of di-n-butyl phthalate (DnBP), which provided a substrate for spore growth (Criado et al. 2005). PET bottles have also been used as an attachment surface for biofilms of *Mycobacterium avium*, an opportunistic pathogen species (Tatchou-Nyamsi-Konig et al. 2009).

PET is not unique in supporting a moderate level of biofilm growth, which also occur on HDPE, cross-linked polyethylene (PEX) and polyvinyl chloride (PVC) surfaces (e.g. Dailloux et al. 2003, Rogers et al. 1994, van der Kooij et al. 2005, Rozej et al. 2015). A number of these experiments, however, were carried out under conditions that are not typical of water service line conditions. The investigators found no evidence that biofilm growth is a problem for PET liners in water service lines, but suggest that it might be worthwhile, given the growing interest in opportunities pathogens in plumbing systems, to examine biofilm growths on PET liners, epoxy coatings, and PUA/PUR coatings, versus those found on copper and plastic service lines under similar conditions, to determine whether some materials are better in this regard than others and if any appear to be enhancing the growth of known or emerging pathogens.

Various organic compounds (hydrocarbons, esters, amides) present in polyurethane polymers represent possible food sources for biofilm growth (Seal and Pathirana 1982). Polyurethanes are susceptible to fungal growth (Darby and Kaplan 1968, Shuttleworh and Seal 1986), and several bacterial strains have also shown the ability to utilize PUR as a sole carbon source for growth (Akutsu et al. 1998, El-Sayed et al. 1996). Polyester polyurethanes appear to be more easily degraded by microbial attack than those from polyethers, which may be due to hydrolysis of ester bonds in the polyester material (Morton and Surman 1994).

There is little evidence of biofilm growth on epoxies. One study by Schoenen (1989) did describe the growth of bacteria on both solvent-containing and solvent-free epoxy resins, but suggested that growth in solvent-free epoxies depended on the mixing proportions of the epoxy precursors and the curing conditions. As with PET, more research is needed to fully assess the likelihood and implications of biofilm growth on epoxy- or PUR-coated pipes under conditions typical of those encountered in water service lines.

Cost Savings in Comparison to LSL Replacement

The potential for cost savings is the most important criterion, directly or indirectly, for all stakeholders – indirectly if one includes costs associated with other criteria, such as the avoided costs associated with traffic disruptions and property damage. If there are no net cost savings (with all costs considered), there is no incentive for water utilities or property owners to use linings or coatings as an alternative to LSL replacement, no reason for manufacturers to develop and market lining and coating technologies for use in LSLs, and no need for state and provincial regulators to assess their potential health impacts or to establish guidelines and regulations for their use.

Despite the importance of costs in the decision-making processes of both public water systems and property owners, good cost estimates are very difficult to obtain and highly site specific. In the past, before the landmark study by Kirmeyer et al. (2000), LSLs were commonly replaced using the standard trenching method, which served as the benchmark for estimated cost savings. Compared to LSL replacement by trenching, lining or coating a 25 to 50 ft. long LSL would likely result in an average cost savings of perhaps 20 to 40 percent or more. Since that time both lining and coating technologies and LSL replacement methods have evolved.

Today, many utilities still use the traditional trenching method to install water service lines in new housing developments and sometimes to replace LSLs, especially shorter LSLs, when there are no obstructions or conflicts with other utilities. However, many utilities commonly employ trenchless LSL replacement methods, such as cable pulling (with a new line dragged in behind), moling, or guided (directional) drilling, especially when they encounter obstructions or must make connections to mains located on the opposite side of the street. The potential cost savings associated with lining or coating depend on the replacement method being used as the baseline for cost comparisons, and the baseline may change depending on conditions encountered in the field. For example, a utility may normally use the cable pulling method to replace LSLs, but if this method cannot be used (e.g., due to soil conditions or the length of the LSL), another method such as trenching or guided directional drilling must be used, which will alter the potential cost savings associated with lining or coating. Some water utilities have chosen to line or coat large numbers of LSLs, maximizing cost savings by taking advantage of economies of scale, while others consider lining or coating primarily as an alternative in situations where replacement is unusually difficult and expensive.

Like LSL replacement methods, lining and coating technologies have also evolved over time. Manufacturers have developed improved cleaning and installation procedures, coatings that cure much more rapidly, better equipment, and software to help optimize installation under site-specific conditions (e.g., ground temperature). These and other improvements have helped maintain the potential for lining and coating technologies to produce cost savings for water utilities and property owners.

Quantifying potential cost savings in a specific service area can be very challenging. One challenge is that installation costs depend on many site-specific factors, including:

- Location and availability of licensed installers (typically the manufacturer or a contractor or utility licensed to use equipment leased or purchased from the manufacturer)
- Number of LSLs to be lined or coated
- Spatial and temporal distribution of the LSLs to be lined or coated
- Length of the LSLs to be lined or coated
- LSL depth below ground
- LSL condition, especially quantity and characteristics of corrosion and scale deposits
- Frequency of LSLs with sharp bends or coils
- Frequency of LSLs with constrictions or sharp protrusions
- Number, size, and depth of access pits needed
- Return-to-service time and need for bypass piping
- Location of LSLs relative to water mains, roads, sidewalks, walls, etc.
- Warranty period (if negotiable)
- Assignment of risks and liability
- Control of scheduling
- Other contract terms

For a specific service area, some of the factors listed above, such as average LSL depth, are likely to be already known to utility personnel, and can be determined without undue effort; but two very important factors depend on development of a specific plan for LSL lining, coating, or replacement. These two factors are the number of LSLs to be lined or coated, and their temporal and spatial distribution within the service area. These factors govern the economy of scale for the lining or coating process, and will therefore significantly affect the estimated cost of the program. Preparing (or updating) a well-organized system-wide LSL replacement program is a good way for a utility to minimize the overall costs of LSL replacement in their service area. However, since the utility will want good cost estimates to use in their planning process, while a manufacturer will want to know the details of the utility's plan before quoting a cost, both parties may find themselves waiting for the other while progress grinds to a standstill. One solution might be for manufacturers to quote a range of costs for representative scenarios involving different numbers and distributions of LSLs. The best approach in a given service area is likely to be to bring all stakeholders together to cooperate in developing (or revising) a good system-wide LSLR program, incorporating lining and coating technologies when and where they help meet the needs of the community, then refining cost estimates as plans progress.

One cost-related complication that can cause misunderstandings is that manufacturers will most likely provide cost quotes or estimates based on the installation costs, including mobilization costs, labor, and materials. However, utilities must also consider other costs, including staff time to communicate with property owners and schedule the work; the time and expense of bypass connections (if provided by the utility); pavement and/or street repair; collection and analysis of samples; and any follow-up required with property owners and consumers. These added costs can exceed the direct cost of lining, coating, or replacement. Thus, it is important, when communicating with various stakeholders about costs, to be clear about what costs are included in cost estimates.

Another complication for utilities is that uncertainty over the service life of a lining or coating makes life-cycle analysis (or calculation of the pay-back period) challenging. Many utilities today, especially those actively engaged in asset management programs, are performing life-cycle analysis on components of their distribution systems. If so, they are likely to have reasonably good information on the service life of water service lines in their system, including LSLs and newer service lines, especially those made of copper. They are likely to have less reliable information about newer materials they may only recently have started using (or do not use) for water service lines, such as HDPE and other plastics. For LSL linings and coatings, there are likely to have almost no information, except for the manufacturers' estimates, unless they extrapolate their experiences from other applications to LSLs, which some may be comfortable doing for epoxy coatings or other technologies they have used in the past.

Caution should be exercised in deciding which costs to include in economic analysis of alternatives. For example, some manufacturers and utilities cite savings in chemical costs (for orthophosphate addition or pH adjustment) as an advantage of lining or coating LSLs; but the same advantage would be gained by replacing LSLs. Cost savings associated with chemical addition should be considered, where applicable, in deciding whether or not to control lead by chemical means versus lining, coating, or replacing LSLs, but not when deciding whether to line, coat, or replace LSLs. Also, the potential for chemical cost savings depends on the regulations and policies applicable to a given utility. For example, a utility in U.S. feeding orthophosphate for corrosion control treatment required by the LCR might not be permitted to stop feeding orthophosphate even after lining, coating, or replacing their LSLs; and continuing to practice corrosion control treatment will help minimize exposure to lead from other sources, such as lead solder and plumbing fixtures. On the other hand, a utility in the UK feeding orthophosphate might be able to stop feeding it after lining, coating, or replacing their LSLs if it is no longer need to comply with the UK's 0.010 mg/L lead standard; and some UK water companies are reportedly lining customer-side LSLs for this very reason (Gillanders 2016a).

Aside from the cost estimates cited in Chapter 1, the investigators were able to obtain relatively little in the way of good cost information pertaining specifically to lining or coating of water service lines. A water company in The Netherlands estimated 5-30% savings on installed costs, excluding avoided damages, noting that costs depend heavily on site layout, depth, pavement type, local labor rates, and other factors (Alferink and Elzink 2010). One manufacturer declined to provide cost information regarding a recently signed contract with a private water company to coat a large number of LSLs, citing a need for confidentiality. When lining or coating is done by utility crews, or by contractors working in concert with utility personnel and others (e.g., street departments and traffic control personnel) the overall costs of lining and coating are likely to be difficult to extract and aggregate from the separate accounting systems that may be involved, making it difficult for a utility to know and publicize the actual installation costs, which may not be particularly important to them if the lining or coating was done primarily to minimize disruptions to traffic or to avoid damage to historic buildings, other utilities, trees, or other things of value. Nevertheless, despite the lack of specific cost information, it is clear that lining or coating LSLs in lieu of replacement can result in significant cost savings, especially when taking advantage of economies of scale. As noted in Chapter 5, several major lining and coating programs are currently underway in the UK and PET liners continue to be installed in LSLs in France.

RECOMMENDED TECHNOLOGIES AND TECHNOLOGIES SELECTED FOR EXPERIMENTAL STUDY

Each of the candidate technologies meets most of the evaluation criteria reasonably well. However, two of them, sliplining of close-fit and loose-fit HDPE liners, are problematic for several reasons:

- It is very difficult to insert HDPE liners through bends, even bends that are not particularly sharp. They are relatively stiff, but using a smaller size reduces the flow and companies that fold HDPE pipe for insertion in larger pipes do not offer this option for pipes smaller than about 4 inches in diameter.
- They are relatively thick walled compared to the inner diameter of an LSL, and just about any size HDPE liner that could be slipped through an LSL would be likely to restrict the flow, which would be especially undesirable for the consumers. Reductions in flow and pressure could be remedied by using a hydropneumatic (bladder) tank, but the added cost and maintenance requirements make this option unacceptable.
- Manufacturers of HDPE pipe make pipes small enough to be sliplined through an LSL, but do not market them for this purpose. Their thinking, accordingly to representatives of several companies, is that the market is small and shrinking, sliplining small-diameter HDPE pipes into LSLs is not a particularly attractive option, and there is little profit to be made since the pipe lengths are short and very little HDPE would be used.

Therefore, the two technologies involving sliplining of HDPE pipes were dropped from further consideration. Two of the other four, PUA and PUR coatings, are similar in some respects and were not evaluated as extensively during this project as were the other technologies, for reasons noted below. Furthermore, hybrid coatings containing both PUA and PUR polymers are available, including one currently being promoted for use in coating LSLs in the UK. Therefore, PUA and PUR coatings are grouped together from this point forward in this report. Thus, three technologies are recommended for evaluation by public water systems and property owners seeking alternatives to LSL replacement. These are:

- Epoxy coatings
- Polyethylene terephthalate (PET) liners
- Polyurea (PUA) and polyurethane (PUR) coatings

An epoxy coating technology and a PET lining technology were experimentally studied as part of this project, as described in Chapter 3, and the results are presented later in Chapter 4. The investigators looked for opportunities to experimentally study a PUA or PUR coating, but during the time when laboratory experiments were being planned and conducted, only a single PUA or PUR product intended for use in LSLs was known to be under development and involved in field trials, and the manufacturer was unwilling to share details or provide a sample to the investigators for experimental purposes. The investigators were later informed by several individuals that the field trial had not been successful, but were never able to obtain any details of the trial or the reason for its failure.

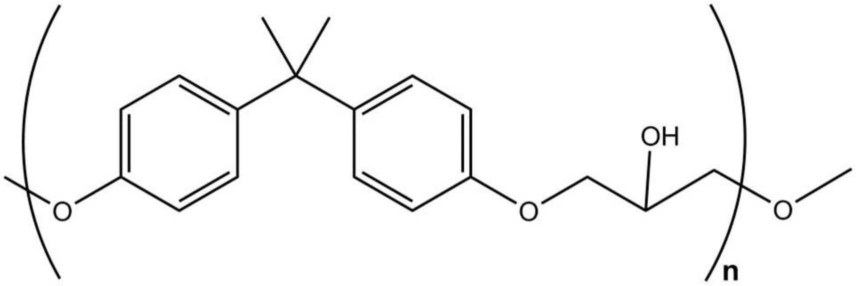
After much of the experimental portion of this project had been completed, the investigators learned of a new PUA/PUR hybrid coating that had recently been approved by the Drinking Water Inspectorate (DWI) for use in LSLs in the UK. This technology appears promising and is reportedly already being applied in the UK. The company that owns the process using this coating is in the process of having it certified as meeting NSF 61 so the technology can be marketed for use in potable water systems, and specifically for coating LSLs, in the U.S. and Canada. Although the investigators have not evaluated this technology as thoroughly as other technologies, and did not study it experimentally, it appears promising enough to recommend to water utilities and property owners for evaluation as an alternative to LSL replacement, provided of course that it is first certified as meeting NSF 61 certification requirements.

EPOXY COATINGS

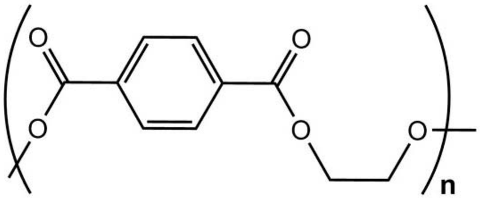
Description

Epoxy coatings are formed through the polymerization of an epoxide containing resin (Ellis 1993). Epoxies are made from a broad range of starting materials and have a range of physical properties (e.g., cure time, flexibility, and functionality). General epoxy characteristics desired for water service lines include adherence to pipe surfaces, a short curing time, long-term durability, and low leaching. Historically, potable water grade epoxies have been used in the rehabilitation of water mains (Deb et al. 2002), but their use in drinking water service lines is a relatively new application.

Epoxy coatings for contact with potable water are formed from two main starting materials (Ellis 1993, AWWA 2008a-c): a resin prepolymer and a hardener. Epoxy formulations can also contain color pigments and fillers or extenders, with specific proprietary formulations varying by manufacturer. The resin prepolymer is designed to facilitate polymerization and is often prepared from a bisphenol with reactive epoxide side chains (Ellis 1993). Common prepolymer starting materials are bisphenol A diglycidyl ether (BADGE) or bisphenol F diglycidyl ether (BFDGE). The diglycidyl ethers are formed through a reaction of bisphenol A (BPA) or bisphenol F (BPF) with an epichlorhydrin (Fried 2014). A BADGE-based resin prepolymer is shown in Figure 2.1. The epoxy mixture often contains novolac glycidyl ethers (NOGE) with approximately 30 to 40% 2-ring NOGE compounds (BADGE or BFDGE) and the remaining percentage is a mixture of 3 to 8-ring NOGE compounds (Brem et al. 2001, Robertson 2013). Although BADGE is a common prepolymer ingredient, the epichlorohydrin can be reacted with other compound classes: phenols (BPF, tetrakis phenylolethane, resorcinol, methylated phenol); alcohols (1,4-butanediol); phenolic resins (cresol, formaldehyde novolac); carboxylic and fatty acids; and aniline and other nitrogen compounds (Ellis 1993).



BADGE-Based Epoxy Resin



PET

Source: Adapted from Lane 2015.

Figure 2.1 Chemical structures of a BADGE-based epoxy resin and PET

The hardener in epoxy coatings is often an ethyleneamine such as ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), or pentaethylenehexamine (PEHA). Ethyleneamines were the first hardeners used in epoxy chemistry due to their reactivity and short chain length between active sites (the unreacted epoxide groups) that enables a tightly cross-linked, three-dimensional polymer structure (Fried 2014, Greenlee 1952). In addition to the ethyleneamines, nitrogen-, oxygen-, and sulphur-containing hardeners can also be used in epoxy chemistry (Ashcroft 1993). Nitrogen curing agents include aliphatic amines, aromatic polyamines, cycloaliphatic polyamines, hydrazine, hydrazides, imidazols, tertiary amines (dimethylaminomethyl phenol or tris(dimethylaminomethyl) phenol), and ureas. Oxygen curing agents include amino formaldehyde resins (urea-formaldehyde and melamine-formaldehyde resins), anhydrides, carboxylic acids, and phenol formaldehyde resins (phenol novolac resin or resole resins). Sulphur curing agents include polysulphides and polymercaptans. Additionally, compounds such as amine-boron trihalide complexes, quaternary phosphonium salts, and cationic salts (such as tri-arylsulphonium) have been used as curing agents.

Epoxy application to water service lines involves cleaning, coating, and curing steps. During the cleaning step the pipe is sandblasted (to remove any residues and roughen the surface to improve adherence of the epoxy), rinsed, and dried (Nu Flow 2015). To coat the interior of the pipe an air pressure system spins the epoxy onto the walls of the pipe. The final step is allowing the epoxy to cure for an appropriate period of time and then rinsing the pipe with water to remove any remaining epoxy materials (Nu Flow 2015). Deb et al. (2006) reported that a typical cure time is often estimated to be 5 to 16 hours and the entire coating process may take more than a day; but epoxies that cure much more rapidly are now available, making it possible to complete the entire application process in less than half a day. Manufacturers have worked to optimize the process such that curing and overall installation times, blistering or bubbling, uncured epoxy, incomplete or thin coverage, ringing or ridging of the coating, slumping (buildup of epoxy), water damage, and holidays (i.e., pinholes or discontinuities) are minimized (Deb et al. 2006).

Providers

There are numerous manufacturers of epoxy coatings, but only four known by the investigators to have been actively engaged in recent years in projects involving epoxy coating of water service lines and/or interior water lines in North America. These are, in alphabetical order by product name:

- CuraFlo®, Burnaby, British Columbia, http://www.curaflo.com/
- ePIPE®, Pipe Restoration Technologies (Las Vegas, Nev.), licensed in the U.S. to ACE DuraFlo Systems, LLC, Santa Ana, CA, http://www.aceduraflo.com/
- Nu Flow Epoxy, Nu Flow Technologies, San Diego, CA, http://www.nuflowtech.com/ (owned by Aquam Corporation)
- Pipe Shield AN500™ Epoxy, Pipe Shield, Mississauga Ontario, http://pipe-shield.com/

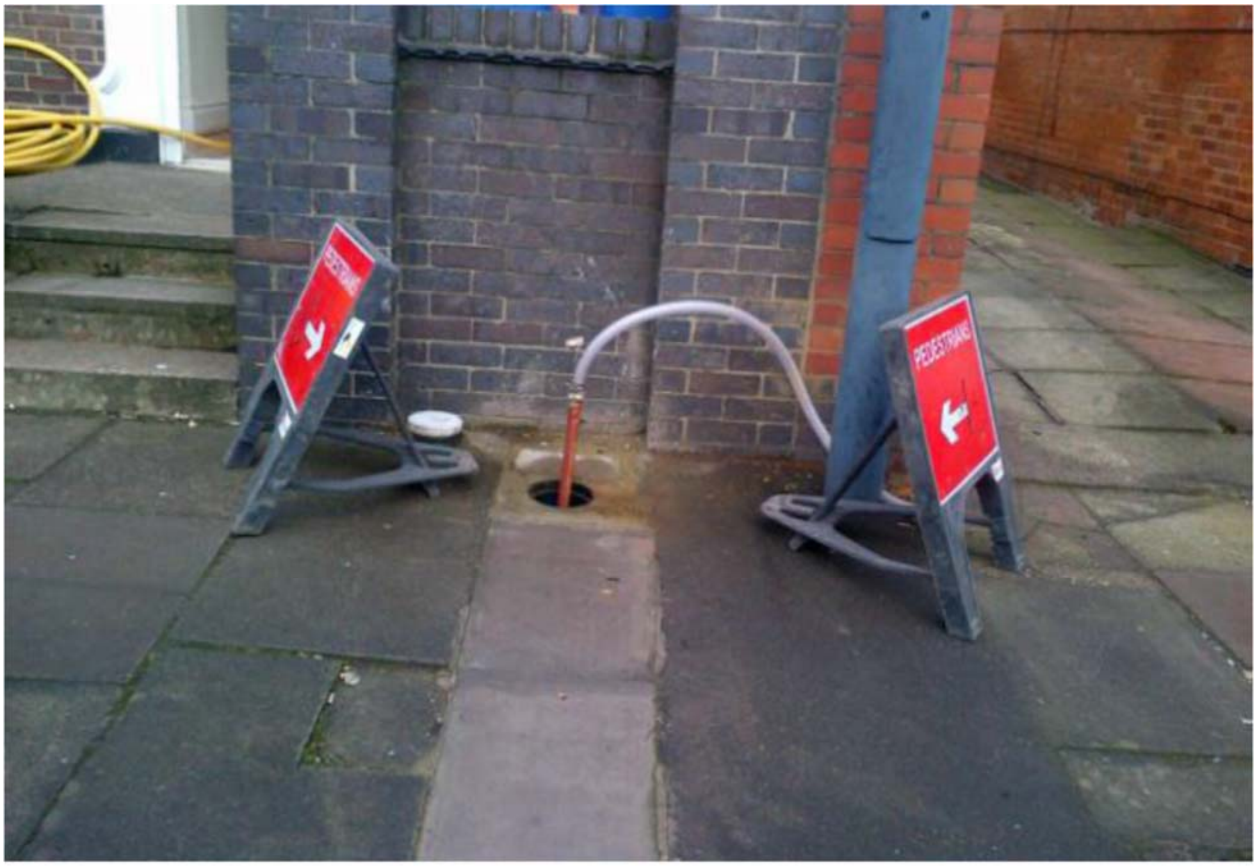
Each of these companies provides other services in addition to epoxy coating of LSLs, and all are either multinational corporations, owned by a multinational corporation, or license their epoxy product or technology in more than one country.

Only one epoxy was used in the experiments described in this report. Since epoxy formulations, applications methods, curing times, and other factors vary among manufacturers and even for different applications involving a single manufacturer, the experimental results presented later in this report (in Chapter 4) are not necessarily representative of those that would be obtained using other epoxy formulations or different application methods. The epoxy used in this study was provided by Nu Flow Technologies and was the same one formerly provided by American Pipe Lining, Inc., a company Nu Flow Technologies acquired in 2007.

Notable Advantages and Disadvantages

Epoxy coatings are known to be very durable and to strongly bond to metal surfaces. Manufacturers generally estimate the service life of an epoxy coating to be about 40 to 60 years, if properly applied to a suitably prepared surface, and there is evidence to support such claims. Deb et al. (2006) estimated a service life of 40 to 60 years for epoxy coatings in water mains, and ASCE (2016) estimates a service life of 40 years or more. Another notable advantage of epoxy coatings is that they typically require only a relatively small access pit, since they are applied as a liquid that can readily pass through tubing with a small bend radius. An extreme example of this is shown in Figure 2.2, which depicts an epoxy coating being applied through a stop tap.

The most obvious disadvantage of epoxy coatings is their relatively long curing time; but the inconvenience to customers can be reduced by using a bypass line, and some epoxy formulations are available that dry in as little as 2 to 5 hours. Another disadvantage of epoxy coatings in that they are relatively inflexible and can be damaged if a pipe is bent beyond the limit of the epoxy, e.g., when it is moved out of the way during repair work.



Source: Pipe Restoration Services, ePIPE, UK.

Figure 2.2 Applying an epoxy coating through a stop tap

Potential Leachates

Bisphenol A (BPA), a common starting ingredient in epoxy formulations, has been reported leaching from epoxy coatings into a wide variety of foods and beverages (Lane 2015), but epoxies certified to NSF 61 for use in contact with drinking water are allowed to leach no more than 10 μg/L of BPA (single product allowable concentration) into water. Compounds other than BPA can leach from epoxies, including those listed in Table 2.1. BADGE, a common starting material identified in the epoxy used experimentally in this project, has been found to leach into canned foods products. Due to public concern over BPA leaching, epoxy manufacturers are considering substituting, or have substituted, structurally similar bisphenol alternatives, such as bisphenols B, D, E, F, and S (BPB, BPD, BPE, BPF, BPS; Figure 2.3), as well as BADGE and BFDGE (bisphenol F diglycidyl ether; Figure 2.4), and some of these compounds have also been observed in foods and the environment, indicating that at least some manufacturers are starting to use them (Lane 2015).

The coatings being applied to water service lines are structurally similar to food can epoxy coatings. Thus, leachates of interest for epoxy can coatings are also of interest as potential leachates from potable water grade epoxy. Due to in-pipe curing, epoxy coatings have a greater potential for leaching when compared with pipe liners not cured in place (e.g., PET liners). There are preliminary data demonstrating that BPA and BPF can leach from potable water grade epoxies (Bruchet et al. 2014, Kosaka et al. 2012).

Hydrolysis and chlorination reactions producing byproducts of bisphenols, BADGE, and BFDGE are discussed in Chapters 3 and 4, and a number of potential byproducts are listed in Table 2.1 and depicted in Figures 2.3 and 2.4. Bisphenol diglycidyl ethers (BDGEs), including BADGE and BFDGE, are susceptible to hydrolysis and have six known by-products: BADGE-H_2O, BADGE-$2H_2O$, BADGE-H_2O-HCl, BFDGE-H_2O, BFDGE-$2H_2O$, and BFDGE-H_2O-HCl (Figure 2.4). These by-products have been reported in many canned foods (Yonebuko et al. 2008, Zou et al. 2012, Gallart-Ayala et al. 2011, Berger et al. 2001, Sendon Garcia et al. 2003). At temperatures above 40 °C reported BADGE half-lives range from 9 to 43 hours (Philo et al. 1997, Losada et al. 1993, Cottier et al. 1998) and from 12 to 52 hours for BFDGE (Losada et al. 1992). Hydrolysis of bisphenols is not expected because their functional groups do not facilitate hydrolysis reactions (Melcer and Klecka 2011).

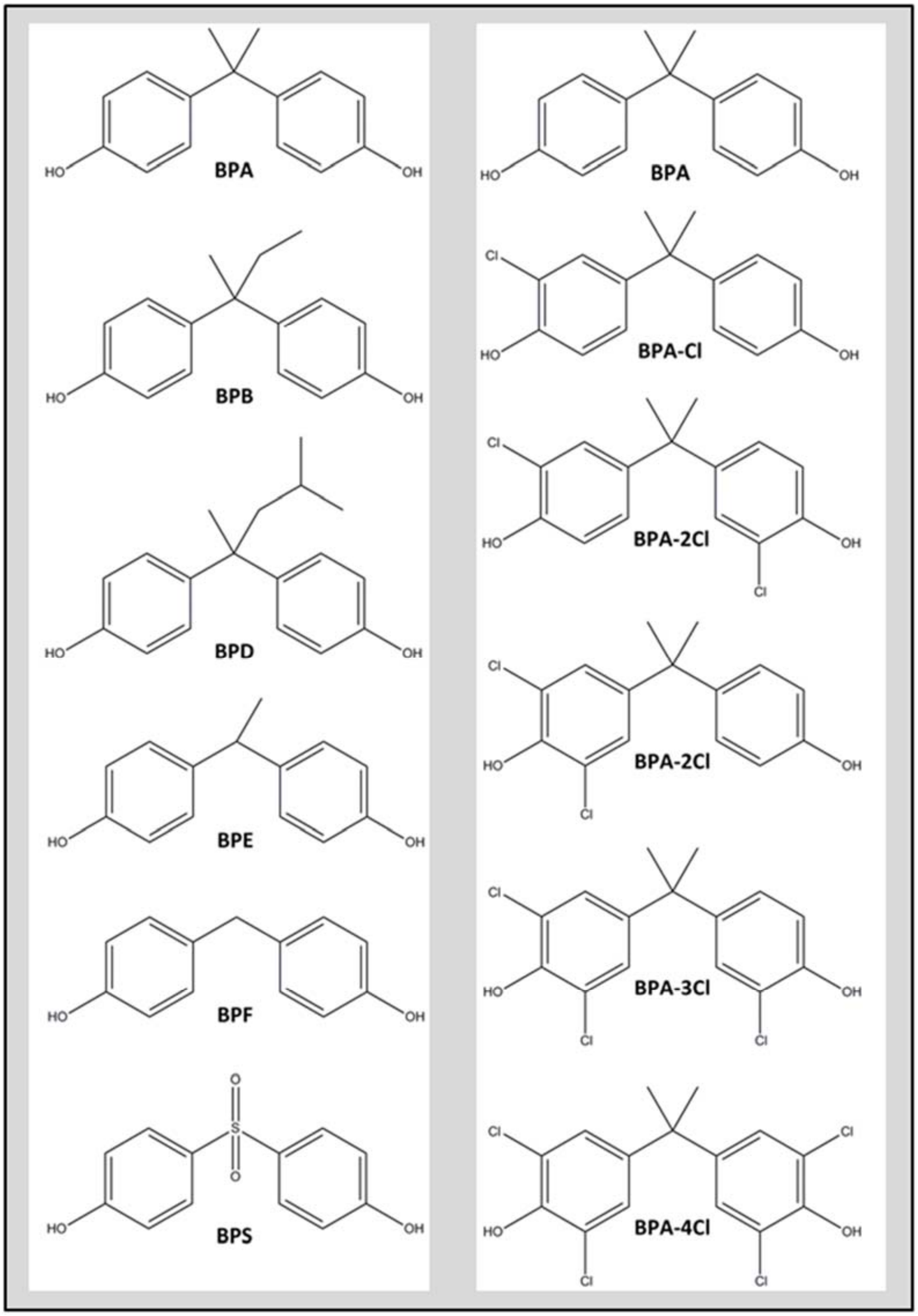
Bisphenol A is susceptible to halogenation reactions. Chlorinated by-products of BPA include mono-, di-, tri-, and tetra-chloro BPA (BPA-Cl, BPA-2Cl, BPA-3Cl, and BPA-4Cl; Figure 2.3) as well as the degradation product trichlorophenol (TCP) (Yamamoto and Yasuhara 2002, Hu et al. 2002, Li et al. 2015, Dupuis et al. 2012). These chlorinated by-products have been detected in drinking water treatment facilities (Li et al. 2015, Dupuis et al. 2012), drinking water (Fan et al. 2013), and water drawn from epoxy-coated drinking water pipes (Kosaka et al. 2012). Chlorination of BPA with free chlorine has been modeled at various pH values (20°C) and the BPA half-life with a chlorine residual of 0.2 mg/L as Cl_2 was 1.5 hours (Gallard et al. 2004). Reactivity of BPA with MCA has not been previously reported and data was not found pertaining to chlorination of bisphenols similar to BPA (i.e., BPB, BPD, BPE, BPF, and BPS).

There are also chlorinated by-products of the BDGEs, i.e., BADGE-H_2O-HCl, BADGE-HCl, BADGE-2HCl, BFDGE-H_2O-HCl, BFDGE-HCl, BFDGE-2HCl, all depicted in Figure 2.4, that have been detected in canned foods (Yonebuko et al. 2008, Zou et al. 2012, Gallart-Ayala et al. 2011, Berger et al. 2001, Uematsu et al. 2001, Sendon Garcia et al. 2003). The mechanism of BDGE chlorination with free chlorine or chloramines has not been reported. Similarly, neither the analysis of chlorinated BDGEs in water or drinking water nor kinetic modeling of BDGE chlorination has been reported.

Table 2.1
Bisphenol and bisphenol diglycidyl ether epoxy leachates and by-products

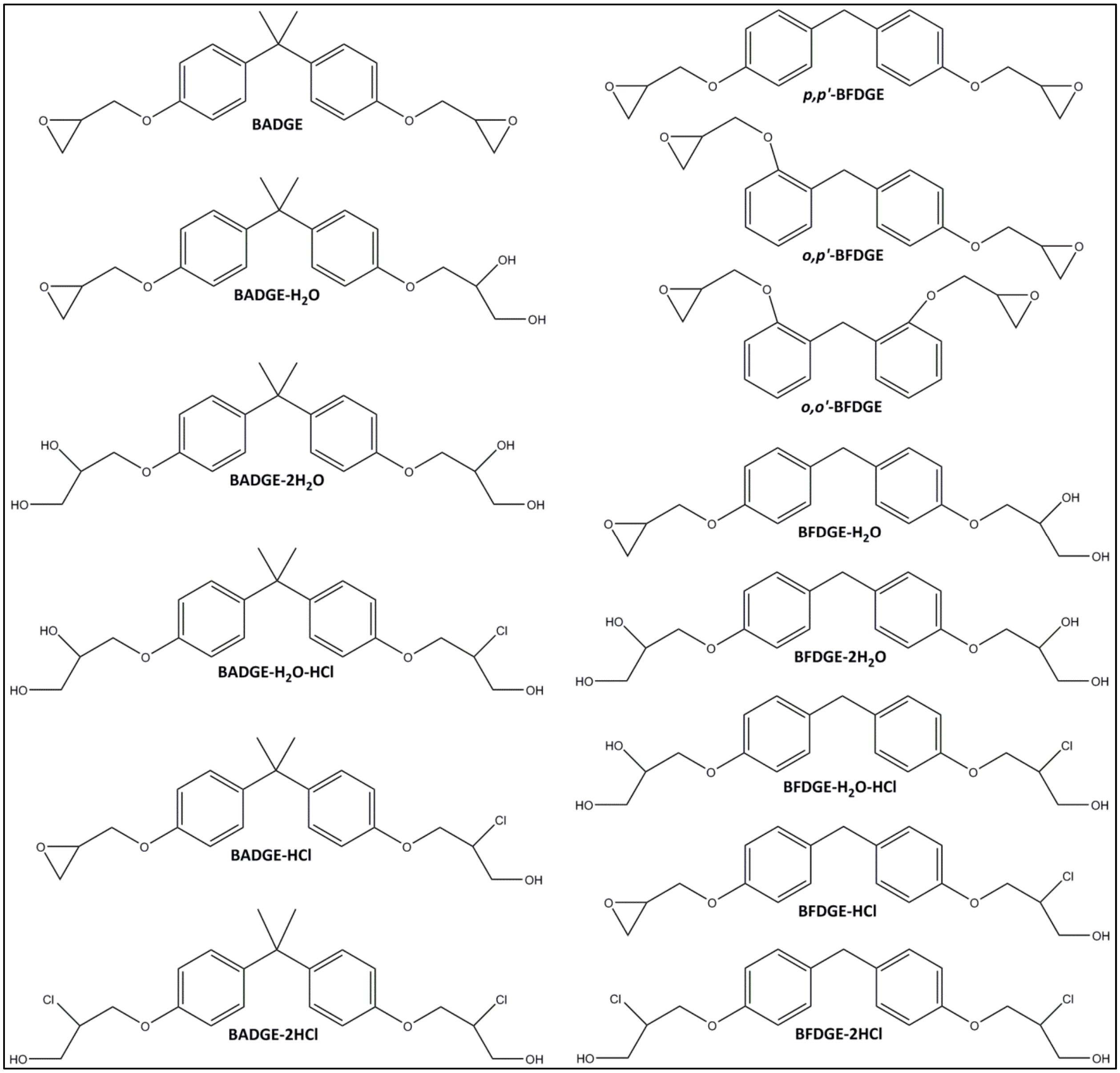
Leachate	Abbreviation	CAS #	Primary Source*
bisphenol A	BPA	80-05-7	resins
monochlorobisphenol A	BPA-Cl	74192-35-1	resin by-product
dichlorobisphenol A	BPA-2Cl	79-98-1	resin by-product
trichlorobisphenol A	BPA-3Cl	40346-55-2	resin by-product
tetrachlorobisphenol A	BPA-4Cl	79-95-8	resin by-product
bisphenol B	BPB	77-40-7	resins
bisphenol D	BPD	6807-17-6	paper
bisphenol E	BPE	2081-08-05	resins
bisphenol F	BPF	620-92-8	resins
bisphenol S	BPS	80-09-1	paper
bisphenol A diglycidyl ether	BADGE	1675-54-3	resins
bisphenol A (2,3-dihydroxypropyl) glycidyl ether	BADGE-H2O	76002-91-0	resin by-product
bisphenol A bis(2,3-dihydroxypropyl) ether	BADGE-2H2O	5581-32-8	resin by-product
bisphenol A (3-chloro-2-hydroxypropyl) (2,3-dihydroxypropyl) ether	BADGE-H2O-HCl	227947-06-0	resin by-product
bisphenol A (3-chloro-2-hydroxypropyl) glycidyl ether	BADGE-HCl	13836-48-1	resin by-product
bisphenol A bis(3-chloro-2-hydroxypropyl) ether	BADGE-2HCl	4809-35-2	resin by-product
bisphenol F diglycidyl ether	BFDGE	2095-03-6	resins
bisphenol F (2,3-dihydroxypropyl) glycidyl ether	BFDGE-H2O	303733-72-4	resin by-product
bisphenol F bis(2,3-dihydroxypropyl) ether	BFDGE-2H2O	72406-26-9	resin by-product
bisphenol F (3-chloro-2-hydroxypropyl) (2,3-dihydroxypropyl) ether	BFDGE-H2O-HCl	638193-72-9	resin by-product
bisphenol F (3-chloro-2-hydroxypropyl) glycidyl ether	BFDGE-HCl	374772-79-9	resin by-product
bisphenol F bis(3-chloro-2-hydroxypropyl) ether	BFDGE-2HCl	194672-61-2	resin by-product

Source: Lane 2015
*resin by-product = leached BPA, BADGE, BPF, or BFDGE that has formed a by-product in solution



Source: Lane 2015.

Figure 2.3 Structures of selected bisphenols and chlorinated BPA by-products



Source: Lane 2015.

Figure 2.4 Structures of selected bisphenol diglycidyl ethers and related by-products

Long-Term Effectiveness and Performance

Expected Service Life

As epoxy coatings age, a number of potential mechanisms can lead to degradation of the material and/or a loss of their protective function, including physical abrasion, stress cracking, and chemical degradation (Maxwell et al. 2005). While direct weathering and photo-oxidative processes are not an issue in lead and copper service lines, aqueous conditions, including water temperature and the presence of reactive chemical species, can impact the useful service life of the epoxy coating. The primary factor in evaluating the useful service life for these coatings is their ability to function as a protective barrier separating potable water from the metal pipe material. When this function breaks down, the utility of the coating is also gone, even if much of the coating physically remains. Unfortunately, the limited ago of existing applications of epoxy coatings to LSLs and CSLs means that there is very little direct evidence available regarding their long-term behavior in these specific applications. However, existing literature on epoxy coating use in water main rehabilitation, as well as the wider scientific literature on epoxy interactions with metal surfaces and aqueous solutions, is helpful in identifying potential issues regarding long-term use of epoxy coatings to control lead and copper release from water service lines.

The most commonly cited estimate for the service life of epoxy coating comes from a WRF report by Deb et al. (2006). This study analyzed characteristics of four epoxy coatings that were applied to steel panels and tubes and then immersed in distilled water for up to eight months. Deb et al. also examined epoxy coatings from existing water mains that had been coated between 1979 and 2000 in the UK or the U.S. Their analysis concluded that the most important single factor in establishing service life was the maintenance of a physical barrier, as measured by electrochemical impedance spectroscopy (EIS). EIS uses measurements of the electrical resistance of an organic lining or coating to estimate how well the coating acts as a barrier (McIntyre and Pham 1996). Deb et al. used EIS measurements of the historical pipe samples to estimate the length of time until the barrier degraded to the end of its useful life. Based on their results, they estimated that properly applied epoxy barriers could have service lives of 40 to 60 years. These values correspond well with existing manufacturer-provided estimates of service life, which indicate a service life of 50 years, or more in some cases (Gillanders 2011).

Before applying this estimate to epoxy coatings in lead and copper pipes, several additional issues should be addressed. The first is the assumption that the overall barrier integrity is the most appropriate measurement for lining performance. In their study, Deb at al. noted that the number of holidays (small holes left in the epoxy coating as it is applied, e.g., due to bubbles or surface impurities) per square foot varied considerably in previously lined pipe samples. Holidays allow for direct connection between the water and the metal surface. In a water main, the overall effect of holidays may not be significant, as the major goal is to slow down bulk corrosion of the pipe material. In a lead pipe, however, corrosion around holidays could, over time, allow Pb concentrations in the water to increase despite overall good coverage by the epoxy coating as measured by EIS. In further investigation, Deb et al. found that, for the most part, there was no visible evidence of rusting or loss of the steel substrate in or around holidays. This suggests that the substrate (pipe surface) below the holidays remained isolated and relatively unreactive. However, the research team did not find any similar information in the literature pertaining specifically to lead or copper service lines; therefore, it should not be assumed that holidays in epoxy coatings in lead and copper service lines are unimportant.

Another commonly cited indicator of the durability of an epoxy coating is how strongly it adheres to the surface, often measured as knife adhesion or pull-off adhesion. The epoxies studied by Deb et al. (2006) had relatively poor knife adhesion but exhibited a range of pull-off adhesion strengths. After examining the totality of their data, they concluded that adhesion strength did not matter much in the absence of holidays, but that it was important if holidays were present because it limited the ability of the corrosion associated with a holiday to work its way under the liner. This finding supports the logical assumption that the most effective and long lasting epoxy coatings are those that bond strongly to the surface and are applied without introducing holidays.

An additional variable in comparing results from water main coatings to LSL coatings is the surface-area-to-volume ratio involved. Not only are residential water service lines far smaller in diameter than a main, but LSLs, most of which were installed a century or so ago, are smaller yet, typically only about 1/2 to 5/8 in. in diameter. In contrast, the pipe sections studied by Deb et al. (2006) ranged from 3 to 12 inches in diameter. As pipe size decreases, the ratio of the surface of the coating to the volume of water in the pipe increases. If Pb is able to leach into the water through holidays in the coating, or through other defects that develop over time (e.g., blistering or loss of permeability due to chemical reactions), the impact on the bulk concentrations in the supplied water would most likely be significantly higher in these smaller pipes, assuming that lead solubility is not limited by other factors. Thus, while long-term use of epoxy linings in larger pipes has typically not shown an impact on the water quality with respect to inorganic constituents (Deb et al. 2010), extrapolation of these results to LSLs could underestimate the potential impacts of small coverage gaps in LSLs and CSLs.

Another factor to consider is temperature. Higher temperatures result in faster degradation of epoxy coatings and similar materials (Maxwell et al. 2005). That is why temperature is usually increased in accelerated aging tests on such materials, and also why epoxies used on interior water lines carrying hot water are formulated (and certified) for use at higher temperatures. In their accelerated-aging tests on epoxy coated materials, Deb et al. (2006) used three temperatures: 8, 25, and 35 ^{0}C. Corrosion of the steel surface around holidays occurred first and most extensively at the highest temperatures, with little visible rusting at 8 ^{0}C, even at the end of the 8-month experiment. Most water systems in the U.S. have average temperatures below 20 ^{0}C (Jana Laboratories 2010), and most lead and copper service lines would not be exposed to significantly higher temperatures, though in some locations in the U.S. water temperatures may reach 30 ^{0}C or more during the summer months. However, water temperatures slightly above average are unlikely to have a significant effect, relatively to other factors, on the service life of an epoxy coating.

Corrosion at the Metal–Metal Interface and Diffusion of Metal Ions

Corrosion at the epoxy-lead or epoxy-copper interface can occur when water, oxygen and charged electrolytes are all present at the pipe surface (Pommersheim 1995). These compounds can reach the interface either by direct diffusion of all constituents through the coating, by diffusion along open spaces in the coating (such as pinhole corrosion points), or a combination of these two processes. Most polymeric coatings, including epoxy resins, are considered permeable to water and oxygen molecules, allowing them to migrate to the metal surface (Sorenson et al. 2010). The diffusion of charged ions through the intact coating, however, is still a subject of some debate (Dong and Zhou 2014). Ions with smaller hydrated radii, such as K^+, diffuse more easily through these coatings than larger ions such as Na^+ (Deflorian and Rossi 2006). This would indicate that Na^+ diffusion occurs along open spaces, or channels. This slows the diffusion process, and corrosion under intact coatings would be limited by the availability of charged ions. In addition, while corrosion may occur at the metal surface, the diffusion of Cu^{2+} and Pb^{2+} back through the lining to the bulk solution would be even slower, due to their even larger size, which would effectively limit ion transport. There is evidence for the diffusion of Cu^{2+} into epoxy coatings (Meiser et al. 2010), but that study took place under a mixed air-water environment substantially different from that found in CSLs. Thus, while corrosion at the pipe surface has the potential to continue in a LSL or CSL under an epoxy lining, the transport of lead and copper back to the solution should be difficult as long as the coating remains mostly intact. The presence of large numbers of pinholes could speed diffusion of these ions back into solution, but it is not clear whether this effect could contribute significantly to aqueous concentrations of either ion.

Reactivity with Chlorine

Deb et al. (2010) observed high levels of consumption of free chlorine in the presence of fresh epoxy coatings. Glass coupons coated with fresh epoxy were exposed to solutions containing either 2.0 mg/L free chlorine or 4-6 mg/L monochloramine in a low hardness water at pH 8. Ninety percent of the free chlorine was consumed during the first 14 hours, with subsequent tests showing persistent loss of chlorine throughout the 30-day test, although the consumption rate decreased. Monochloramine losses were lower (about 40% in the first day) and also decreased with time. When epoxy-lined copper pipes were tested after five years in service, the consumption of free chlorine was higher and did not appear to decrease over the 30-day test period. These results suggest that epoxy linings may maintain a persistent free chlorine demand. This disinfectant demand may need to be taken into account when collecting tap-water samples that will be analyzed for compliance with requirements for maintaining a minimum concentration of chlorine in the distribution system.

PET LINERS

Description

PET is a strong, lightweight, and relatively inexpensive plastic used in many consumer products and is identified by resin code 1 (♳) (PETRA 2015). The formation of PET involves the reaction of terephthalic acid (TPA) or dimethyl phthalate (DMTP) with ethylene glycol to form the polymerized PET (Figure 2.1) (Weissermel and Arpe 2003). TPA is commonly used but phthalic acid (PA) and isophthalic acid (IPA) can also be polymerized and other diols (e.g., 1,4-butanediol and 1,4-dimethylolcyclohexane) can be used in place of ethylene glycol.

PET's strong yet lightweight nature make it an attractive option for lining of drinking water service lines. Since it is a thermoplastic, PET can be softened under heat and pressure but becomes firm when cooled. This process can be repeated multiple times but continued remolding will cause degradation of the material (Harper and Petrie 2003). For service line applications, a small diameter PET pipe is inserted into the old pipe and the PET is expanded to form a close-fit lining within the pipe. The installation process typically requires 13 minutes (excluding equipment setup and takedown time) and involves cleaning the internal surface of the pipe with foam swabs, inserting an unexpanded PET liner into the pipe, and running hot water (90 °C) through the liner while pressurizing (28 to 43 psi) it so that it expands (Kirmeyer et al. 2000). Sandblasting is not required since the liner does not need to bond to the inner pipe wall. Scraping or pigging is performed to remove deposits, to restore water flow capacity, and to ensure – by recovering the pig and examining its condition (Kirmeyer et al. 2000) – that no obstructions will block insertion of the liner and no sharp protrusions will compromise its integrity. Following installation, the liner is flushed and can immediately be placed back into service since it is factory cured. Connection of the liner to end-fittings is important because improper seating of the liner could allow water to flow behind it, which could at least partially negate the benefit of the liner (Breault 2014).

Notable Advantages and Disadvantages

The two most notable advantages of PET liners are their very short installation time (when no difficulties are encountered), which increase the productivity of work crews and increases satisfaction among water utility customers; and consumer familiarity with PET. Since most people frequently consume beverages from PET containers, multiple times each day in many cases, they tend to be less fearful of drinking water passing through a PET liner than they might be of other lining or coating materials. Although other lining and coating products are also widely used in applications familiar to consumers, they are generally not used to make beverage containers, and their use in familiar products, such as epoxy coatings in food cans, goes largely unnoticed.

The most notable disadvantage of PET liners is their limited bend radius, which can make it difficult to insert them in LSLs with bends or obstructions (e.g., joints), and nearly impossible if the LSL was coiled when it was originally installed. For this reason, the manufacturer of PET liners for LSLs recommends using a slightly smaller diameter unexpanded liner when lining a water service line that is not relatively straight (Wavin 2010).

Providers

To the investigators' knowledge, only a single manufacturer (Wavin) licenses and markets a PET pipe lining technology, which they have named Neofit®. This technology is used in many countries around the globe. In the U.S., Neofit® is represented by Flow-Liner Systems, Ltd. (Zanesville, OH; http://www.flow-liner.com), and in Canada, Pipe Shield (Mississauga, Ontario; http://pipe-shield.com/) is a licensed installer. Lining LSLs is the primary purpose for which it was developed (Alferink and Elzink 2010), though it is also used to eliminate or prevent leaks in service lines made of copper or plastic, and in other applications involving small-diameter pipes (0.5 to 2 in. ID). According to the manufacturer the liner has a life expectancy of 50+ years.

Potential Leachates

PET can potentially leach phthalate esters (PAEs) and phthalic acids (Table 2.2 and Figure 2.5). The wide range of possible leachates is attributed to the use of recycled PET. During prior use and during the recycling process, PET can adsorb many phthalates which can later leach into anything made from the recycled PET (Safa and Bourelle 1999, Sax 2010). Washing steps can significantly reduce contaminants but are not mandatory in the recycling process (Nerin et al. 2003). While virgin PET minimally leaches PAEs, recycled PET is still widely used due to concerns about environmental waste (Sax 2010, Nerin et al. 2003, Welle 2011). Of the possible leachates, three phthalic acids and ten phthalate esters (checked in Table 2.2) are of specific interest for PET liners due to their prevalence of detection, regulatory concerns, and inclusion in EPA Method 625 (Munch 1995); and these specific chemical compounds were included in the experimental work on PET liners described in Chapters 3 and 4.

Phthalates are used in a wide variety of applications, thereby contributing a steady influx of phthalates into the aquatic environment (Staples et al. 1997). Phthalates are susceptible to hydrolysis but not under conditions found in aquatic environments. While phthalate hydrolysis is rapid at acidic and basic pH values, hydrolysis under drinking water conditions is slow, with half-lives ranging from 3.2 to 2000 years (Table 2.2). Photodegradation by sunlight also provides a very slow mechanism of decay, with estimated of half-lives from 0.12 to 12 years. Both long and short chain phthalates can be biodegraded by aerobic and anaerobic bacteria with half-lives of less than a day to two weeks.

While drinking water treatment can expose the phthalates to a variety of oxidants, there has not been reported decay of phthalates with oxidants typically used as disinfectants. Chlorine and monochloramine (MCA) are very commonly used; others, less commonly used, include ozone (O_3), chlorine dioxide, and hydroxyl radicals produced by advanced oxidation processes (AOPs) (Black & Veatch 2010). Chlorinated by-products of phthalates have not been reported because the phthalates' chemical structures are not conducive to chlorination reactions. AOPs that have been found to degrade phthalates are UV/H_2O_2, UV/H_2O_2/Fe, UV/TiO_2/O_3, UV/TiO_2, O_3, O_3/H_2O_2, O_3/UV, O_3/UV/TiO_2 (supported by γ-Al_2O_3), O_3/TiO_2, O_3/Ru-Al_2O_3, O_3/activated carbon, O_3/Fe, O_3/Fe-Silica (SBA-15), and O_3/zeolite (Abdel-Daiem et al. 2012, Medellin-Castillo et al. 2013).

Therefore, taking all of these various mechanisms discussed above into consideration, any phthalic acids or phthalate esters that might happen to leach from a PET liner in a water service line would not be expected to form byproducts before the water reaches the tap.

Table 2.2
Potential PET leachates, regulated levels, and environmental persistence

Potential PET Leachate*	Abbreviation	CAS #	Leachate of Interest	NSF TAC† (ppb)	Hydrolysis Half Life (years)§
phthalic acid	PA	88-99-3	✓	10,000	
dimethyl phthalate	DMP	131-11-3	✓	50	3.2
diethyl phthalate	DEP	84-66-2	✓	6,000	8.8
dipropyl phthalate	DPP	131-16-8			
diallyl phthalate	DAP	131-17-9			
di-n-butyl phthalate	DNBP	84-74-2	✓	700	22
diisobutyl phthalate	DIBP	84-69-5		800	
benzylbutyl phthalate	BBP	85-68-7	✓	1000	> 0.3
bis(2-ethylhexyl) phthalate	DEHP	117-81-7	✓	6‡	2000
di-n-pentyl phthalate	DNPnP	131-18-0			
di-n-hexyl phthalate	DNHxP	84-75-3			
diphenyl phthalate	DPhP	84-62-8			
di-n-heptyl phthalate	DNHP	3648-21-3			
di-n-octyl phthalate	DNOP	117-84-0	✓		107
dinonyl phthalate	DNP	84-76-4			
diisononyl phthalate	DINP	28553-12-0		50	
di-n-dodecyl phthalate	DDP	2432-90-8			
diisodecyl phthalate	DIDP	26761-40-0			
isophthalic acid	IPA	121-91-5	✓	10	
dimethyl isophthalic acid	DMIP	1459-93-4	✓		
terephthalic acid	TPA	100-21-0	✓	3,000	
dimethyl terephthalate	DMTP	120-61-6	✓	3,000	
diethyl terephthalate	DETP	636-09-9	✓		
di(2-ethylhexyl)adipate	DEHA	103-23-1	✓	400‡	
4-nonylphenol	4-NP	104-40-5			
4-tert-octylphenol	4-TOP	140-66-9			
ethylene glycol	EG	107-21-1		10,000	
formaldehyde	FA	50-00-0		1,000	
acetaldehyde	AA	75-07-0		10	

Source: Lane 2015

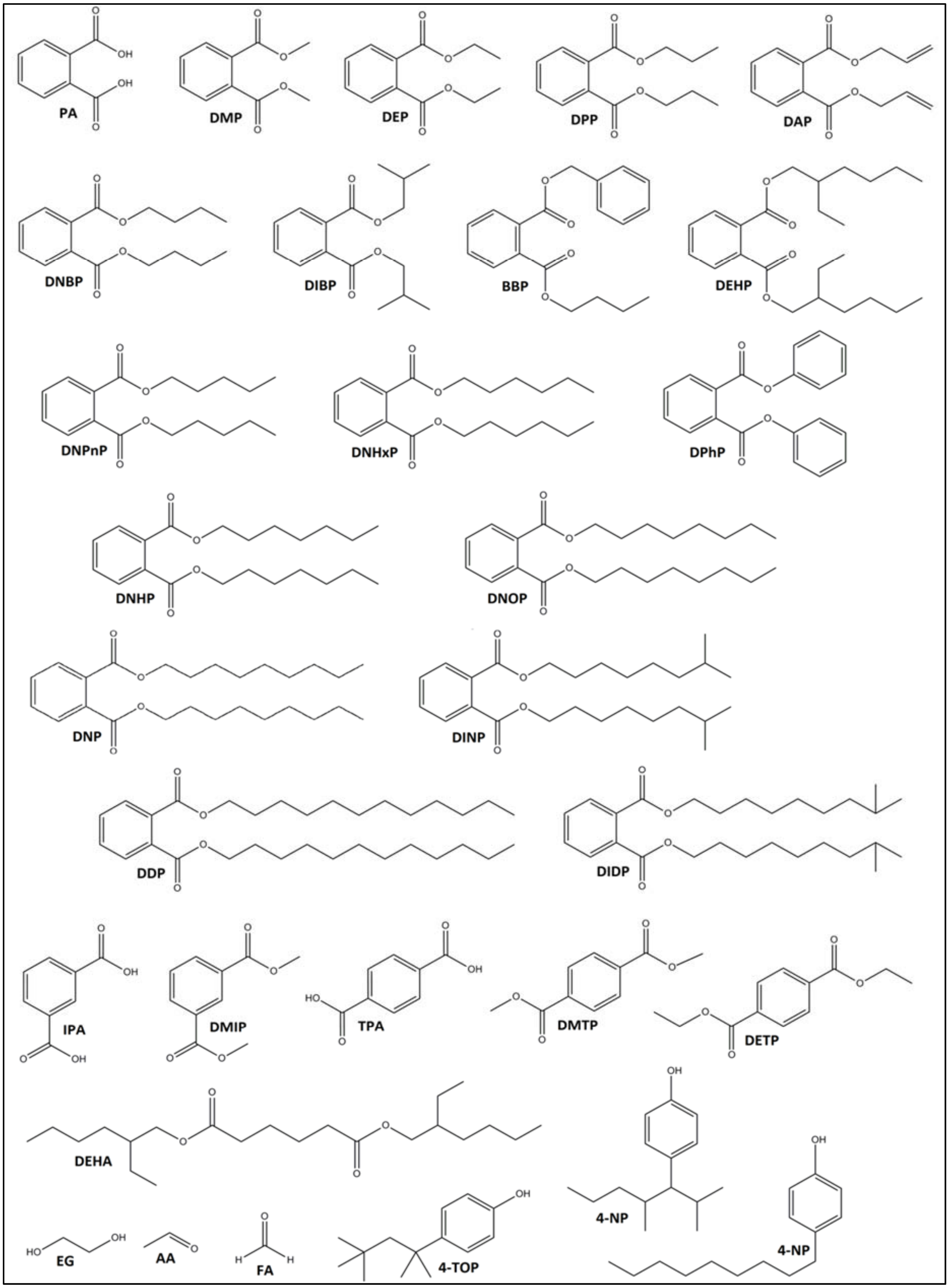
* See Lane (2015) for additional references pertaining to individual compounds.

† TAC = Total Allowable Concentration as reported in NSF/ANSI Standard 61, Table D-1 (NSF 2016a)

§ Half-life as reported by Staples et al. (1997)

‡ EPA Maximum Concentration Level (MCL)

Source: Lane 2015.



Source: Lane 2015.

Figure 2.5 Structures of potential leachates from PET plastics

Long-Term Effectiveness and Performance

Expected Service Life

Development of PET lining technology dates to the early 1990s (Boyd et al. 2000b). Kirmeyer et al. (2000) described several field studies demonstrating early applications of PET liners in drinking water distribution systems. PET liners are referenced as having an expected service life of greater than 50 years in the commercial literature and in one EPA report (Morrison et al. 2013). Mesman et al. (1995), based on data from tests on PET bottles and from laboratory tests on PET liners, estimated the service life of PET liners to be at least 50 years under water service line conditions; and they also noted that the burst strength of an expanded PET liner is similar to that of PVC pipe. These estimates are consistent with design life estimates for PE potable water pipes (Vibien et al. 2009, Najafi et al. 2015), the most similar commonly used pipe material.

For lead and copper service line rehabilitation, the primary factor in determining service life is the ability of the PET liner to act as a protective barrier between the pipe material and potable water carried inside the liner. Breakdown of this protective barrier could occur through physical degradation of the liner material or through increased permeability that could allow metal ions to migrate into and through the liner. A number of studies have been carried out on PET materials to examine degradation under various conditions. While none of these studies reproduced either the exact nature of PET liners used in water service line or the conditions found in distribution pipes, they can provide information on the primary factors affecting long-term PET behavior. A summary of significant results from these publications is therefore presented in the following paragraph.

PET can be degraded through several processes under different conditions, including photodegradation, thermal or thermal-oxidative degradation, and hydrolytic degradation (Mohammadian et al. 1991). Photodegradation is not of concern inside water service lines. PET appears to have good stability with respect to thermal degradation up to 80 ^{0}C or more (Edge et al. 1991, Pirzadeh et al. 2007, Turnbull et al. 2012), a temperature far above those ever experienced by most service lines. The most significant reactive pathway for PET breakdown in wet conditions at lower temperatures is hydrolysis, which can result in the material becoming more brittle (Bellenger et al. 1995), and thus more prone to physical failure. Hydrolytic degradation rates depend on humidity, temperature, and the degree of polymer crystallinity, with reactions occurring primarily in amorphous regions (Sammon et al. 2000). Most published studies in dry conditions show that hydrolysis is faster above the glass transition temperature (80 ^{0}C). Saturation of the PET with water, however, lowers this transition temperature to around 57 ^{0}C (Launay et al. 1999), and humid conditions result in more hydrolytic degradation. Mohammadian et al. (1991) estimated that PET bottles would have life expectancies of 27-48 years at ambient temperatures based on studies at 60-90 ^{0}C and 0-100% relative humidity. Ioakeimidis et al. (2016) found that PET bottles in marine environments began to show signs of increased breakdown after 15 years; however, those bottles could have been influenced by UV degradation, as well as exposure to high concentrations of multiple ions, relative to potable water.

Overall, PET does not appear to be particularly reactive under typical conditions for lead and copper service lines, although long-term studies are limited. One study carried out seven years after PET liner installation did show continued effective performance of the liners (Ball 2016). Further details of this study are presented in the Louisville Water Company case study in Chapter 5. Exposure to elevated water temperatures in household and residential plumbing lines could result in higher reactivity of the material, which has the potential to reduce service life through increased hydrolytic degradation; but PET liners are generally used only on water service lines and not on interior water lines. More direct experimental evidence for PET liner aging in service line use would improve the ability to estimate service life. Accelerated aging studies could also be carried out, although the notably different behavior observed at higher temperatures in the above studies would complicate such studies.

Migration of Metal Ions in PET

Amorphous PET does contain some void spaces allowing water to absorb into the material (Launay et al. 1999). Even if service lines are completely dried prior to liner installation, therefore, it is likely that water will eventually migrate to the outer edge of the PET liner and contact the lead or copper pipe. Under these conditions, some continued corrosion of the pipe material could occur, although low oxygen diffusion rates (Auras et al. 2004) should limit this process. Even if some corrosion occurs at the pipe surface, this does not present an issue for water quality within the liner unless the released Pb and Cu ions can diffuse back through the liner. Diffusion of copper into the liner should be somewhat faster than lead due to its lower molecular weight; but neither is expected to be significant for water service line applications.

The metal that has received the most study with respect to PET migration is antimony. Antimony is used as a catalyst in the production process for around 90% of PETs (Hansen and Pergantis 2006). This generally results in Sb concentrations of 190-300 ppm in the final material (Duh 2002). A number of studies have looked at antimony leaching from PET water bottles under various conditions designed to simulate short and longer-term water storage. The majority of these studies observed Sb concentrations below 1 μg/L when stored at room temperature or below (Bach et al. 2012), even after several months' storage. At higher temperature conditions, Sb concentrations increased substantially, with 45 ^{0}C representing an apparent critical temperature for increased leaching, and Sb levels exceeding drinking water standards at 80 ^{0}C (Westerhoff et al. 2008, Reimann et al. 2012, Greifenstein et al. 2013). Diffusion coefficients for Sb were calculated at 2.2×10^{-21} to 3.4×10^{-18} cm^2/s in deionized water across a temperature range of 25-70 ^{0}C (Rungchang et al. 2013). Given that Sb levels in finite volumes stored for days to months were below drinking water standards at service line temperatures, concentrations in flowing water should be even lower for waters in contact with PET liners. Additionally, the Sb leaching levels were only a small fraction of the total Sb in the bottles (Westerhoff et al. 2008), which suggests that cation diffusion through PET liners would also be relatively small.

While PET is relatively unreactive with chlorine, as discussed in greater detail in Chapter 4, one study indicates that polyethylene pipe materials are affected by long term exposure to chlorinated water (Whelton et al. 2011). In that work, HDPE and PEX pipes showed increases in diffusion rates for polar organic contaminants. This may or may not indicate that PET lining materials exposed to chlorine will be more likely to leach cations as they age, but the investigators did not identify any studies directly addressing this issue.

POLYUREA AND POLYURETHANE COATINGS

Description

PUA and PUR coatings represent a potentially attractive alternative to LSL replacement. Polyurethane polymers are most commonly formed from reaction of polyisocyanate with a polyol to form a long chain molecule with a 'urethane linkage' (CIEC Promoting Science 2013). Both rigid and elastomeric polyurethane formulations can be prepared, with the former distinguished by cross-linking between the polymer chains. This cross-linking produces a harder, denser material with good chemical and corrosion resistance (Walker and Guan 1997). Polyurea is an elastomeric polymer produced by reacting various isocyanate starting products together to produce a longer chain polymer. Both polymers have been used as protective coatings for a variety of applications since their introduction in the 1930s. Hybrid coatings containing both PUA and PUR linkages are also possible, including one that recently entered the LSL coating market in the UK.

Polyurethane coatings have been used to line water transmission pipelines since the late 1980s (Bambei Jr. et al. 2011). However, the first version of AWWA Standard C222 for polyurethane coating of steel pipe and fittings was not approved until 1999. Their use to rehabilitate water mains and service lines has become common in the United Kingdom, where they have become as or more popular than other lining technologies (Deb et al. 2006, Ellison et al. 2010). A significant advantage of polyurethanes for this application is a short curing time, which can allow for a rapid return of treated lines to service in several hours (Rockaway and Ball 2007). Their historical use for water mains and service lines in the U.S. has been minimal. More recently, polyurea resin materials have also been approved (certified as meeting NSF 61) for use in potable water supply pipes.

Installation of a PUA/PUR hybrid coating using the Serline^{TM} process, the only process known to the investigators to be currently available for PUA or PUR coating of LSLs, is evidently similar to processes used to apply epoxy coatings. According the Nu Flow (n.d.) and Manners (2017a), hot air is blown through the service line to dry the pipe to 10 °C above the dew point, and garnet grit is added as needed to clean the pipe. More grit and longer drying times are typically needed for galvanized pipes than for LSLs. After the LSL is cleaned and dry, a PUA/PUR hybrid coating is blown into the pipe using a forced air vortex and cures (dry to the touch) in 15 minutes, forming a seamless barrier. For use in the UK (DWI 2016), the coating must be applied by a certified contractor and cured for at least 4 hours at a temperature of at least 7 °C. A patented bypass system can be used to keep the customer supplied with water while the coating is installed. The process is designed for pipes having a ID of 10–50 mm and has been approved for use in the UK under DWI and WRAS requirements.

Notable Advantages and Disadvantages

The most obvious advantage of the Serline^{TM} coating technology is that the very rapid curing rate of the coating facilitates rapid return to service, although this feature is currently limited in the UK by DWI's requirement of a curing time of at least four hours. Another notable feature is that the coating is flexible enough to allow movement of the pipe without damaging the coating. Like epoxy coatings, the hybrid PUA/PUR coating can bridge gaps, seal pinholes, and control corrosion.

The most notable disadvantage of this technology for use in LSLs is its short history of success in this particular application and, therefore, less confidence in its effectiveness and in estimates of its expected service life. Manufacturers estimate the service life of other PUA and PUR coatings to be about 50 years (Morrison et al. 2013), and the manufacturer of the Serline^{TM} process is reportedly in negotiations with the manufacturer of the coating to provide a warranty commensurate with the estimated service life of the coating (Manners 2017a). Another potential disadvantage of PUR coatings in general is the need to thoroughly dry the interior surface of the pipe (Younis et al. 2016), which can be challenging in a water service line environment.

Providers

The Serline^{TM} process is the only process involving a PUA or PUR coating known to the investigators to be currently available for use in coating LSLs. This process is owned by Aquam Corporation (Manchester, UK; http://www.aquamcorp.co.uk/), a company with offices in the U.S., Canada, and the UK, and which also owns Nu Flow Technologies. The coating used in the process is 3M^{TM} Scotchkote^{TM} Rapid Setting Polymeric Lining 166L(3M 2013). This coating is currently approved for use in small diameter pipes (such as LSLs) for public water supply purposes in the UK (DWI 2016), and is also WRAS approved for use in LSLs on private property.

Potential Leachates

The water quality impacts of PUA and PUR coatings are not extensively described in the literature. In a study addressing water quality implications of coating use (Deb et al. 2010), a PUR coated coupon was tested with three waters at pH 8 with, respectively, no chlorine, 2 mg/L of free chlorine, and 4-6 mg/L of monochloramine for 30 days, with fresh water added at intervals. All waters showed a pH decrease of 2-3 units (to ~ pH 6), with longer exposure times decreasing the pH more. The specific reason for this pH decrease could not be determined. Free chlorine levels decreased by $\geq$75% in the first few days of exposure, and by 50% later in the experiment. Monochloramine consumption was much lower, with no trend observed with time. An immersion study of a PUA polymer used to coat storm-water pipes also showed an initial pH decrease of 1.0 to 1.2 units, with a smaller but consistent pH decrease at longer times (Whelton et al. 2013). This study suggested that pH changes could be due to reaction between the isocyanate resin and the water. In both cases, some TOC release to solution was observed.

NSF 61 requires testing of PUR coatings for leaching of VOCs and for other organic constituents using GC/MS (base/neutral/acid scan). PUR products must also be tested for regulated metals and phenolics. Potential leaching of these and any additional compounds is likely highly dependent on the specific resin formulation. Tullo (2016) recently reported that a common PUR curative, 4,4′-methylenebis 2-chloroaniline, faces a ban in Europe due to fears that it may be toxic, leaving manufacturers scrambling to identify suitable replacements.

Long-Term Effectiveness and Performance

The published technical literature on the use, long-term performance and water quality impacts of PUA and PUR coatings in drinking water distribution systems is rather sparse. Field tests have occurred in Tacoma, Washington, for rehabilitating a steel transmission pipeline (Peloquin and Weisenberg 2014), and in Bangor, Maine, for cast-iron water mains (Jani 2015). Walker and Guan (1997) stated that rigid polyurethanes would perform better than elastomeric polyurethane for pipe lining due to low undercutting and high abrasion and impact resistance. Deb et al. (2006) assessed one PUR coating for use in service lines through a series of accelerated-aging studies at three temperatures: 8, 25, and 35 ^{0}C. PUR coatings showed only isolated instances of undercreep and did not develop underfill rusting of the steel test panels. Measurement of coating barrier properties using electrochemical impedance spectroscopy (EIS) did not show a significant effect of temperature on the performance of the polyurethane coating. This result, in particular, was considered important in suggesting a long service life for the PUR coating, although a quantitative analysis of service life was not conducted. Denver Water conducted tests from 1999 to 2011 on an early-generation PUR coating system installed in 1997, to examine its longer-term performance (Bambei Jr. et al. 2011). Based on adhesion tests and other results, they found that the lining was in excellent condition after 14 years. Information sheets supplied by manufacturers for current PUR and PUA coatings typically indicate design lives of 50 years (Morrison et al. 2013), but no specific data for those coatings were available for review for the report.

Deb et al. (2010) conducted tests on PUR-coated coupons using three different water, all at pH 8: one with no disinfectant, one with 2.0 mg/L chlorine, and one with 4.0-6.0 mg/L monochloramine. The coatings exhibited significant chlorine demand (as expected, given the structure of PUR). Free chlorine was consumed more rapidly than combined chlorine. The consumption rate decreased over time, but was still significant after 30 days of testing. TOC leached from the PUR, with about 1 mg/L leaching out during the first 24 h period; but over a 15-day period, the TOC values in the extraction waters converged on the values of the control samples.

The long-term performance of PUA and PUR coatings, and their potential to leach organic constituents into the water, or to react with drinking water constituents, particularly disinfectants, are not well characterized at this time. As discussed previously for epoxy linings, when used in LSLs, the overall lifespan of a coating material is not the only important consideration. If holidays are present in the coating, or if the coating becomes more permeable over time (e.g., due to reactions with chlorine), this could result in direct contact between potable water and the lead surface, potentially causing increased lead levels at the tap prior to failure of the coating as judged by more traditional criteria such as adhesion. Studies assessing these issues for PUA or PUR coatings should be included in future long-term testing to assess these materials for specific use in water service lines.

CHAPTER 3
MATERIALS AND METHODS

REAGENTS

Reagent Water

Reagent water was ultrapure, filtered and deionized 18.2 megohm (MΩ) water. To obtain reagent water, Lawrence, KS tap water was processed using a reverse osmosis system (Model Elix 10, EMD Millipore, Billerica, MA) followed by an ultrapure water polishing system (Model Milli-Q® Advantage A10®, EMD Millipore, Billerica, MA). Unless otherwise noted, this reagent water was used in all solutions, stocks, standards, and extraction waters.

Water used during LC/MS analyte optimization was Optima LC/MS grade water from Fisher Scientific (Pittsburgh, PA). After optimization, reagent water was found to yield results equivalent to those obtained using Optima LC/MS grade water, so reagent water was used for all subsequent LC/MS analyses.

Chemical Reagents

Except where noted otherwise, American Chemical Society (ACS) reagent-grade chemicals were used to make all solutions, stock solutions, and standards. Standards for lead analysis were made from Claritas PPT® grade lead standard (1000 mg/L, Cat. No. CLPB2-2Y, SPEX Certiprep®, Metuchen, NJ). Standards for copper analysis were made from Claritas PPT® grade copper standard (1000 mg/L, Cat. No. CLCU2-2Y, SPEX Certiprep®, Metuchen, NJ). Standards for antimony analysis were made from Claritas PPT® grade antimony standard (1000 mg/L, Cat. No. CLSB7-2Y, SPEX Certiprep®, Metuchen, NJ). Standards for Ca, Mg, Na, and K were made by dissolving ACS-grade nitrate or sulfate salts (Fisher Chemical, Pittsburg, PA) in reagent water. TraceMetal™ grade concentrated nitric acid (67 – 70%, Cat. No. A509-P212, Fisher Chemical™, Pittsburg, PA) was used to preserve samples for metals analysis. TraceMetal™ grade concentrated hydrochloric acid (HCl) (30 – 32%, Cat. No. A508-4, Fisher Chemical™, Pittsburg, PA) was used to generate 1.0 and 0.1 M solutions of HCl for pH adjustment. Laboratory-grade sodium hypochlorite solution (5.65 – 6.00%, Cat. No. SS290-1, Fisher Scientific™, Pittsburg, PA) was used to create chlorinated and chloraminated solutions, with the latter also involving addition of ammonium chloride purchased from Fisher Scientific (Pittsburgh, PA).

For organics analysis, HPLC grade acetonitrile, HPLC grade chloroform, HPLC grade hexanes, LC/MS grade methanol (Optima), hydrochloric acid, calcium chloride, monobasic and dibasic sodium phosphate, sodium bicarbonate, sodium bisulfite, sodium chloride, sodium hydroxide, and the chlorine quenching agents 99% L-ascorbic acid sodium salt, sodium bisulfite, sodium thiosulfate, and sodium sulfite were purchased from Fisher Scientific (Pittsburgh, PA). Ammonium formate, formic acid, and trichlorophenol were purchased from Sigma Aldrich (St. Louis, MO).

Bisphenols (i.e., BPA, BPB, BPD, BPE), were purchased from TCI America (Portland, OR), BPF and the deuterated internal standard (BPA-D16) from Sigma Aldrich (St. Louis, MO), and the deuterated surrogate internal standard (BPA-D8) from Cambridge Isotopes Laboratory (Tewksbury, MA). Chlorinated bisphenol A standards (BPA-Cl, BPA-2Cl, BPA-3Cl) were purchased from Santa Cruz Biotechnology (Dallas, TX) and BPA-4Cl from TCI America

(Portland, OR). Diglycidyl ether compounds (BADGE, BADGE-H_2O, BADGE-2H_2O, BADGE-H_2O-HCl, BADGE-HCl, BADGE-2HCl) were purchased from Sigma Aldrich (St. Louis, MO), BFDGE from Crescent Chemical Co. (Islandia, NY), and the deuterated internal standard sulfamethoxazole-D4 (SMXL-D4) from Toronto Research Company (Toronto, Ontario, Canada).

The following phthalate esters were ordered from Fisher Scientific (Pittsburgh, PA): 99% di-n-butyl phthalate (DNBP) (Acros Organics), 99% diethyl phthalate (DEP) (Acros Organics), 98% diethyl hexyl phthalate (DEHP) (Acros Organics), 97% butyl benzyl phthalate (BBP) (Acros Organics), 99% dimethyl phthalate (DMP) (Acros Organics), 99% Dimethyl isophthalate (DMIP) (Acros Organics), 99% dimethyl terephthalate (DMTP) (Acros Organics), 99% bis(2-ethylhexyl) adipate (DEHA) (Acros Organics), 98% di-n-octyl phthalate (DNOP) (Alfa Aesar), and 95% diethyl terephthalate (DETP) (Alfa Aesar). One phthalate ester, 95(+)% diethyl phthalate (DEP), was ordered from Ultra Scientific (North Kingstown, RI). The deuterated surrogate internal standard di-n-hexylphthalate-D4 (DNHP-D4) and deuterated internal standard phenanthrene-D10 (PANE-D10) were ordered from Sigma Aldrich (St. Louis, MO). The phthalic acids, 99% phthalic acid (PA), 99% isophthalic acid (IPA), and >99% terephthalic acid (TPA), were ordered from Fisher Scientific (Pittsburgh, PA).

Extraction Waters

The extraction waters used to fill the pipe sections for the fill-and-dump experiments were adapted from, and similar to, extraction waters specified by NSF 61. Three waters were used in the fill-and-dump experiments:

- Chlorinated pH 8 extraction water (CL)
- Low pH (pH 6.5) extraction water (LP)
- Dechlorinated pH 8 tap water (DT)

Preparation of these waters is summarized immediately below and described in detail in the standard operating procedures (SOPs) in Appendices A and B.

These waters were also used in various other experiments, along with an unchlorinated pH 8 extraction water (the same as CL, but with no chlorine added) and a chloraminated pH 8 extraction water. Chloraminated pH 8 extraction water was prepared by dosing unchlorinated pH 8 extraction water with ammonium chloride at a molar concentration equivalent to the desired chloramine concentration, e.g., 0.0282 M NH_4Cl for a desired combined chlorine concentration of 2 mg/L as Cl_2 (0.0282 M), then adding chlorine while stirring rapidly. Under these conditions (pH 8 and a Cl_2:NH_3-N weight ratio of about 5:1), monochloramine is the predominant chlorine species and very little free ammonia remains following chlorine addition.

Chlorinated pH 8 Extraction Water (CL)

Chlorinated pH 8 extraction water was prepared from reagent water stored in 4 L amber glass bottles tightly sealed with caps with polytetrafluoroethylene (PTFE) liners. The reagent water was adjusted to room temperature by storing it overnight in the same temperature-controlled room used for the fill-and-dump tests. Prior to use, this water was dosed with 1.00 mM reagent-grade $CaCl_2$ to obtain a hardness of 100 mg/L as $CaCO_3$. For the first fill-and-dump experiment (FD1), this water was dosed with 1.00 mM $NaHCO_3$, then adjusted to pH 8.0 ± 0.1 using 1.0 and 0.1 N hydrochloric acid. Since this water was not in equilibrium with the atmosphere with respect to carbon dioxide, its pH was prone to large and variable fluctuations as the water was poured into and dumped out of the pipe sections. Therefore, for subsequent tests, this water was prepared to have an initial composition of 0.56 mM $NaHCO_3$ and 0.44 mM NaCl, such that its initial pH would be close to 8 and it would also be close to equilibrium with the atmosphere with respect to carbon dioxide. Immediately prior to use, this extraction water was dosed with sodium hypochlorite to obtain a free chlorine concentration of 2 mg/L as Cl_2. The pH of the water was then adjusted to 8.0 ± 0.1 using 0.1 N HCl.

Low pH (pH 6.5) Extraction Water (LP)

The pH 6.5 extraction water was prepared in similar fashion to the chlorinated pH 8 extraction water, including addition of 1.00 mM reagent-grade $CaCl_2$ to obtain a hardness of 100 mg/L as $CaCO_3$. For FD1, LP extraction water was prepared by adding 1.00 mM $NaHCO_3$, then adjusting the pH to 6.5 immediately prior to use using 1.0 and 0.1 N HCl. For reasons similar to those stated above for the pH 8 extraction water, batches of pH 6.5 extraction water used in subsequent fill-and-dump experiments (after FD1) were prepared using 0.018 mM $NaHCO_3$ and 0.982 mM NaCl to produce a pH close to 6.5 and a carbon dioxide concentration close equilibrium with the atmosphere. Immediately prior to use of this water, its pH was checked and adjusted, if necessary, using 0.1 N HCl. No chlorine was added to the pH 6.5 extraction water.

Dechlorinated pH 8 Tap Water (DT)

Dechlorinated pH 8 tap water was prepared using water drawn from a tap in a laboratory at the University of Kansas, which obtains water from the City of Lawrence, KS. Monitored concentrations of constituents in Lawrence tap water in 2011 are shown in Appendix C – City of Lawrence, KS Drinking Water Consumer Confidence Report. After running the tap for 5 min., a 28 L HDPE cylindrical tank (Nalgene™, Thermo-Scientific™, Waltham, MA) was filled with 13 – 20 L of tap water. The tap water, which is chloraminated, was dechlorinated by drop-wise addition of a 0.14 M solution of $NaHSO_3$ while stirring with a 2-ft. section of 3/4 in. HDPE tubing (Advanced Technology Products, Milford Center, OH; meets NSF 61) until the total chlorine concentration was non-detectable (below 0.1 mg/L as Cl_2). The pH of the dechlorinated tap water (initially 8.3 – 8.4) was then adjusted to pH 8.0 ± 0.1 using 0.1 N hydrochloric acid. Prior to dechlorination and pH adjustment, the alkalinity of the tap water was determined. After pH adjustment, the tap water was analyzed for dissolved oxygen (DO) and samples were collected for analysis of TOC and metals.

LSL AND CSL SECTIONS

Source and Preparation

LSL Sections

LSLs approximately 100 years old and recently removed from service were cut into sections 3.5 to 4.0 ft. long and sent to the University of Kansas (KU) by the Rochester (New York) Water Bureau. All but two of the sections had an inner diameter (ID) of ~5/8 in.; the other two had an ID of ~1/2 in. Some of the LSLs had been excavated, but most had been pulled from the ground by inserting a chain through the pipe's length and securing it on the end. This process has the potential to damage the inner surface of the LSL as the chain rubs against it, or due to the compressive and tensile stresses exerted on a ductile lead pipe as it is pulled through the soil. Consequently, the pipes were inspected for damage once received, and those showing signs of damage were set aside and not used. The external surfaces of the pipes were cleaned using tap water to remove excess dirt. After drying, the pipes were wrapped with duct tape to minimize potential contamination from handling the outer surfaces. To prevent extraction waters from coming into contact with lead, as would happen if they were poured out directly over the lip of a pipe, and to allow a lining or coating to extend 2 to 3 in. past the cut ends of the LSL sections, stainless steel (SS) end fittings were installed on both ends of each pipe, as shown in Figure 3.1.

The ends of each LSL pipe section were reamed and then threaded with a nominal 1/2 in. die. Threaded 1/2 in. (nom.) by 2-1/2 in. long SS pipe nipples (Part No. 1XAB2, Grainger, Lake Forest, IL; actual ID ~5/8 in.) were installed on both ends of each LSL pipe section after the threads were wrapped three times around with PTFE tape (Poly-Temp® XHD, Anti-Seize Technology, Inc., Franklin Park, IL; meeting C.I.D. Spec A-A-58092). Before installation, the nipples were scrubbed with a stiff brush to remove any loose residue from the manufacturing process, rinsed with warm tap water, then agitated and soaked in hexane for at least 5 minutes to remove any remaining cutting oil. SS hose clamps (Breeze Aero-Seal® Model 200 12H, Norma Group, Auburn Hills, MI) were installed over the pipe ends and nipples to tightly secure the nipples and to prevent leaks. The pipes were then wrapped in foam insulation to minimize any damage from shipping and handling and to provide an extra layer of protection from surface lead contamination.

LSL sections were also received from another utility (Providence Water, Providence RI), These sections were similar to those described above, but were shorter in length, so they were not used in the fill-and-dump experiments. However, one of them was used in a follow-on experiment examining the amount of antimony present in scale deposits and in the lead from which the LSLs were made.

Source: Photo by Zachary A. Breault.

Note: Top: LSL with threaded SS nipples and silicone stoppers. Bottom: CSL with unthreaded SS pipe nipples connected with polypropylene compression fittings and fitted with HDPE stoppers.

Figure 3.1 Image of fully prepared pipe sections

CSL Sections

CSL sections 45 in. long were cut from 50 ft. rolls of Type L potable water grade ‘soft’ annealed copper tubing (ASTM B-88, Great Lakes Copper Inc., London, Ontario, Canada) with a nominal size of 0.625 (5/8) in. and an actual ID slightly larger than 5/8 in. As the sections were cut, the tubing was carefully straightened to avoid kinking, and the ends were reamed and sanded to remove burrs and to improve contact with end-fittings, which were used for the reasons noted above for the LSL sections.

Polypropylene compression fittings (tube bulkhead union, JACO Manufacturing Company, Berea, OH) soaked and rinsed in reagent water were installed on both ends of each CSL section. Unthreaded SS pipe nipples 3 in. long were cut from SS pipe (1/2 in. nom. ID, ~5/8 in actual ID; Part No. 4NTN6, Grainger, Lake Forest, IL; meeting ASTM A269/A213 and ASME SA213 standards). The unthreaded SS nipples were scrubbed with a stiff brush then rinsed with tap water and finally hexane (to remove any residual cutting oil) before being inserted into the polypropylene fittings. The pipes were then wrapped with foam insulation to minimize damage during shipping and handling and to cover all exposed copper.

Epoxy Coating Application

Eighteen 18 pipe sections were selected for epoxy coating: 8 LSL sections with an ID of ~5/8 in., 2 LSL sections with an actual ID of ~1/2 in., and 8 CSL sections with a nominal size of 5/8 in. These sections were shipped to an epoxy manufacturer (Nu Flow Technologies, San Diego, CA) to be coated with epoxy in a manner similar to the way service lines would be coated in the field, ensuring proper application and curing. The same equipment used in the field was used for this application, including an air compressor, an air filtration system, heating elements, hoses, connectors, and a sand hopper.

The pipe sections were mounted horizontally on a wall in 9 pairs, with 2 pipes of identical material and similar ID in each pair. This configuration allowed the application process to go more quickly than if each pipe were coated individually. To connect the pairs of LSL sections, brass fittings were used. The SS nipples were removed from the copper pipes and replaced with transparent acrylic pipe nipples to connect them to each other and to the equipment used to prepare and coat the pipe sections.

The first step in the coating process was to sandblast the inside of the pipes to give the epoxy a fresh, rough surface to adhere to. If done properly, the surface will have what is commonly referred to as an "anchor tooth" pattern. Approximately one cup of sand was used for each blast (of about 8 total) applied to the copper pipes. The sand used to roughen the internal surfaces of the CSL sections was added manually, to reduce the pressure load on the connectors used. The LSL sections were able to withstand the pressure required to use the sand hopper, and were given about ten 3 or 4-second-long shots of sand. When the desired anchor tooth pattern was thought to have been attained, a small camera mounted on a long USB cable and connected to a computer was used to inspect the inner wall texture. If the texture did not look quite right, further sandblasting was performed until the proper texture was achieved.

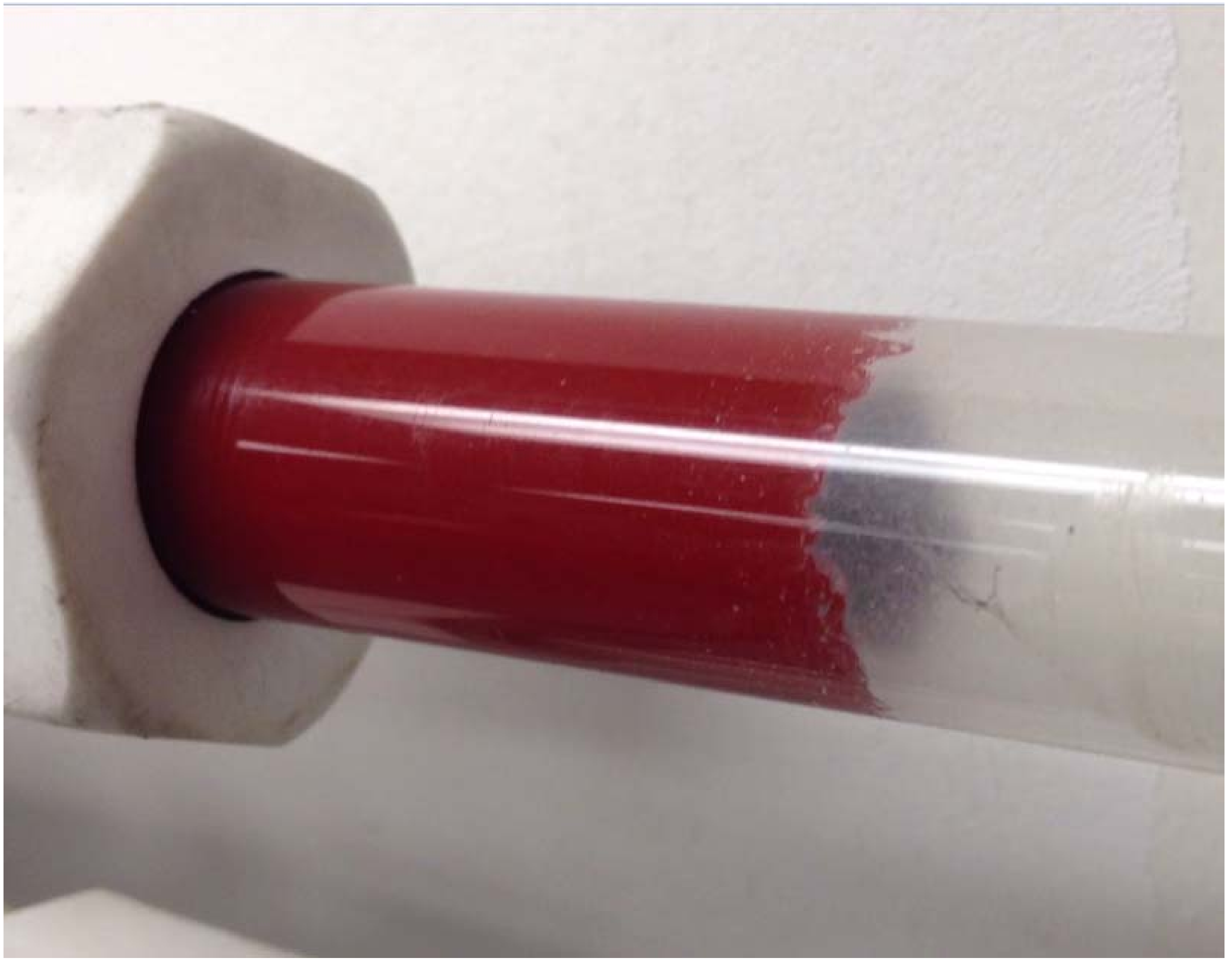
The pipes were then flushed with tap water to remove lead dust. In the field, copper pipes are flushed only if lead solder is present. For this study, all pipes were flushed, including the copper pipes. A second flush was performed in the opposite direction to rinse threads, fittings, and transitions evenly. In the field, the flush water is typically drawn from a hydrant or pump truck and a higher pressure is used. After flushing, the pipes were dried using heated, filtered air. The air was heated using a heating element located between the filter and pipes. An infrared thermometer was used to measure the temperature of the outer pipe. Feeling the heat by touch was also employed to get a good sense of when the pipe had finished drying.

The pipe sections were coated using a two-part potable-water-grade epoxy certified as meeting NSF 61. According to the epoxy's Material Safety Data Sheets (MSDS; Nu Flow Technologies 2011a; 2011b), Part A (the epoxy resin) contains 5% iron oxide by weight, which is assumed to be the source of the red color, and Part B (the hardener) contains triethylenetetramine

(TETA, <10%) and reaction products of TETA, a primary aliphatic polyamine. The epoxy used to coat the pipes was prepared by mixing 70% part A and 30% part B, by weight.

The amount of epoxy mixed was based on an estimate of the amount that could be applied before the epoxy's working time expired. The first batch proved sufficient to coat all 8 copper pipes. Immediately prior to epoxy application, the pipes were heated once again to improve the epoxy's adherence and to extend its working time. The pipes were coated in pairs. Enough epoxy to coat two pipes was poured into a 4-ft. shot tube, which was coiled into a single loop that allowed the epoxy to pool at the bottom as it was connected to the pipe. The other end of the epoxy-filled loop was connected to the air flow system. Air pressure and flow were applied to spread the epoxy along the inner walls of the pipe. The air pressure and flow were determined based on the inner diameter and length of the pipe. Using acrylic pipe connectors made the coating process easy to see, as shown in Figure 3.2. The epoxy was not a slug of liquid being pushed through the pipe; instead, a channel of air flowed through the liquid epoxy, creating a vortex. The epoxy was thereby spun into the wall of the pipe as it moved along the length of the pipe.

Once the epoxy was applied, all of the equipment was disconnected and the pairs of pipe sections were separated from one another, which had to be done before the epoxy hardened. The unthreaded SS nipples were re-attached to the copper pipes. In the field, air would be blown through the pipes for an additional 2 – 3 hours, expediting curing and minimizing pooling effects. Since this demonstration involved 9 separate connections (one for each pair of pipes), the air flow could not be reasonably continued for that long. Therefore, the pipes were hung vertically on a rack and allowed to cure. One coated and one uncoated LSL section (used as a control) are depicted in Figure 3.3 to illustrate their appearance before and after epoxy coating.



Source: Photo by Zachary A. Breault.

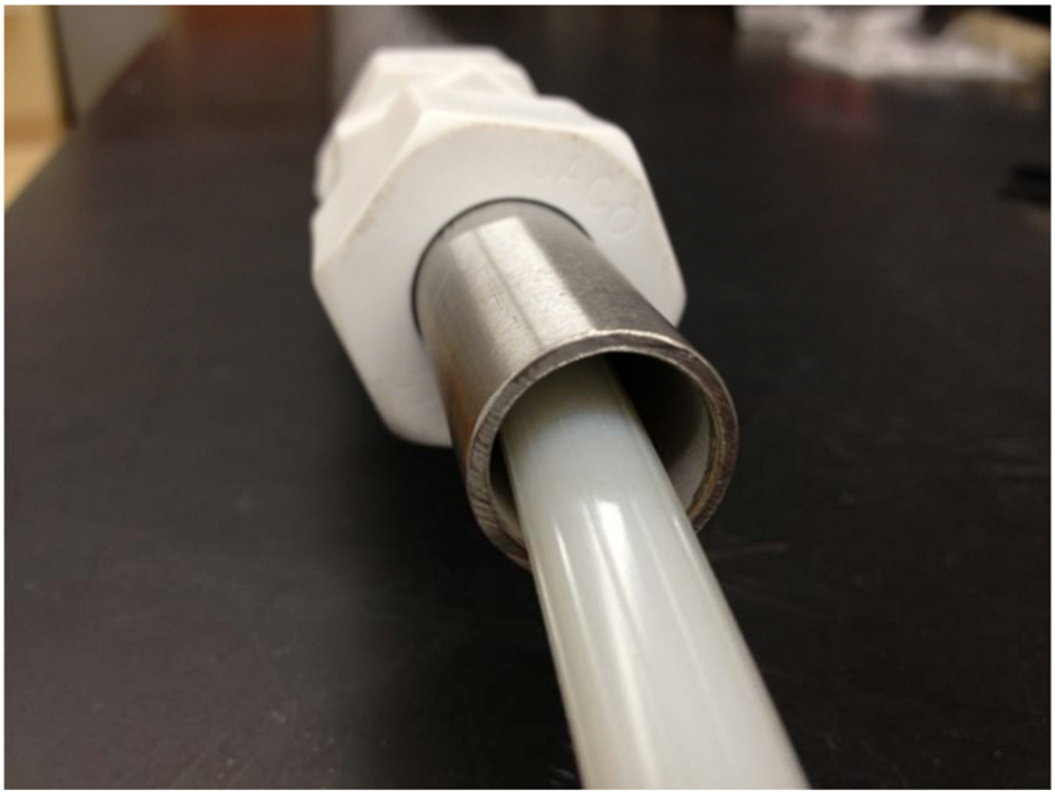
Figure 3.2 Image of epoxy coating as it is being installed through transparent acrylic pipe

Source: Photo by Zachary A. Breault.

Figure 3.3 Image comparing an epoxy-coated LSL (left) to an uncoated LSL (right)

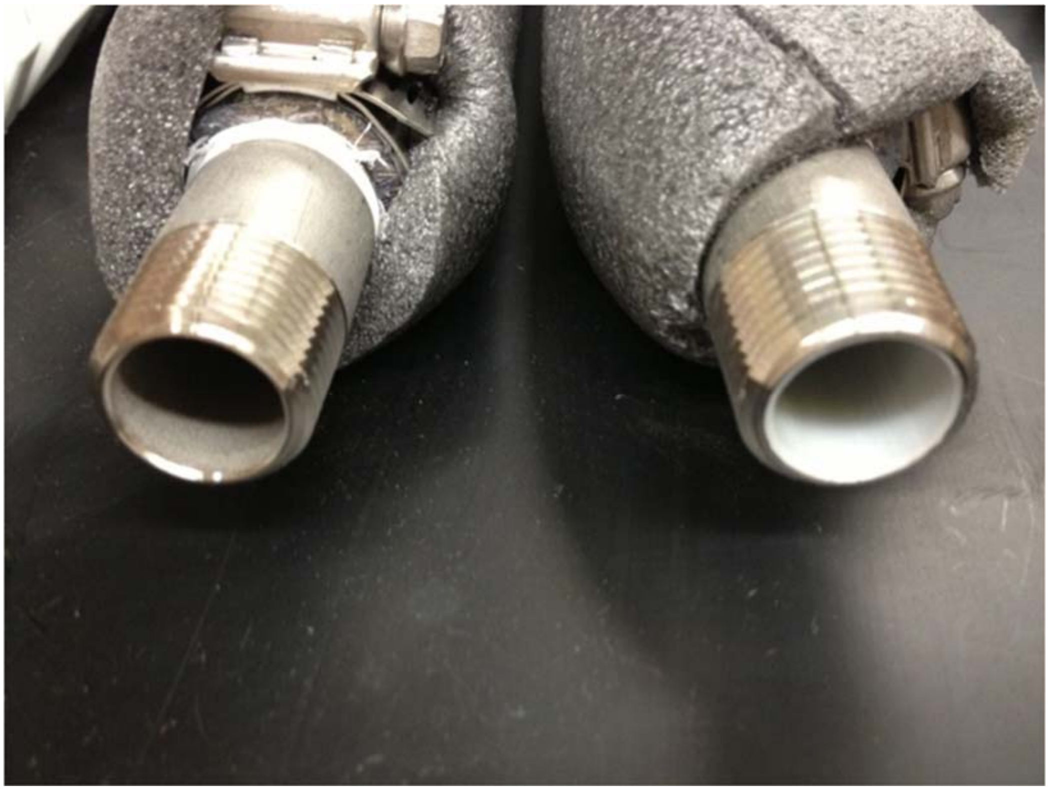
PET Liner Installation

PET (polyethylene terephthalate) liners certified as meeting NSF 61 and NSF 61-G[48] were installed in a second set of LSL and CSL sections by the manufacturer (Flow-Liner Systems, Zanesville, OH). Before lining the LSL sections, they were first cleaned by scraping / pigging to remove loose deposits. The CSL sections were made of virgin material, so they did not require cleaning. The lining process consisted of inserting PET tubing through the pipe sections, which were connected in series, then pumping hot water under pressure through the PET tubing to expand it and press it tightly against the internal surface of each pipe section. The tubing was then flushed with pressurized cold water to complete the lining process, and the PET-lined pipe sections were shipped back to the University of Kansas. Figure 3.4 shows an unexpanded PET liner protruding from an unthreaded SS pipe nipple attached to a CSL section. Figure 3.5 shows the ends of lined and unlined LSL sections, the latter serving as a control section.



Source: Photo by Zachary A. Breault.

Figure 3.4 Unexpanded PET liner inserted into an unthreaded SS pipe nipple



Source: Photo by Zachary A. Breault.

Figure 3.5 Unlined (left) and PET-lined SS pipe nipples on LSL sections

ANALYTICAL METHODS

General Procedures for Sample Collection, Preservation, and Analysis

Unless noted otherwise, all samples were collected, preserved, stored in a suitable container, and analyzed as specified in *Standard Methods* (APHA et al. 2005). More detailed information for specific methods is provided below. Method detection limits, precision, and bias were determined as described in *Standard Methods*.

To ensure the quality of the data, strict quality assurance (QA) guidelines were developed and followed; quality control (QC) processes were incorporated into a standard operating procedure (SOP) for each analytical method; and each data set was carefully reviewed to see that QC guidelines were met and to attempt to detect any experimental or instrumental problems. Where applicable, the QA/QC guidelines in *Standard Methods* were followed, including not only those for a specific method but also the general guidelines in Part 1000 and those applicable to specific groups of contaminant, such as Part 3020 for metals. Similar guidelines were adopted for non-standard methods, such as those used to identify and quantify various organic constituents. Quality control practices included:

- Initial demonstration of proficiency by each analyst for each method
- Instrument calibration prior to analyzing each set of samples

- Diluting and re-analyzing samples whenever the analyte concentration falls outside the range of the calibration curve
- Analysis of check samples during each run to verify instrument calibration and linearity (at least one every 10th sample)
- Analysis of independently prepared standards to verify accuracy
- Analysis of reagent blanks and experimental control samples
- Analysis of replicate samples (at least one every 10th sample) to verify precision
- Analysis of matrix spikes (at least one in every sample set) to verify analyte recovery
- Analysis of samples in groups, rather than individually
- Labeling each sample with a unique code

In addition, for analysis of organic constituents, calibration curves were not used unless they had a coefficient of determination (r^2) of at least 0.98 for a 5-point calibration curve. For analysis of bisphenols and the diglycidyl ether derivatives, samples were spiked with both internal standards and surrogate internal standards; and recovery of the surrogate standard was required to be within 25% of the target value.

If QC guidelines were not met, or if the results were not within acceptable limits of precision and accuracy, such as those stated in Section 1020 of *Standard Methods,* the data were discarded, corrective action was taken, and the samples were re-analyzed. Possible corrective actions included recalibrating the instrument; running diagnostic checks and correcting any problems that are identified; preparing fresh standards; checking reagents for contamination and discarding any found to be contaminated; and taking the instrument out of service for maintenance or repair.

For most analyses, enough sample volume was collected to re-run any samples that did not initially meet the QC guidelines. In a few cases, the volume of sample collected for TOC analysis was only sufficient for one analysis consisting of five replicate injections; and if QC guidelines were not met, the data were carefully reviewed, the results were marked with a footnote indicating the deviation from the QC guidelines, and justification was given for including or excluding results based on a statistical analysis of the data.

pH, Alkalinity, Dissolved Oxygen, and Conductivity

Standard Method 4500-H^+ (APHA et al. 2005) was used to determine pH. For the fill-and-dump experiments, including preparation of the extraction waters, and for chlorine demand testing, pH was determined using either: 1) a pH meter (Accumet™ AB15, Fisher Scientific™, Pittsburg, PA) equipped with a double junction pH electrode (Ag/AgCl, Orion™ 9107BN Triode™, Thermo Scientific™, Waltham, MA); or 2) a pH meter (Accumet™ XL25, Fisher Scientific™, Pittsburg, PA) equipped with fast-response research-grade electrode (pHASE model S10101CD, Sensorex Corp., Garden Grove, CA). The latter was used for all other experiments, including those to determine the hydrolysis rates of bisphenol diglycidyl ethers and bisphenol A and the reactions of chlorine and monochloramine with bisphenol A, bisphenol F, and bisphenol A diglycidyl ether. Each meter was equipped with an automatic temperature compensation probe.

Alkalinity was analyzed according to Standard Method 2320 using an automatic titrator (Model DL15, Mettler Toledo, Columbus, OH). Dissolved oxygen (DO) was measured following Standard Method 4500-O using a DO meter (Model 5000, YSI Incorporated, Yellow Springs, OH). Conductivity was measured according to Standard Method 2510 using a portable conductivity meter (Orion Star A222, Thermo Scientific™, Waltham, MA). Samples analyzed for pH, alkalinity, dissolved oxygen, and conductivity were analyzed immediately and not stored.

Hardness, Sodium, and Potassium

Hardness was determined by analyzing samples for calcium and magnesium and summing their concentrations in units of mg/L as $CaCO_3$. Calcium, magnesium, sodium, and potassium were analyzed using flame atomic absorption spectrometry (FLAAS) following Standard Method 3111 (APHA et al. 2005) and using a flame atomic absorption spectrometer (Varian 240, Agilent Technologies, Santa Clara, CA). Sodium and potassium concentrations were determined in emission mode. Samples for analysis of hardness, sodium, and potassium were stored at 4º C in polypropylene centrifuge tubes (50 mL, Cat. No. 05-539-13, Fisherbrand™, Pittsburg, PA) and preserved by adding 4 drops of nitric acid per 10 mL of sample.

Free and Combined Chlorine and Free Ammonia-Nitrogen

Concentrations of free and combined chlorine and free ammonia-nitrogen were determined using a spectrophotometer (DR 5000 UV-Vis Spectrophotometer), vials (AccuVac® Ampuls), and reagents purchased from Hach Co. (Loveland Colo.). Total chlorine concentrations in mg/L as Cl_2 were determined using Hach Method 8167 (Hach 2014), a method based on the reaction of chlorine with iodide and N,N-diethyl-p-phenylenediamine (DPD), adapted from Standard Method 4500-Cl G (DPD Colorimetric Method; APHA et al. 2005). Monochloramine and free ammonia-nitrogen concentrations were determined using Hach Method 10200 (Hach 2015). Spot tests to verify the presence or absence of free or combined chlorine in selected samples were conducted using reagents prepared as described in Standard Method 4500-Cl G. Samples analyzed for free or combined chlorine were analyzed immediately and not stored.

Total Organic Carbon (TOC)

TOC concentrations were determined using a portable TOC analyzer (Sievers Model 900, GE Instruments, Boulder, Colo.) located at the Clinton Lake Lawrence Water Treatment Plant in Lawrence, KS Each time the instrument was used, the analyst used at least three calibration standards (high, medium, and low) and analyzed 1 reagent blank and 1 calibration check for every 10 samples, 1 duplicate sample, 1 matrix spike, and 1 sample spiked with inorganic carbon (sodium bicarbonate, to verify complete stripping of carbon dioxide from the acidified samples). Five replicate injections were made for each sample, with the first two omitted to minimize instrument "memory". The remaining replicates were required to have a relative standard deviation (RSD) of ≤ 2% for TOC levels > 2000 µg/L, ≤ 3% for TOC levels ≤ 2000 µg/L, ≤ 5% for TOC levels ≤ 1000 µg/L, and ≤ 10% for TOC levels ≤ 500 µg/L. If the RSD criterion for a given sample was not met, the sample was re-analyzed until the RSD criterion was satisfied. If a sample was analyzed more than once for TOC and none of the results met QA guidelines, the result based on replicates having the lowest relative standard deviation (RSD) was used, with a note added to indicate that the RSD criterion was not met. See Appendix D for the standard operating procedure (SOP) for TOC.

The method detection limit (MDL) for TOC, based on analysis of a 1.00 mg/L standard on 8 different days, was 0.10 mg/L. However, caution should be exercised when drawing conclusions from low-level TOC measurements (≤ 0.30 mg/L). Small and variable amounts of TOC are present in reagent water and introduced during sample handling, and there is no universally agreed upon method of handling the instrumental response produced when ultrapure water is injected into a TOC analyzer.

Samples collected for TOC analysis were stored at 4º C in amber borosilicate glass vials with screw caps and PTFE-lined septa (40 mL, Cat. No. 2122-40mlT, QEC, Beaver, W. Va.) and were at first preserved by adding 5 drops phosphoric acid per 10 mL of sample. Some samples from the first fill-and-dump experiment were found to contain minute amounts of a white fluffy precipitate, possibly due to precipitation of a phosphate salt. For subsequent experiments, samples for TOC analysis were preserved by adding only 1 drop of phosphoric acid per 10 mL of samples, which was still more than enough to drop the pH of the samples to below 2; and this resolved the problem.

Lead, Copper, and Chromium

Lead, copper, and chromium were determined in accord with Standard Method 3113 (APHA et al. 2005) using an atomic absorption spectrophotometer equipped with a graphite furnace (Varian Model 120, Agilent Technologies, Santa Clara, CA). Ammonium di-hydrogen phosphate (5,000 mg/L) and palladium (500 mg/L) were used as matrix modifiers for analysis of lead and copper, respectively. QC samples analyzed with every 20 samples in each run of the instrument included: a duplicate sample, a laboratory-fortified blank (LFB), a laboratory-fortified matrix (LFM) sample, and a reagent blank. To meet QC guidelines, the measured concentrations for the LFM and LFB had to be within 20% of their actual value and the concentration in the reagent blank had to be below the MDL. Furthermore, the RSD had to be less than 5% for lead results > 2 ppb and less than 10% for lead results < 2 ppb. The RSD had to be less than 5% for copper results > 1 ppb and less than 10% for copper results < 1 ppb. If any of these QC guidelines were not met, corrective measures were taken, including: instrument recalibration, re-analysis of a failed sample, or re-analysis of the entire batch of samples. The MDLs for lead and copper using these methods were 0.5 µg/L and 0.25 µg/L, respectively. Samples collected for analysis of lead and copper were stored at 4º C in polypropylene centrifuge tubes (15 mL, Cat. No. 05-539-12, Fisherbrand™, Pittsburg, PA) and preserved by adding 4 drops of nitric acid per 10 mL of sample. See Appendices E and F for the SOPs for analysis of lead and copper, respectively, in aqueous samples.

Antimony (Sb)

Antimony analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS) (PlasmaQuad II+XS, VG Elemental, Thermo Scientific™, Waltham, MA). At least 5 standards were analyzed at the beginning and end of each run of the instrument to establish and check the calibration curve. A continuing calibration check and LFM were analyzed with every 10 samples. To meet QC guidelines, the LFM and continuing calibration check had to be measured within 20% of their actual value. The MDL for antimony using these methods was 0.06 µg/L. Samples collected for analysis of antimony were stored at 4º C in polypropylene centrifuge tubes (15 mL, Cat. No. 05-539-12, Fisherbrand™, Pittsburg, PA) and preserved by adding 4 drops of nitric acid per 10 mL of sample. See Appendix G for the SOP for analysis of antimony in aqueous samples.

Metals by ICP-MS and Laser-Ablation ICP-MS

Samples of the epoxy and PET liners used in the fill-and-dump experiments were analyzed for acid extractable metals using the PlasmaQuad II+ ICP-MS in scanning mode to identify elements present in the samples. For the epoxy, aqueous samples were prepared for ICP-MS analysis using hot-plate digestion, as described in the section on epoxy analysis below. For the PET liner, samples were initially analyzed using laser ablation followed by ICP-MS. The laser converted liner material into an aerosol, which was subsequently ionized in an argon plasma before entering a quadrupole mass spectrometer, which in turn produced a continuous signal (counts per sec.) for each mass-to-charge ratio detected. This method is very sensitive, and was useful for identifying elements present in the liner, even if present in small amounts. A laser ablation microprobe (LA: Merchanteck LUV266X Laser Ablation Station) was used to ablate the samples; the aerosols generated were then conducted to the PlasmaQuad II+ ICP-MS using argon as a carrier gas. However, the exact amount of material drawn from the solid into the detector is unknown and no matrix standards were available, so the results of this analysis were strictly qualitative. Subsequently, aqueous samples were prepared by microwave digestion of the PET liner materials and analyzed by ICP-MS for antimony and other metals.

Bisphenols

The liquid chromatography / triple quadruple mass spectrometry (LC/MS/MS) method used for bisphenols was adapted from a previously described method (Gallart-Ayala et al. 2011). The LC/MS system consisted of a Shimadzu (Columbia, MD) Prominence High Performance LC (HPLC) equipped with a LC-20AB binary pump, DGU-20A3 degasser, and SIL-20A autosampler coupled to a 4000 QTrap triple-quadrupole linear ion-trap mass spectrometer with a turbo ion-spray source (AB SciEx, Framingham, MA). A Gemini-NX C18-with-TMS-endcapping column (150 × 3.0 mm, 3-micron particle size; Phenomenex, Torrance, CA) was selected to provide reverse phase chromatographic separation over a broad pH range (2 to 12). A 50 µL aliquot of sample was injected and carried by a water and methanol mobile phase at a flow rate of 0.4 mL/min. The gradient mobile phase was applied with the following percentages of methanol: held at 65% for 1 min., ramped from 65% to 85% over 5 min., held at 85% for 6 min., ramped from 85% to 100% over 3 min., held at 100% for 2 min., then returned to 65% over 4 min. and held for 5 min.

The MS electrospray source was operated with nitrogen gas for nebulization. The MS/MS parameters were optimized for each analyte and are summarized, along with the MDL for each analyte, in Table 3.1. BPA-D8 was used as the surrogate internal standard (to provide correction for filter losses and instrumental variation) and BPA-D16 was used as the internal standard (to provide corrections for instrumental variation). A linear calibration curve was used for quantitation and the method detection limits (MDLs) were determined as described in *Standard Methods* Method 1030C, Method Detection Limit (APHA et al. 2005). Additionally, the signal-to-noise (S/N) value was always kept above 2 for quantitation; anything below 2 was considered noise (Skoog et al. 2007). Examples of chromatograms with elution times and calibration curves used for quantitation are shown in Figure 3.6. See Lane (2015) for additional information, including a detailed SOP.

To prevent clogging of the LC column and LC system with debris in samples from the unlined and uncoated control pipe sections, these samples had to be filtered. So that all samples for a given experiment would be processed in the same way, all samples collected for bisphenol analysis during the fill-and-dump experiments were filtered using sterile mixed cellulose ester (MCE) syringe filters (0.22 µm pore size, 25 mm dia.; Fisherbrand™, Pittsburg, PA). These filters were selected over other types tested because they were found not to leach bisphenols and exhibited relatively low adsorption of bisphenol D (Lane 2015). Prior to use the filters were conditioned with reagent water.

To obtain bisphenol data at specific time points during the chlorination experiments, a quenching agent was required. Since changes in solution matrix (including addition of quenching agents) can alter the ionization efficiency of the MS electrospray, experiments were conducted to determine which quenching agent would exert the least impact on the electrospray. Sodium bisulfite was selected from among those tested because it did not significantly suppress or enhance the BPA signal at high concentrations. See Lane (2015) for additional information.

Table 3.1
MS parameters for LC/MS/MS analysis of bisphenols and chlorinated by-products

Compound	CAS Number	Precursor Ion (m/z)		Product Ion (m/z)	DP (V)	CE (V)	CXP (V)	MDL (µg/L)
BPA	80-05-7	**$[M-H]^-$**	**227.0**	**212.0**	-76.02	-24.87	-3.12	0.057
		$[M-H]^-$	227.0	133.0	-76.02	-31.26	-10.35	
BPA-Cl	74192-35-1	**$[M-H]^-$**	**261.7**	**181.9**	-69.59	-41.39	-12.97	13.6
		$[M-H]^-$	261.7	245.8	-44.96	-29.12	-14.74	
BPA-2Cl	79-98-1	**$[M-H]^-$**	**295.0**	**243.8**	-84.88	-32.91	-5.10	1.8
		$[M-H]^-$	295.0	216.1	-49.95	-41.35	-32.37	
BPA-3Cl	40346-55-2	**$[M-H]^-$**	**330.6**	**252.0**	-40.15	-44.21	-8.36	3.2
		$[M-H]^-$	330.6	278.0	-52.96	-35.24	-12.26	
BPA-4Cl	79-95-8	**$[M-H]^-$**	**365.0**	**314.0**	-81.19	-35.77	-13.06	5.9
		$[M-H]^-$	365.0	286.0	-33.04	-45.66	-13.26	
BPB	77-40-7	**$[M-H]^-$**	**241.0**	**212.0**	-66.98	-24.20	-9.44	0.18
		$[M-H]^-$	241.0	211.0	-66.98	-34.76	-13.10	
BPD	6807-17-6	**$[M-H]^-$**	**269.0**	**212.0**	-82.07	-25.08	-16.67	0.1
		$[M-H]^-$	269.0	211.0	-82.07	-35.56	-3.60	
BPE	2081-08-5	**$[M-H]^-$**	**213.0**	**198.0**	-68.21	-23.37	-3.02	0.07
		$[M-H]^-$	213.0	199.0	-68.21	-37.54	-3.44	
BPF	620-92-8	**$[M-H]^-$**	**199.0**	**93.0**	-67.19	-29.07	-6.88	0.18
		$[M-H]^-$	199.0	105.0	-70.68	-28.42	-5.56	
BPA-D8	92739-58-7	**$[M-H]^-$**	**235.0**	**220.0**	-76.20	-25.68	-4.58	NA
		$[M-H]^-$	235.0	137.0	-78.04	-35.62	-8.86	
BPA-D16	96210-87-6	**$[M-H]^-$**	**241.0**	**142.0**	-84.38	-37.51	-10.54	NA
		$[M-H]^-$	241.0	222.0	-71.80	-40.84	-15.26	
TCP	88-06-2	**$[M-H]^-$**	**194.7**	**35.0**	-29.98	-44.79	-3.50	NA
		$[M-H]^-$	194.7	158.8	-64.45	-29.97	-24.66	

Source: Adapted from *Water Research*, vol. 72, Lane, R. F., C. D. Adams, S. J. Randtke, and R. E. Carter, Jr. Bisphenol Diglycidyl Ethers and Bisphenol A and Their Hydrolysis in Drinking Water, Copyright 2015, with permission from Elsevier.

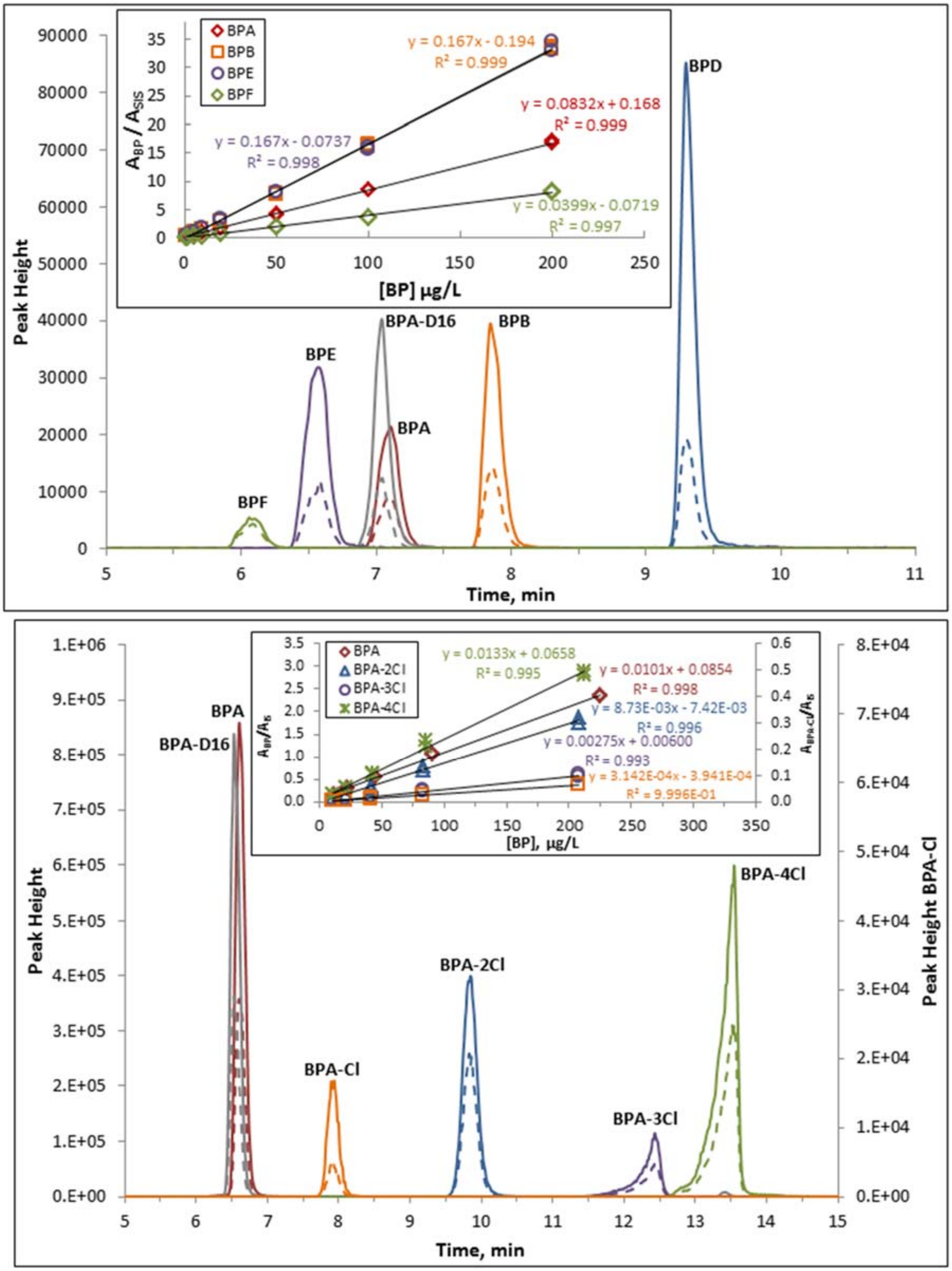
Transitions in bold are quantitation ions

NA = Not applicable

DP = Declustering potential

CE = Collision energy

CXP = Collision cell exit potential



Source: Lane 2015.

Figure 3.6 LC/MS/MS chromatogram of a 20 µg/L mixed bisphenols standard and calibration curves (top); LC/MS/MS chromatogram of an 80 µg/L mixed chlorinated bisphenol A standard and calibration curves (bottom)

Bisphenol Diglycidyl Ethers (BDGEs)

The LC/MS/MS method for BDGEs was adapted from a previously described method (Gallart-Ayala et al. 2011) and the instrumental system described for the bisphenols was also used for the BDGEs. A Gemini-NX C18-with-TMS-endcapping column(Phenomenex, Torrance, CA), 150 × 3.0 mm, 3-micron particle size was selected such that reverse phase chromatographic separation could be achieved with samples in the pH range of 2 to 12. A 50 µL aliquot of sample was injected at a flow rate of 0.4 mL/min. The gradient mobile phase was ammonium formate at pH 3.75 and methanol. The gradient used was 30% to 60% methanol over 4.5 min., then from 60% to 84% methanol over 5 min., from 84% to 90% methanol over 10 min., from 90% to 100% methanol over 5 min., held at 100% methanol for 2 min., and then returned to 60% methanol over 5 min.

The MS electrospray source was operated with nitrogen gas for nebulization. The ammonium in the mobile phase was present to facilitate formation of a BDGE adduct. The BDGE ion is not stable in the electrospray but BDGE ammonium adducts are stable. The MS/MS parameters were optimized for each analyte and are summarized, with MDLs, in Table 3.2. Because BADGE is susceptible to hydrolysis, calibration standards and run standards were prepared every 24 hours and all samples were run within 24 hours of sampling. A deuterated analog of sulfamethoxazole (SMXL-D4) was selected as the internal standard because a deuterated BDGE compound was not commercially available. The BDGE response was linear from 0 to 200 µg/L and non-linear from 200 µg/L and above (Figure 3.7). To avoid using a non-linear polynomial calibration curve, samples were diluted to within the range of the linear calibration curve. See Lane (2015) for additional information, including a detailed SOP.

Table 3.2
MS parameters for LC/MS/MS analysis of bisphenol diglycidyl ethers

Compound	CAS Number	Precursor Ion (m/z)		Product Ion (m/z)	DP (V)	CE (V)	CXP (V)	MDL (µg/L)
BADGE	1675-54-3	**[M+NH4]$^+$**	**358.2**	**191.0**	51.95	21.49	12.04	7.00
		[M+NH4]$^+$	358.2	135.0	51.95	43.41	7.61	
BADGE-H_2O	76002-91-0	**[M+NH4]$^+$**	**376.4**	**209.0**	46.49	20.47	12.37	1.50
		[M+NH4]$^+$	376.4	135.0	46.49	40.38	6.46	
BADGE-2H_2O	5581-32-8	**[M+NH4]$^+$**	**394.4**	**209.0**	46.87	23.71	12.24	1.40
		[M+NH4]$^+$	394.4	135.0	46.87	46.16	6.32	
BADGE-H_2O-HCl	227947-06-0	**[M+NH4]$^+$**	**412.8**	**135.0**	38.50	48.57	6.11	7.60
		[M+NH4]$^+$	412.8	227.1	38.50	21.93	13.80	
BADGE-HCl	13836-48-1	**[M+NH4]$^+$**	**394.0**	**227.0**	42.89	19.78	14.17	0.48
		[M+NH4]$^+$	394.0	135.0	42.89	45.21	6.71	
BADGE-2HCl	4809-35-2	**[M+NH4]$^+$**	**431.3**	**229.0**	51.65	22.45	15.11	2.90
		[M+NH4]$^+$	431.1	227.0	54.59	23.48	13.81	
BFDGE	2095-03-6	**[M+NH4]$^+$**	**328.8**	**163.0**	41.97	19.35	8.93	0.24
		[M+NH4]$^+$	328.8	133.0	42.96	24.33	6.35	
SMXL-D4	1020719-86-1	**[M+H]$^+$**	**258.0**	**96.0**	56.36	45.25	17.08	NA
		[M+H]$^+$	258.0	112.0	72.14	35.41	5.62	

Source: Adapted from *Water Research*, vol. 79, Lane, R.F., Adams, C.D., Randtke, S.J., and Carter, Jr., R.E. Chlorination and Chloramination of Bisphenol A, Bisphenol F, and Bisphenol A Diglycidyl Ether in Drinking Water, Copyright 2015, with permission from Elsevier.

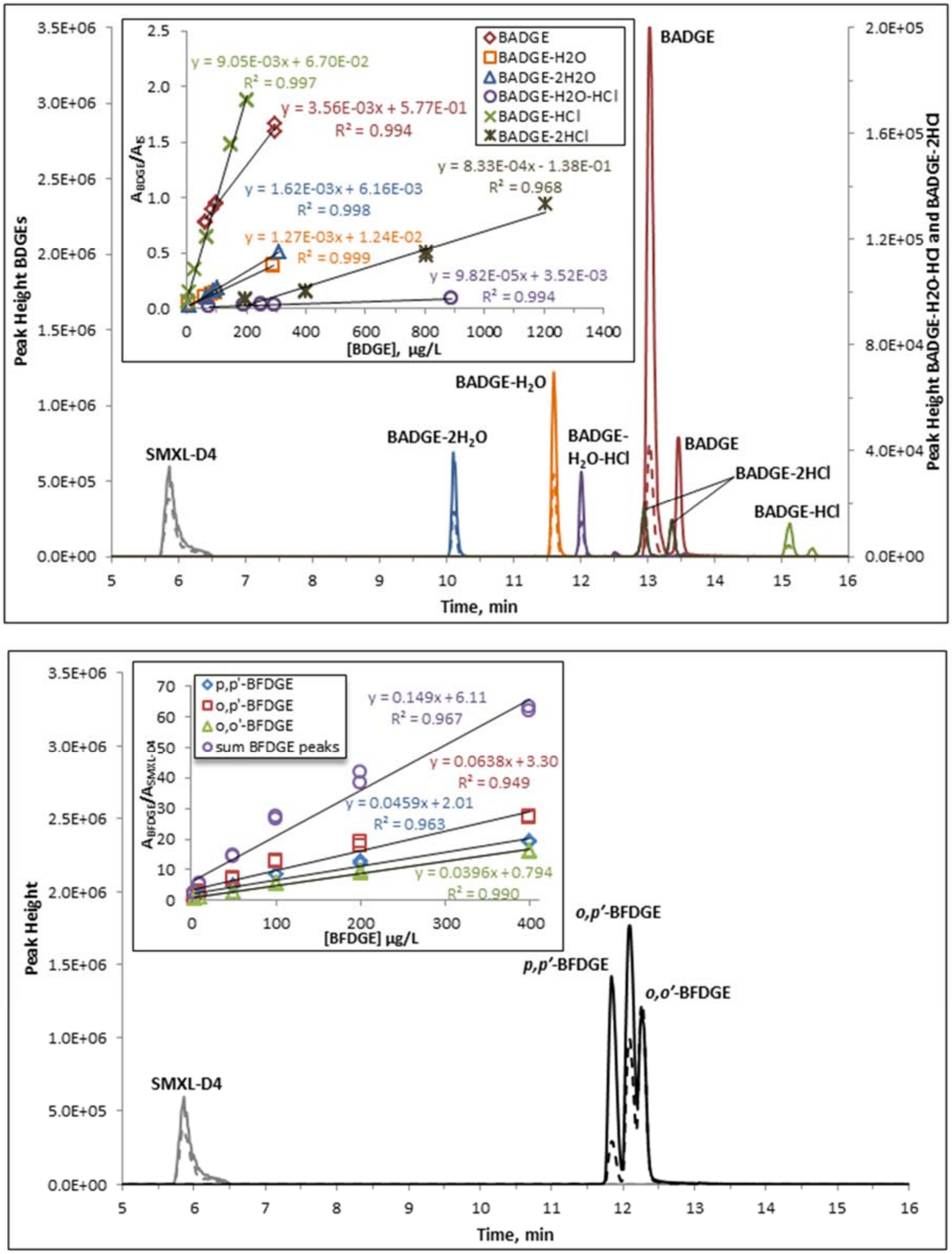
Transitions in bold are quantitation ions

NA = Not applicable

DP = Declustering potential

CE = Collision energy

CXP = Collision cell exit potential



Source: Lane 2015.

Note: The BDGE mix standard contained 296 µg/L BADGE, 294 µg/L BADGE-H$_2$O, 310 µg/L BADGE-2H$_2$O, 893 µg/L BADGE-H$_2$O-HCl, 204 µg/L BADGE-HCl, 805 µg/L BADGE-2HCl.

Figure 3.7 LC/MS/MS chromatogram of BDGE mix standard and calibration curve (top); chromatogram of an 800 µg/L BFDGE standard and calibration curve (bottom)

Bisphenols and BADGE in Epoxy

A gas chromatography / mass spectrometry (GC/MS) method was used to determine key starting materials in the epoxy resin. Due to reactivity of the epoxy starting materials (part A and part B), a GC/MS method was selected to prevent contamination and epoxy coating of the LC/MS system. A GC (Agilent 6890A, Agilent Technologies, Santa Clara, CA) equipped with an MS detector (Agilent 5973N), an autosampler (Model 7683) and a capillary GC column (HP-5MS, 0.25 mm ID x 30 m, with a 0.25-µm film thickness) was operated in scan mode from 40 to 550 Da. Helium was used as the carrier gas and the transfer line temperature was 270 °C. The sample solvent was methanol (with a 3.5 min solvent delay), and a 1.0 µL splitless injection was made at an injection temperature of 270 °C with a constant carrier gas flow rate of 1.0 mL/ min. The oven temperature was held at 100 °C for 0.5 min then ramped at 9 °C/min to 300 °C. Bisphenol and BADGE standards were run prior to any MS scans to confirm the retention times of the analytes of interest.

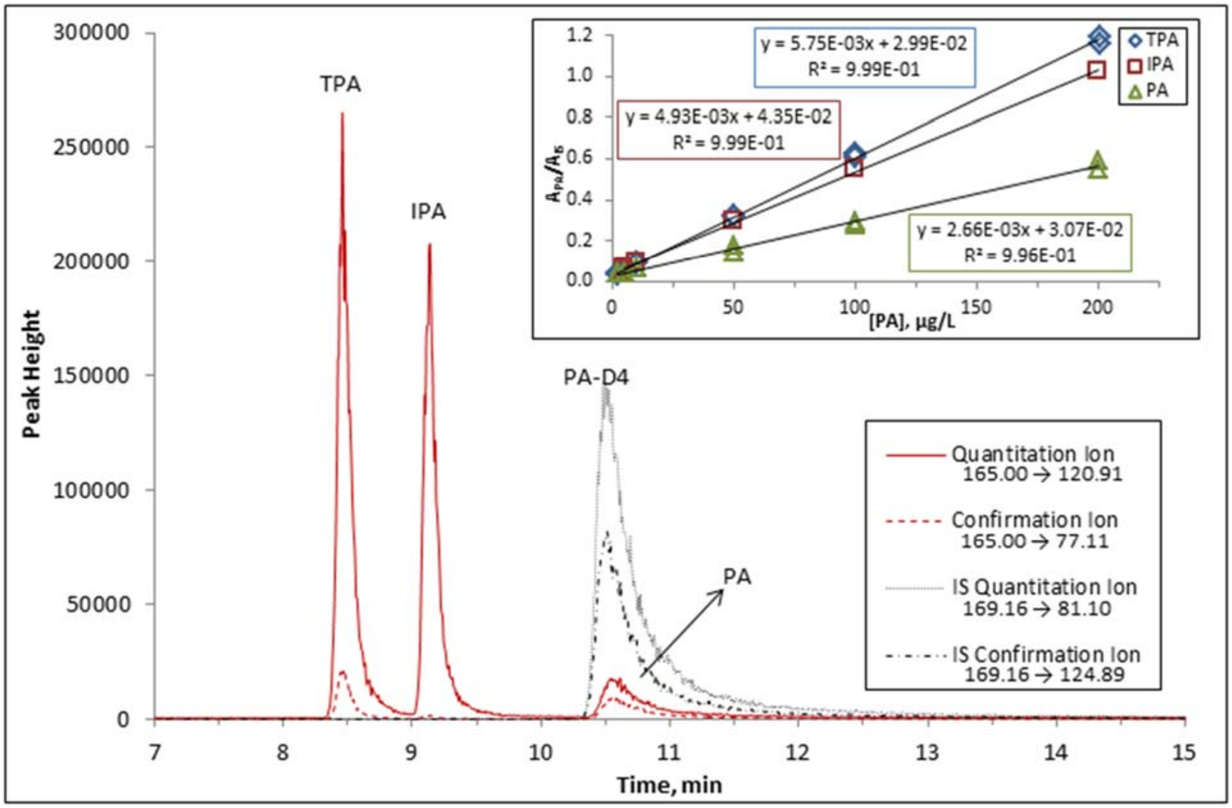
Time-of-Flight Mass Spectrometry (TOF-MS)

Time-of-flight mass spectrometry (TOF-MS) analysis was performed by the University of Kansas (KU) Mass Spectrometry & Analytical Proteomics Laboratory on a Micromass Q-TOF-2 mass spectrometer (Micromass Ltd., Manchester UK).

Phthalic Acids (PAs)

The same LC/MS/MS system and chromatographic column used for the analysis of bisphenols was also used for phthalic acid analysis. A 50 µL aliquot of sample was injected at a flow rate of 0.4 mL/min. The gradient mobile phase was 0.1% formic acid and acetonitrile. The following percentages of acetonitrile were applied as the gradient: held at 15% for 3 min., then from 15% to 36% over 7.8 min., from 36% to 49% over 10.2 min., then 49% to 100% over 2 min., held at 100% for 2 min., and then returned to 15% over 5 min.

The quantitation ion for the PAs had a MRM transition of 165.00 → 120.91 and collision cell exit potential (CXP, volts) of -8.63, collision energy (CE, volts) of -17.45, and declustering potential (DP, volts) -52.58. The PAs confirmation ion had a MRM transition of 165.00 → 77.11 and CXP (volts) of -4.51, CE (volts) of -26.68, and DP (volts) -52.58. The internal standard, deuterated phthalic acid (PA-D4), had a quantitation ion MRM transition of 169.16 → 81.10 and CXP (volts) of -3.55, CE (volts) of -22.59, and DP (volts) -25.89. The internal standard had a confirmation ion MRM transition of 169.16 → 81.10 and CXP (volts) of -7.07, CE (volts) of -15.26, and DP (volts) -28.91. The phthalic acids are isomers so it was not possible to have separate MRM transition ions. Therefore, a specific acid was identified by its retention time, which was confirmed with a standard prior to every run, that is: ~10.6 min. for PA, 9.14 min. for IPA, and ~8.62 min. for TPA (Figure 3.8). In reagent water, the MDLs were 1.4 µg/L, 0.53 µg/L, and 0.70 µg/L for PA, IPA, and TPA respectively. In dechlorinated tap water, 10% (by volume) acetonitrile was added to all samples and standards (to control the degradation of IPA and TPA, and the MDLs were 4.0, 2.1, and 3.1 µg/L for PA, IPA, and TPA respectively. See Lane (2015) for additional information, including a detailed SOP.



Source: Lane 2015.

Figure 3.8 LC/MS/MS chromatogram and calibration curve for a 500 µg/L mixed phthalic acids standard

Phthalate Esters

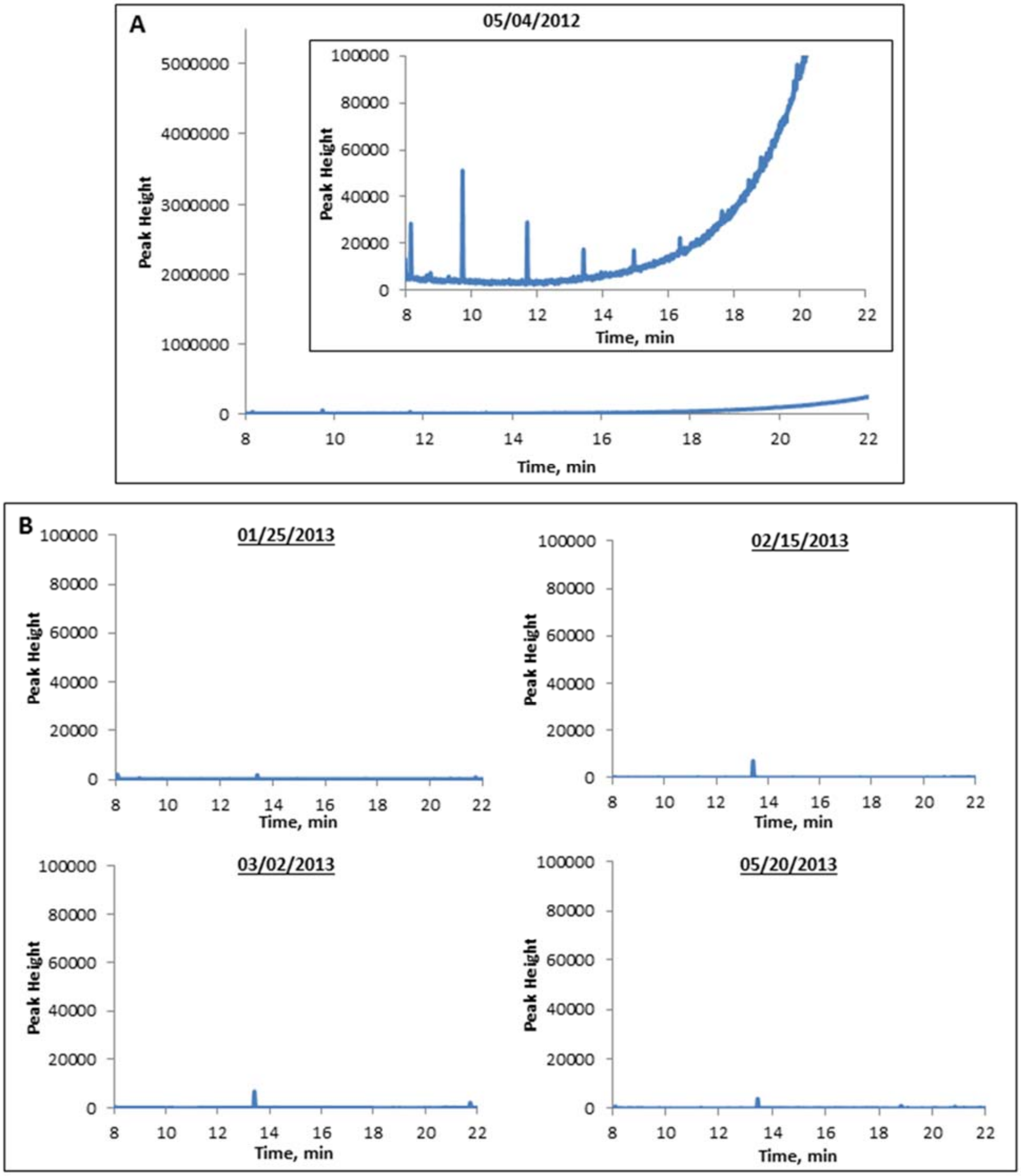
The same GC/MS system described above (see Bisphenols and BADGE in Epoxy) was used for the analysis of phthalate esters, but with a different capillary column (Varian FactorFour VF-5MS 0.32 mm ID, 30 m length, and 0.5 µm film thickness). Helium was used as the carrier gas and the transfer line temperature was 270 °C. The sample solvent was hexanes/chloroform (50/50 by volume) with a 4.5 min solvent delay; a 1.0 µL splitless injection was made at an injection temperature of 270 °C, and the carrier gas flow rate was 1.0 mL/min. The oven temperature started at 120 °C and was ramped at 20 °C/min to 200 °C, then ramped at 30 °C/min to 220 °C, then ramped at 10 °C/min to 250 °C, held at 250 °C for 5 min, then ramped at 10 °C/min to 300 °C, and held for 4 min. The MS was operated in SIM mode and transitions and elution times are reported in Table 3.3.

Prior to GC/MS analysis, phthalate esters were extracted from samples and standards using liquid-liquid extraction (LLE). To each 20-mL sample aliquot, 500 g of sodium chloride and the surrogate internal standard (DNHP-D4) were added. The sample was extracted with 1 mL of chloroform, followed by extraction with 1 mL of hexane, and the organic layer was collected for analysis. The background level of the phthalates could not be reduced to below the noise (Figure 3.9A); the background levels were reduced from those observed during initial method optimization but were never completely eliminated (Figure 3.9B). The background levels varied between run days but were stable during the runs. A linear calibration curve based on the surrogate internal standard was used for quantitation and the S/N was used to determine the MDLs for each run day, which ranged from ≤ 1 to 10 µg/L (with a S/N of greater than 2 considered a relevant signal). The MDL was based on the S/N due to the low level variable phthalate background. A chromatogram with all phthalate esters included in the analysis is provided in Figure 3.10. See Lane (2015) for additional information, including a detailed SOP.

Table 3.3
MS parameters for GC/MS analysis of phthalate esters

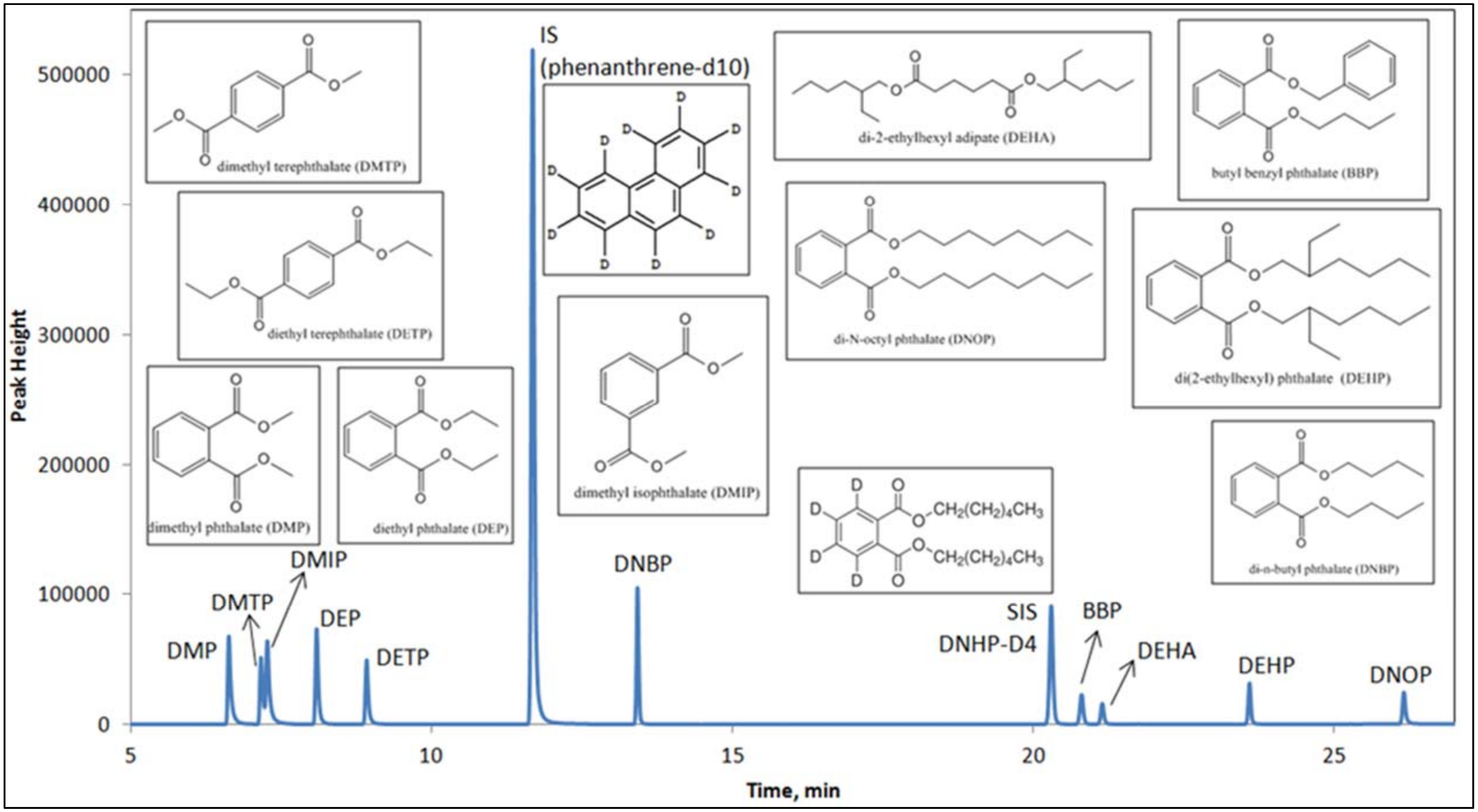
Compound	CAS Number	Retention Time, min	MS Ions Monitored Time, min	MS Ions Monitored Ions, Da
DMP	131-11-3	6.604	4.5 to 7.7	163.1 & 194.1
DMTP	120-61-6	7.136	4.5 to 7.7	163.1 & 194.1
DMIP	1459-93-4	7.243	4.5 to 7.7	163.1 & 194.1
DEP	84-66-2	8.063	7.7 to 10.0	149.1 & 177.1
DETP	636-09-9	8.892	7.7 to 10.0	149.1 & 177.1
DNBP	84-74-2	13.401	12.6 to 18.0	149.1 & 223.1
BBP	85-68-7	20.776	20.6 to 21.0	149.1 & 206.1
DEHA	103-23-1	21.126	21.0 to 22.5	129.1 & 147.1
DEHP	117-81-7	23.583	22.5 to 25.0	149.1 & 167.1
DNOP	117-84-0	26.158	25.0 to 26.7	149.1 & 279.1
DNHP-D4	1015854-55-3	20.276	18.0 to 20.6	153.1 & 255.1
PANE-D10	1517-22-2	11.657	10.0 to 12.6	160.0 & 188.2

Source: Lane 2015



Source: Lane 2015.

Figure 3.9 GC/MS chromatograms of control blanks for analysis of phthalate esters: (A) control blank used during method optimization, with inlay zoomed in to show low-level phthalates in the background; (B) control blanks from different dates illustrating the variable low-level phthalate background.



Source: Lane 2015.

Figure 3.10 GC/MS with LLE extraction of an 800 µg/L mixed phthalate ester standard

EXPERIMENTAL PROCEDURES

Physical Characteristics of Pipe Sections before and after Lining or Coating

The internal volume of each LSL section was determined, before and after coating or lining, by stoppering one end, filling the LSL with reagent water, pouring the water into a tared beaker, weighing the beaker to determine the mass of water held by the LSL, which was used to calculate the volume. A similar procedure was used for the CSL sections, but since the CSL sections were all cut to the same length from two coils (one coil for the epoxy-coating sections and the other for the PET-lined sections) the volumes of the unlined CSL sections were expected to be virtually the same, so the initial volumes were estimated based on the (nearly identical) calculated volumes of three CSL sections from each coil.

The length of each pipe section was measured and divided into the calculated volume to determine the average inner cross-sectional surface area and average inner diameter of each pipe section. The calculated average inner diameter of each coated or lined pipe section was subtracted from its pre-coated or pre-lined average inner diameter, then divided by two to determine the average coating or lining thickness. The average inner diameter was used to calculate the inner circumference then multiplied by the pipe's length to determine the inner surface area of each pipe.

Epoxy Analysis

Samples of the epoxy used to coat the pipe sections for the fill-and-dump experiments were analyzed for both organic and inorganic constituents, in part to assist in interpreting the results of the fill-and-dump experiments and in part in an effort to determine if other constituents should be included in analyzing samples from the fill-and dump experiments. Samples of Part A and Part B of the epoxy were dissolved and diluted (1:150) in methanol and analyzed for organic constituents as described above (see Analytical Methods – Bisphenols and BADGE in Epoxy).

A sample of hardened epoxy was digested and analyzed for lead, copper, and chromium, elements likely to be present in the pipe sections and some of the end-fittings used in the fill-and-dump experiments, and which could potentially compromise the results or complicate their interpretation. Approximately 3 grams of epoxy were mixed and allowed to cure as a thin layer on a polystyrene weighing dish (Hexagonal Type, Fisherbrand™, Pittsburg, PA). The cured epoxy was then carefully chipped away from the plate and placed in an Erlenmeyer flask with 9 mL nitric acid and 3 mL of hydrochloric acid. The mass of the cured epoxy chips was 1.1 grams. The flask was then topped with a lens and placed on a hot plate set to a temperature of 85 ^{o}C. The mixture was allowed to digest for 24 h after which another 10 mL nitric acid, 4 mL hydrochloric acid, and 5 mL of 30% hydrogen peroxide were added. The temperature was then raised to 90 ^{o}C. Peroxide was added periodically (134 mL total) to quicken the digestion. Nitric and hydrochloric acids were also added periodically (totaling 27 mL and 10 mL, respectively). The epoxy was never fully digested, but the remaining mass was bleached from red to yellow. The digestate was analyzed for lead, copper, and chromium using the graphite furnace atomic absorption spectrometry (GFAAS) method described above (see Analytical Methods), and a scan for other elements in the digestate was performed using ICP-MS.

PET Liner Analysis

A small section of PET liner cut from a longer piece of unexpanded PET liner obtained during a demonstration test conducted in Providence, RI (described later in this report) was initially analyzed for multiple elements using laser ablation ICP-MS as described above (see Metals by ICP-MS and Laser-Ablation ICP-MS). To obtain quantitative results for the elements identified in the initial (laser ablation) ICP-MS analysis, PET liner samples of known mass were digested, and the digestates were diluted in a known volume of solution to provide samples for quantitative ICP-MS analysis. Triplicate samples of PET liner, approximately 2 mm^2 in size and weighing 0.1 – 0.3 mg, were each placed in a PTFE vessel containing 10 mL 65% nitric acid and 2 mL 30 – 32% hydrochloric acid. A control sample containing only the combined nitric and hydrochloric acid mixture was also prepared. The vessels were then placed in a microwave digester (Multiwave 3000, Anton Paar, Ashland, Va.). Digestion proceeded in two stages. In the first stage, elevated temperature and pressure were achieved by setting the microwave power output at 400 W, with a pressure increase rate of 0.3 bar/s for 15 min. This condition was held for 60 min. In the second "cool down" stage, the power output was reduced to 0 W but pressure was maintained for 20 min. After digestion, the vessels were rinsed into a volumetric flask and diluted to 100 mL with reagent water. The digested solids contained small amounts of solids that were removed by filtration through a 0.45 µm PTFE syringe filter (Fisherbrand™, Pittsburg, PA) prior to ICP-MS analysis (to avoid plugging the inlet of the instrument). Concentrations of constituents in the liner were calculated by dividing their concentration in the digestate by the mass of PET liner digested, and then averaging the results for three PET liner samples that were digested. Since the PET liner material was not completely digested, the results of this analysis could be biased low with respect to total metal concentrations in the liner. These results thus are reported as the "acid extractable" concentrations for each metal.

To investigate whether selected phthalic acids or phthalate esters could be leached from a PET liner under extreme conditions, pieces of the liner were extracted with a mixture of hexane and chloroform (50:50), with acetonitrile, and with methanol and water (10:90). These organic extracts were then analyzed for phthalic acids and phthalate esters using the methods described above for the fill-and-dump samples, but the samples were not filtered nor was additional acetonitrile added.

Leaching and Adsorption of Constituents by End Fittings

To minimize potential experimental artifacts, and to facilitate comparison of results for control sections with those for lined or coated sections, end-fitting materials used in the fill-and-dump experiments were tested to determine their potential to leach or adsorb constituents of interest, such as lead, copper, antimony, TOC, bisphenols, BDGEs, phthalic acids, and phthalate esters.

In coated or lined pipe sections, the extraction water would be in direct contact with the ends of silicone or HDPE stoppers, respectively. Extraction water in uncoated and unlined pipe sections (controls) would also be in contact with the SS pipe nipples and potentially with small amounts of PTFE thread tape in the LSL pipe sections. Furthermore, extraction water from coated and lined pipe sections would have brief contact with the ends of the SS pipe nipples as the water was poured into a beaker. Consequently, SS pipe nipples, silicone and HDPE stoppers, and PTFE tape were all tested to determine their ability to leach or adsorb lead, copper, antimony, and the organic constituents of interest. Each type of stopper (silicone and HDPE) was also tested for chlorine demand and for leaching of TOC.

Leaching or adsorption of the various end-fitting materials was examined by immersing them, or where appropriate by filling them, with either reagent water or with solutions containing known concentrations of the constituents of interest. After a specified holding time at room temperature (20-25 °C), the solutions were sampled and later analyzed for the constituents of interest. Increase or decreases in the concentration of a constituent provided evidence of leaching or adsorption, respectively. In setting up each experiment, care was taken to be sure the surface-to-volume ratio of the end-fitting equaled or exceeded the ratio applicable to the fill-and-dump experiments. In addition, slices of the silicone stoppers used in the fill-and-dump texts on the epoxy-coated pipe sections were analyzed using laser ablation ICP-MS, using the same procedure described above for laser ablation of the PET liner.

Fill-and-Dump Experiments

Fill-and-dump experiments were conducted to determine the concentrations of various constituents of interest leaching from epoxy-coated or PET-lined LSL and CSL sections. Three different extraction waters and holding times varying from 6 hours to 10 days were used to simulate a broad range of field conditions. Two fill-and-dump experiments (FD1 and FD2) were conducted on epoxy-coated sections, and three (FD3, FD4, and FD5) on PET-lined sections. All of the experiments were conducted at room temperature (20-25 °C) using the procedures summarized in the paragraphs below. The SOPs for FD1, FD2, and FD3 are presented in Appendices H, I, and J, respectively.

The initial fill-and-dump experiment on each lining or coating material was designed to examine the effects of freshly cured epoxy (FD1) or freshly installed PET liners (FD3 and FD5) on water quality under reasonable worst-case, i.e., minimal flushing, and holding times up to 10 days. Additional fill-and-dump experiments, to investigate the leaching of selected constituents over time, were initially planned, but few such experiments were conducted because in the initial experiments the concentrations of many constituents of interest were either below the detection limit or low relative to applicable standards or guidelines. The second fill-and-dump experiment (FD2) examined leaching of constituents from epoxy-coated pipe sections after they had been stored under various conditions; and FD4 was conducted on PET-lined sections as a follow-up experiment to FD3. Additional fill-and-dump tests were conducted to examine in greater detail the chlorine demand associated with the epoxy coatings and PET liners, and later to examine leaching of antimony from selected pipe sections.

Each fill-and-dump experiment consisted of pouring extraction waters of known quality into a series of pipe sections, sealing the ends of the pipe sections and holding each section for a specified time, pouring the water into a beaker, and analyzing the sample for the constituents of interest. Since the number of pipe sections available for each experiment was limited, many of the pipe sections were refilled and used again, in the same experiment, with a different holding time. To ensure against experimental artifacts, the end-fitting materials used in the fill-and-dump experiments were tested for leaching and adsorption of compounds of interest, e.g., lead, copper, antimony, TOC, and selected organic constituents, as described above (see “Leaching and Adsorption of Constituents by End Fittings”).

In the field, lining and coating installers typically flush the pipes after installation, before putting the pipes back into service. To simulate this practice, lined or coated pipe sections were flushed in the laboratory after they were received from the manufacturers. Unlined and uncoated control sections were also flushed. Groups of two to four pipe sections were connected in series and flushed with tap water for 15 min. When an unlined and uncoated control section was included in the pipe manifold, it was placed last in the direction of flow to avoid contaminating a lined or coated pipe section with metals released from a control pipe section. After flushing, and immediately before filling a pipe section with extraction water, it was first rinsed with approximately 100 mL of extraction water to rinse away any tap water remaining after flushing.

Holding times used in the fill-and-dump experiments were 6 hours, 24 hours, 4 days, 7 days, and 10 days. The 6-hour holding time was chosen to be representative of the time water is typically left standing in a service line overnight, before water use continues again in the morning. Longer periods of time (24 hours to 10 days) were used for two purposes: 1) to examine the potential release of specific constituents over an extended period of time; and 2) to represent reasonable worst-case scenarios, such as all members of a household on a week-long trip.

When the desired holding time was reached for a given pipe section, the extraction water was immediately and carefully poured into a glass beaker that had been acid washed, rinsed with reagent water, dried, and protected from contamination by dust. From this glass beaker, samples were immediately poured into other containers (smaller beakers or storage vials) for analysis of pH, lead, copper, TOC, and selected organic constituents, and for analysis of residual chlorine when the extraction water initially contained chlorine. Samples collected from PET-lined pipes were also analyzed for antimony. Residual chlorine and pH were determined immediately, and samples for analysis of other constituents were preserved and stored for later analysis.

Samples of the extraction water were also collected immediately before each fill-and-dump experiment to determine the initial concentration of each constituent analyzed for in samples collected from the pipe sections. The chlorinated pH 8 extraction water was analyzed for residual chlorine immediately before and after each fill-and-dump test, to serve as a control. It was stored in a tightly capped 4 L amber-glass bottle placed next to the pipe sections to keep it at the same temperature as the extraction water in the pipe sections. Amber glass was used to reduce exposure to light, which could potentially reduce the residual chlorine concentration.

Readers should note that although the procedures used for the fill-and-dump experiments, as well as the recipes for the extraction water, were similar to those specified in NSF 61, the purpose of these experiments was not to simulate or verify the results of NSF 61 testing. The differences in the extraction waters, flushing procedures, holding times, sampling procedures, and analytical methods are such that equivalent results would not necessarily be obtained; and no conclusions should be drawn based on the results presented herein as to whether or not the materials tested meet NSF 61 or other certification or specification requirements.

Procedures for Fill-and-Dump Experiments Using Epoxy-Coated Pipe Sections

The purpose of the first fill-and-dump experiment (FD1) was to examine constituents leaching into the water from or through freshly applied epoxy. After the pipe sections were coated by the manufacturer, they were shipped (from California) back to the investigators' laboratory in Lawrence, KS where the fill-and-dump experiment was performed. For logistical reasons, approximately 72 hours passed between the completion of the epoxy application process and the start of FD1. Therefore, the epoxy cured for a much longer time than it would have in a typically field application (less than a day versus 3 days). However, the curing process may have been essentially complete after the first day, and the epoxy was still very fresh relative to its expected service life (many decades).

Randomly selected epoxy-coated pipe sections of each type (LSL and CSL) and one control pipe of each type were filled with dechlorinated pH 8 tap water and held for 6 h, 24 h, or 4 d. Two pipes of each type were held for 6 h, serving as duplicates. When the pipes that held dechlorinated pH 8 tap water for 24 hours were emptied, they were immediately filled again with dechlorinated pH 8 tap water and held for 10 more days. A second set of epoxy-coated pipes were filled with chlorinated pH 8 extraction water employing the same holding times as for those filled with dechlorinated pH 8 tap water, but without a duplicate for the 6-h holding time.

Selected pipe sections previously extracted with either dechlorinated pH 8 tap water or chlorinated pH 8 extraction water were filled with pH 6.5 extraction water and held for 6 hours. The pipes selected included: the control pipes (one of each type), the duplicate pipes that held dechlorinated tap water, and pipes (one of each type) that held chlorinated pH 8 extraction water. Once emptied, the pipes were refilled with pH 6.5 extraction water and held for 7 more days. The full testing matrix for FD1 is illustrated in Table 3.4 and the SOP presented in Appendix H. Since the pipe sections used in a given experiment were often refilled several times, using different extraction waters and holding times, the history of each section was carefully recorded and taken into consideration in interpreting the results.

As the pipe sections used in FD1 were emptied for the last time, all except one section of each type were allowed to drip dry, sealed on each end with air tight polypropylene caps, and stored at room temperature for later use. The two pipes not stored dry were filled with reagent water and the ends were sealed with silicone stoppers (LabPure® PX 18D and 21D, Saint-Gobain Performance Plastics, Portage, Wis.). Every seven days, these "wet-stored" pipes were emptied and filled with fresh reagent water.

Seven months after FD1, a second fill-and-dump experiment (FD2) was performed on selected epoxy-coated pipe sections using chlorinated pH 8 extraction water and holding times of 6 h, 24 h, and 7 d, with the sections held for 6 and 24 h being refilled and then held for 7d. The pipe sections used in FD2 included the two wet-stored pipes described immediately above, two pairs of dry-stored pipes (each pair consisting of one LSL and one CSL section), one pair of dry-stored pipes that had not been previously used (or flushed), and the uncoated LSL and CSL control sections. Before being used in FD2, the two previously unused epoxy-coated pipe sections were flushed (for the first time) for 15 minutes using tap water. The other (previously used) pipes were not flushed again prior to commencing FD2; however, every pipe was rinsed with 100 mL of reagent water immediately before being filled with chlorinated pH 8 extraction water. Note that the recipe for the extraction water for FD2 was revised from that used in FD1, as noted above (see "Extraction Waters") so that its pH would be about 8 without adjustment.

Table 3.4
FD1 and FD2 test matrix using epoxy-coated pipe sections

	Extraction Water	Holding Time, h	Pipe No.		Notes
			LSLs	CSLs	
Fill-and-Dump Experiment 1 (FD1)	Dechlorinated Tap Water, pH 8	6	Pb04	Cu10	Uncoated Controls
		6	Pb01	Cu01	
		6	Pb02	Cu02	
		24	Pb05	Cu05	
		96	Pb07	Cu07	
		240	Pb05	Cu05	
	Chlorinated pH 8 Extraction Water	6	Pb03	Cu03	
		24	Pb06	Cu06	
		96	Pb08	Cu08	
		240	Pb06	Cu06	
	pH 6.5 Extraction Water	6	Pb04	Cu10	Uncoated Controls
		168	Pb04	Cu10	Uncoated Controls
		6	Pb01	Cu01	
		6	Pb02	Cu02	
		168	Pb01	Cu01	
		168	Pb02	Cu02	
		6	Pb03	Cu03	
		168	Pb03	Cu03	
Seven-Month Wait, then Fill-and-Dump Experiment 2 (FD2)	Chlorinated pH 8 Extraction Water	6	Pb04	Cu10	Uncoated Controls, Stored Dry
		168	Pb04	Cu10	Uncoated Controls
		6	Pb08	Cu08	Stored Dry
		24	Pb02	Cu02	Stored Wet
		24	Pb05	Cu05	Stored Dry
		24	Pb09	Cu09	Previously Unused
		168	Pb02	Cu02	
		168	Pb05	Cu05	
		168	Pb09	Cu09	
	Re-Flushed, then Chlorinated pH 8 Extraction Water	6	Pb02	Cu02	
		6	Pb05	Cu05	
		6	Pb08	Cu08	
		6	Pb09	Cu09	
		24	Pb02	Cu02	
		24	Pb05	Cu05	
		24	Pb08	Cu08	
		24	Pb09	Cu09	
		168	Pb02	Cu02	
		168	Pb05	Cu05	
		168	Pb08	Cu08	
		168	Pb09	Cu09	

Source: Breault 2014

FD2 included a second stage of testing, which began by flushing all of the pipe sections except the control sections (which were not used in the second stage) for 15 min. with tap water. Each of the 8 pipe sections was then rinsed with 100 mL of reagent water, refilled with chlorinated pH 8 extraction water, held for 6 h, refilled again and held for 24 h, and then refilled again and held for 7d. The samples collected during the second stage were all analyzed for residual chlorine and organic constituents of interest; and selected samples were analyzed for other constituents as needed to address various questions and concerns that arose during FD1 and the first stage of FD2. The order of pipe section reuse during FD2 is indicated in Table 3.5 and the detailed SOP for FD2 is provided in Appendix I.

FD2 was designed to serve the following purposes: 1) to examine the effects of time and storage conditions on the results for selected analytes; 2) to test for analytes for which the methods had not yet been developed when FD1 was conducted (i.e., BADGE hydrolysis and chlorination products); 3) to collect additional data on chlorine demand; and 4) to collect additional data on three epoxy-coated pipe sections (each of which had been stored dry): LSL and CSL sections that yielded anomalous Pb results during the first stage, and an LSL section that yielded an anomalously high TOC concentration during FD1.

A pair of epoxy-coated LSL and CSL pipe sections, previously filled with chlorinated pH 8 extraction water and held for 24 hours, then refilled and held 10 days, was selected for a series of sequential one-hour fill-and-dump tests using chlorinated pH 8 extraction water to determine the effect on chlorine demand after repeated exposure to chlorinated water. After 9 one-hour tests, the pipes were filled with chlorinated pH 8 extraction water dosed with 100 mg/L free chlorine as Cl_2 and dumped after three hours in a test modeled after the slug method for disinfecting water mains (AWWA 2005). The samples were then analyzed to determine the remaining concentration of free chlorine. This test was repeated three times in an effort to exhaust the epoxy coating's chlorine demand. Another series of six 1-hour fill-and-dump tests with chlorinated pH 8 extraction water dosed with 2 mg/L of free chlorine as Cl_2 was performed again on the same pipe sections, and the samples were immediately analyzed to determine the residual free chlorine concentration.

To test for combined chlorine demand, epoxy-coated pipe sections were filled with chloraminated pH 8 extraction water and held for 6 hours, 24 hours, and 4 days. The extraction water samples were analyzed immediately after dumping to determine the residual combined chlorine concentration.

Table 3.5
Pipe section filling order history and holding times for FD1 and FD2

Pipe Section	FD1 Extraction Water and Holding Time (Sequential Filling Order →)			Storage Condition*	FD2 Extraction Water & Holding Time (Sequential Filling Order →)					
Pb01	DT, 6 h	LP, 6 h	LP, 168 h	dry			Pipe sections flushed 15 min with tap water, then rinsed with 100 mL extraction water			
Pb02	DT, 6 h	LP, 6 h	LP, 168 h	wet	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Pb03	CL, 6 h	LP, 6 h	LP, 168 h	dry						
Pb04 (Control)	DT, 6 h	LP, 6 h	LP, 168 h	dry	CL, 6 h	CL, 168 h				
Pb05	DT, 24 h	DT, 240 h		dry	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Pb06	CL, 24 h	CL, 240 h		dry						
Pb07	DT, 96 h			dry						
Pb08	CL, 96 h			dry	CL, 6 h			CL, 6 h	CL, 24 h	CL, 168 h
Pb09				dry	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Cu01	DT, 6 h	LP, 6 h	LP, 168 h	dry						
Cu02	DT, 6 h	LP, 6 h	LP, 168 h	wet	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Cu03	CL, 6 h	LP, 6 h	LP, 168 h	dry						
Cu05	DT, 24 h	DT, 240 h		dry	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Cu06	CL, 24 h	CL, 240 h		dry						
Cu07	DT, 96 h			dry						
Cu08	CL, 96 h			dry	CL, 6 h			CL, 6 h	CL, 24 h	CL, 168 h
Cu09				dry	CL, 24 h	CL, 168 h		CL, 6 h	CL, 24 h	CL, 168 h
Cu10 (Control)	DT, 6 h	LP, 6 h	LP, 168 h	dry	CL, 6 h	CL, 168 h				

*Stored for 7 months at room temperature (20-25 °C)

Source: Lane 2015.

Procedures for Fill-and-Dump Experiments Using PET-Lined Pipe Sections

The third fill-and-dump experiment (FD3) examined leaching of constituents of interest from or through PET liners installed by the manufacturer inside LSL and CSL pipe sections as described above. The procedure (see Appendix J) was similar to those used for FD1 and FD2, and the full testing matrix is shown in Table 3.6. When FD3 was concluded, the pipe sections used were allowed to drip dry and were then capped with air-tight polypropylene caps and stored at room temperature for possible later use.

As the pipe sections were being flushed with tap water during FD3, water was observed dripping from some of the PET-lined LSL sections, from where the SS nipple was threaded into the lead pipe, and from some of the PET-lined CSL sections, from where the unthreaded SS nipple was inserted into the polypropylene compression fitting. Since the inner wall of these connections was sealed with a PET liner, these leaks indicated that water was traveling between the pipe wall and the liner itself. Such leakage would not have been possible using fittings provided by the manufacturer, but the pipe sections were lined with fittings provided by the investigators, which were designed to connect to the flushing manifold using in the laboratory to flush the pipe sections. Despite the leakage, FD3 was carried out as planned, and the leakage was taken into consideration in presenting and evaluating the results (see Chapter 3).

A fourth fill-and-dump experiment (FD4) was designed as a follow-up experiment to FD3, after corrective action was taken to address the leakage, which compromised the results for Pb and Cu, as discussed in Chapter 3. Five pairs of pipe sections (a pair consisting of one LSL and one CSL) were selected for testing in FD4: three pairs exposed to dechlorinated tap and pH 6.5 extraction waters in FD3, one pair exposed to pH 6.5 and pH 8 chlorinated extraction waters in FD3, one pair not previously used (held out of FD3), and the control pair. The SS nipples were carefully removed, leaving exposed PET liner extending approximately 2.5 – 3 in. from each end of each pipe section. The newly exposed ends of PET liner on many of the pipes were found to be wet, confirming that water had passed between the liners and SS nipples. The exposed outer surface of each liner end was carefully cleaned with a new laboratory wipe (Wypall Type L30, Kimberly-Clark, Roswell, Ga.) starting on the outer rim before wiping the rest of the outer surface. A fresh clean laboratory wipe moistened with 0.5% HCl was then applied in the same manner. Another fresh clean laboratory wipe moistened with 0.5% HCl was then applied to the inner liner wall, extending approximately 1 in. into the liner. The entire wiping procedure was performed once more with clean laboratory cloths and reagent water. The pipes were then flushed with two 150 mL volumes of pH 6.5 extraction water, once from each end. These altered pipe sections were then filled with pH 6.5 extraction water and hold first for 6 h and then for 4 d.

One set of the altered PET-lined lead and copper pipes and an unexpanded section of PET liner were selected for a series of sequential 24-hour fill-and-dump tests using chlorinated pH 8 extraction water to provide additional data for evaluating chlorine demand.

A fifth fill-and-dump experiment (FD5) was conducted on four pairs of pipe sections that were relined by the manufacturer using end-fittings supplied by the manufacturer, so that no leakage would occur. The procedure was similar to that used in FD3. The sections were first filled with dechlorinated pH 8 tap water with holding times of 6 h for two pairs, 24 h for the third pair, and 4 d for the fourth pair. When the 6-h samples were collected, the pipes were promptly rinsed, refilled with chlorinated pH 8 reagent water, and held for 6 h. After the 24-h dechlorinated tap water samples were collected, the first three pairs of pipe sections were rinsed, refilled with pH

6.5 extraction water, and held for 6 h, 6 h, and 24 h respectively. Those held for 6-h were later rinsed, refilled with pH 6.5 extraction water, and held for 4 d.

Table 3.6
FD3 and FD4 testing matrix using PET-lined pipe sections

Experiment	Extraction Water	Holding Time, h	Pipe No.		Notes
			LSLs	CSLs	
Fill-and-Dump Experiment 3 (FD3)	Dechlorinated Tap Water, pH 8	6	Pb11	Cu11	Unlined Control
		6	Pb12	Cu12	
		6	Pb13	Cu13	
		24	Pb15	Cu15	
		96	Pb17	Cu17	
	Chlorinated pH 8 Extraction Water	6	Pb14	Cu14	
		24	Pb16	Cu16	
		96	Pb18	Cu18	
	pH 6.5 Extraction Water	6	Pb11	Cu11	Unlined Control
		96	Pb11	Cu11	Unlined Control
		6	Pb12	Cu12	
		6	Pb13	Cu13	
		96	Pb12	Cu12	
		96	Pb13	Cu13	
		6	Pb14	Cu14	
		96	Pb14	Cu14	
Stainless Steel Nipples Removed, Liners Cleaned, then Fill-and-Dump Experiment 4 (FD4)	pH 6.5 Extraction Water	6	Pb11	Cu11	Unlined Control
		96	Pb11	Cu11	Unlined Control
		6	Pb19	Cu19	
		96	Pb19	Cu19	
		6	Pb12	Cu12	
		6	Pb13	Cu13	
		96	Pb12	Cu12	
		96	Pb13	Cu13	
		6	Pb14	Cu14	
		96	Pb14	Cu14	

Source: Breault 2014

Hydrolysis of Bisphenol Diglycidyl Ethers (BDGEs) and BPA

The hydrolysis rates of BADGE, BFDGE, and BPA were determined under a range of conditions broader than those that might reasonably be expected to occur in water service lines. BADGE, BFDGE, or BPA (depending on the analyte being studied) was spiked into 5 mM sodium phosphate buffer solutions adjusted to pH values ranging from 2 to 12 and held at temperatures of 5, 15, 25, and 40 °C. BFDGE hydrolysis was studied only at 25 °C, for comparison with BADGE. BPA hydrolysis was studied only at 25 and 40 °C (since no hydrolysis or decay was observed in 30 d at higher temperatures). Solution pH was monitored at the beginning, middle, and end of each experiment, and the mean and median pH drifts were 0.3 and 0.1 pH units, respectively. The experiments were designed using a pseudo-first-order kinetics approach in which all conditions except the analyte concentration(s) were held constant. Once the pseudo-first-order rate constants were determined for various pH values and temperatures, the hydrolysis rate of each analyte, as well as some of the byproducts formed, could be modeled and expressed as a function of pH and temperature. See Lane (2015) and Lane et al. (2015a) for additional details.

Chlorination of BPA, BPF, BADGE

The experimental approach used to examine the rates of reaction of BPA, BPF, and BADGE with free chlorine and monochloramine (MCA) was similar to that used to study the hydrolysis of these compounds, i.e., a pseudo-first-order kinetic approach. Free chlorine or MCA was added in sufficient excess that its concentration remained nearly constant (decreasing no more than 36% for free chlorine and no more than 37% for MCA) as the BPA, BPF or BADGE degraded.

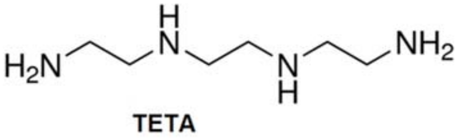
BPA and BPF were spiked (individually) at a nominal concentration of 200 µg/L each into 5 mM sodium phosphate buffer solutions adjusted to pH values from 2 to 12 and containing 2 mg/L of free chlorine (as Cl_2). The buffer concentration was chosen to effectively control pH while keeping activity corrections to less than one percent, which could be (and were) ignored in the subsequent kinetic and equilibrium modeling efforts. Temperature was held constant at either 10 or 25 °C for the bisphenol experiments. The procedure was similar for BADGE, but pH was varied only from 7 to 9 and all samples were held at 25 °C.

At predetermined times, samples were collected for LC/MS/MS analysis to quantify concentrations of unreacted bisphenols and selected chlorination by-products (see Table 3.1) or, for samples spiked with BADGE, BADGE and selected hydrolysis and chlorination byproducts of BADGE (see Table 3.2). Immediately after sampling, and prior to LC/MS/MS analysis, residual chlorine was quenched using sodium bisulfite, keeping excess sodium bisulfite to a minimum. Initial and final concentrations of free residual chlorine were determined using the Hach Total Chlorine Method 8167 (an EPA-approved DPD Method, Hach 2014) with a Hach DR 5000 UV-Vis Spectrophotometer (Loveland, CO).

The chloramination experiments were conducted in the same manner as the free chlorination experiments. MCA was prepared by spiking a predetermined quantity of sodium hypochlorite into an ammonium chloride solution at pH 8.9, producing an MCA concentration of 3.5 to 4 mg/L as Cl_2, which was measured using the Hach Chloramine (Mono) Indophenol Method 10200 (Hach 2015). The sodium hypochlorite dosage was chosen to produce a chloramine solution containing mostly MCA, with only a minimal amount of dichloramine and an ammonium-N concentration of no more than 0.1 mg/L as N, which was verified (using the Nitrogen, Free, Ammonia Indophenol Method 10200; Hach 2015). See Lane (2015) and Lane et al. (2015b) for additional details.

Reactivity of Free and Combined Chlorine with Triethylenetetramine (TETA)

Laboratory experiments were conducted to examine the reactivity of free and combined chlorine with triethylenetetramine (TETA), a major component of some epoxies that is also representative of the amines used in other amine-based epoxies. The underlying objective was to determine whether the reactivity of free and combined chlorine with TETA provided a reasonable explanation for their reactivity with epoxy coatings, given that both free and combined chlorine had been found, in the chlorination experiments described above, to be relatively unreactive with BADGE, the major component in the other part of the two-part epoxy used to coat pipe sections in the fill-and-dump experiments. Since TETA has a primary amine group on each of its terminal ends, as shown in Figure 3.11, it is expected to readily react with both free and combined chlorine.



Source: Lane 2015.

Figure 3.11 Chemical structure of triethylenetetramine (TETA)

Chlorine solutions were dosed with TETA at a 1:1 molar ratio of chlorine (as Cl_2) to TETA, and concentrations of free chlorine, monochloramine (MCA), total chlorine, and free ammonia-N were monitored over time. The controls were chlorine solutions not dosed with TETA. Solutions of free chlorine and MCA were prepared from a laboratory grade sodium hypochlorite solution (Fisher Scientific, Pittsburgh, PA). All solutions were prepared using 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl (pH 8) to mimic the pH 8 extraction water used during the fill-and-dump experiments. Free chlorine, total chlorine, MCA, and free ammonia-N were determined using the methods described above (see Analytical Methods).

A supplemental fill-and-dump test was conducted to more closely examine the decay of free and combined chlorine in epoxy-coated pipe sections under conditions similar to those used to study the reactivity of free and combined chlorine with TETA. Two epoxy-coated pipe sections, Pb03 and Cu03, were filled with a free chlorine solution prepared in the same manner as the solution used to examine the reactivity of free chlorine with TETA. Over the next 24 hours, aliquots were removed from the pipe sections and analyzed for free chlorine, total chlorine, MCA, and free ammonia-N using the same methods described above. This experiment was then repeated using an MCA solution instead of a free chlorine solution.

Source of the Antimony (Sb) in Samples from Unlined LSL Sections

In FD3, significant concentrations of Sb were found in the extraction water samples drawn from the unlined (control) LSL pipe section. However, it was not clear whether the Sb was associated with the lead from which the LSL was made or with the deposits inside the LSL, nor whether Sb was present in other LSLs. To shed light on this, three previously unused (and unlined and uncoated) LSL sections were selected for testing – two received from the Rochester (NY) Water Bureau (one having lighter colored deposits than the other) and one from Providence Water (via Mr. John Phillips, O'Brien & Gere). The section from Providence (P1) contained deposits that were light gray in color, while the deposits in the sections from Rochester (R1 and R2) were dark brown in color (perhaps indicating the presence of iron and/or manganese), with those in R2 being noticeably darker than those in R1.

From each LSL section, two 12-in. subsections were cut, providing duplicate sections to help assess the variability of results for a given pipe section and among the three different pipe sections. A countersink drill bit was inserted into each end of each pipe subsection and gently turned by hand to provide a round, smooth opening that could be tightly sealed using a silicone stopper. Each subsection was rinsed with reagent water then rinsed with pH 6.5 extraction water (LP), the same low-pH extraction water used in FD2 and subsequent fill-and-dump experiments. Each subsection was then filled with the LP extraction water and held for 24 hours. At that time the extraction water in each subsection was dumped into a clean beaker from which a subsample was poured into a clean storage container (centrifuge tube), acidified with 0.1 mL of concentrated nitric acid (trace-metal grade), and stored for analysis of Pb and Sb. Each subsection was then extracted three more times in the same manner – first with pH 6.5 extraction water, then with two successive rounds of a mildly acidic solution (~0.01% HNO_3 in reagent water, resulting in an initial pH of ~3.0). The samples were acidified and stored for analysis in the same manner as the earlier samples. Sb was determined using ICP-MS, but due to the high concentrations of Pb in these samples, Pb was determined using flame AAS (Varian Model AA240 FS, Agilent Technologies, Santa Clara, CA) rather than GFAAS.

Another subsection was cut from each of the same three LSLs sections described above (two from the Rochester Water Bureau and one from Providence Water). The ends of each subsection were trimmed, by turning them on a lathe, so they would fit smoothly into a 50-mL centrifuge tube. Samples of clean cuttings (i.e., cutting obtained after the outer surface was stripped away on the lathe) were collected from each subsection and stored for analysis of Pb and Sb. Samples of the deposits inside each subsection were then collected in two stages: 1) using a stiff nylon brush (5 minutes from each end) to dislodge deposits into a clean 50 mL centrifuge tube; and 2) using a round file (3 minutes from each end) to dislodge some of the remaining deposits into another clean 50 mL centrifuge tube. Lastly, using a utility knife, more samples of lead were collected from one end of each subsection where the lathe had freshly exposed "clean" lead. The deposits and cuttings were labeled and stored for analysis of Pb and Sb. Clean cuttings were also taken from one end of the LSL control pipe section used in FD3 (Pb11).

Acid digestion of the cuttings and scale deposits was carried out using a modified version of EPA Method 3051A (EPA 2007c). Approximately 0.3 g of scale material from each pipe subsection were digested in a Multiwave 3000 microwave digestion unit (Anton Paar GmbH) with 6 mL of concentrated nitric acid and 2 mL of concentrated hydrochloric acid (both trace metal grade, Fisher Scientific). Digestion vessels were pre-cleaned with a 0.5% nitric acid solution and triple-rinsed with reagent water prior to use. The resulting digestates were filtered through a 0.45 µm PTFE filter (25 mm, Fisher Scientific, Pittsburgh, PA) to remove undigested materials (such as silicates) and diluted to 100 mL with reagent water. The diluted samples were analyzed for Pb using flame AAS and for Sb using ICP-MS.

DATA HANDLING AND STATISTICAL METHODS

As the data for a particular experiment were obtained, they were first examined to see if the QC guidelines were met, if the results made sense, if significant trends could be discerned, if there appeared to be a need for follow-up experiments, and if there appeared to be any outliers present. For a data set involving multiple samples or replicates, one of the first steps taken was to determine the mean and standard deviation (SD) of the data and/or of specific subsets of the data corresponding to selected variables such as holding time or the extraction water used. Grubb's test ($\alpha = 0.05$) was used to examine possible statistical outliers (Rohlf and Sokal 1981); and if a data point was determined to be a statistical outlier, it was marked as such with a footnote and excluded from further statistical analysis.

In some cases, concentration changes were examined rather than absolute concentrations, e.g., to compare results among different extraction waters having different initial concentrations of a given constituent, such as TOC or antimony. The increase in concentration in an individual sample was determined by subtracting the initial concentration from the final concentration. If the initial concentration was below the method detection limit (MDL), it was assumed to be zero for the purpose of calculating the increase in concentration.

T-tests were used to determine whether the means of two sets or subsets of data were significantly different. First, the variances of the two data sets were examined using an F-test, to determine if they were statistically different, by rejecting the null hypothesis that the variances were equal if the p-value was less than the α-value (0.05). If the null hypothesis of the F-test was rejected, the subsequent t-test would assume unequal variance. If the null hypothesis of the F-test was not rejected, the subsequent t-test would assume equal variance. The means of the two data sets were determined to be statistically different, using a two-tailed t-test, by rejecting the null hypothesis that the means were equal if the p-value was less than the α-value (0.05). The mean of one data set was determined to be statistically greater than the mean of another data set (or greater than the concentration in the control samples) by using a one-tailed t-test and rejecting the null hypothesis that the means were equal if the p-value was less than the α-value (0.05). The significance of the relationship between two variables was evaluated by performing a regression analysis and rejecting the null hypothesis (slope = 0; not statically significant) if the p-value was less than the α-value (0.05).

Box plots are used in Chapter 4 to display the range of lead, copper, and antimony concentrations measured in various sets of samples. Each box represents the middle 50% of the data points, and the line dividing each box into two smaller boxes represents the median value. The top and bottom error bars represent the top and bottom 25% of the measured values, respectively, with the end-caps of the error bars representing the maximum and minimum values. To display values below the MDL, a value of 0.5 times the MDL was used. Variables such as extraction water composition, the number of times a given pipe section was exposed, holding time, etc., were often not separated out in a given plot. Box plots were used primarily to graphically display the range of concentrations measured in broad subsets of samples, and not necessarily for other statistical purposes. Therefore, caution should be exercised in interpreting them, to avoid drawing conclusions not supported by the data.

CHAPTER 4
RESULTS AND DISCUSSION

LEACHING AND ADSORPTION OF CONSTITUENTS BY END-FITTINGS

Leaching and adsorption tests were conducted to determine if the various end-fitting materials used in this study were leaching or adsorbing either organic or inorganic constituents of interest, or reacting with free or combined chlorine. The results are summarized in the following paragraphs and described in greater detail by Breault (2014) and Lane (2015).

Leaching and Adsorption of Inorganic Constituents

Silicone stoppers examined using the laser ablation ICP-MS method described in Chapter 3 showed no evidence of detectable Pb, Cu or Sb, so leaching tests with these stoppers were not conducted. Adsorption studies were conducted by immersing different amounts of stopper materials, sized to equal or exceed the surface-area-to-volume ratios corresponding to a particular end-fitting, in a solution containing 0.072 µM Pb and Cu. For the silicone stoppers, the changes in concentration were only 1-3% after 7 days. For HDPE stoppers, used in place of the silicone stoppers in some fill-and-dump tests, the Pb and Cu concentrations were within 5% of the control solution. Adsorption studies on PTFE tape showed that Pb, Cu and Sb remained within 6% of the original concentrations. Based on these results, and taking into consideration the surface-area-to-volume ratios of both the end-fittings and pipe sections, it does not appear that any of these end-fitting materials would significantly impact the concentrations of inorganic constituents measured in the fill-and-dump samples.

Leaching tests showed no detectable lead concentrations in reagent water in contact with both threaded and unthreaded SS pipe nipples, while adsorption studies showed that lead concentrations remained within 2% of the control samples after 7 d contact time. Copper concentrations increased both in the reagent water and in the adsorption solution after contact with threaded and unthreaded SS pipe nipples. The Cu concentrations in the reagent water were < 10 µg/L, while concentrations in the adsorption solution increased by an average of 20 µg/L in the threaded SS pipe nipples and 14 µg/L in the unthreaded SS pipe nipples. These concentrations are significant relative to the MDL for Cu, but insignificant relative to the AL for copper (1,300 µg/L) and relative to the concentrations observed in the CSL control pipe section in the fill-and-dump experiments described later in this chapter. Antimony showed small amounts of adsorption, with losses of 26% and 10% of the initial Sb in the threaded and unthreaded SS pipe nipples, respectively; but given the surface area and volume of the end-fittings, antimony adsorption would not be expected to significantly impact antimony concentrations in the LSL and CSL pipe fill-and-dump samples.

Based on these results, the impact of the SS pipe nipples on lead concentrations appear to be insignificant. Pipe nipples could contribute to increases in observed Cu concentrations and decreases in observed Sb concentrations. However, in fill-and-dump experiments, contact between extraction waters and pipe nipples is negligible, except in the control samples. The lining or coating extended past the cut ends of each lead or copper pipe section, including the pipe nipples, so only the end of each pipe nipple represented an uncoated surface. Water came into contact with ends the pipe nipples only as it was poured out of the pipe at the end of the experiment. The pipe nipples could potentially exert a great effect on metal concentrations in the unlined (control) pipe sections, but such effects would be expected to be small given the relative surface-area-to-volume ratios of the end-fittings and unlined pipe sections.

The end-fittings for FD5 consisted of PEX tubing and compression fittings (believed to be polybutylene) provided by the manufacturer that lined the pipe sections. Extra end-fittings, identical to those used but shipped separately, were scrupulously cleaned, in the same manner as described by Breault (2014) and then tested for adsorption and leaching of lead and copper, the only constituents analyzed in the FD5 samples. Leaching studies using reagent water acidified to a pH of about 4.7 (by adding 0.81 µL of concentrated HNO_3 per L of reagent water) showed no detectable lead concentrations in the reagent water after seven days. Copper concentrations between 1 and 5 µg/L were observed in the acidified reagent water after contact with the gray end-fitting pieces, and were 6 µg/L after contact with the plastic pipe. These results show potential for release of trace amounts of Cu from the end fittings during FD5. Traces of copper were unexpectedly detected in two of the three control samples, suggesting some initial level of Cu may have been present in the batch of the acidic reagent water used in this experiment, but the levels detected (< 1.0 µg/L) were well below the concentrations measured in the end-fitting tests and in the FD5 samples.

Adsorption experiments on the FD5 end fittings were conducted using a mixed-metal standard of Pb, Cu and Sb acidified (by the HNO_3 in the standards) to a pH of about 4.7. The results showed lead concentrations within 15% of the control sample for the gray end-fitting pieces, indicating a small loss of Pb from solution over 7 days. Cu concentrations increased by 10-15%, consistent with the leaching study results showing release of Cu from these pieces. Lead concentrations decreased by more than 50% in contact with the plastic pipe, indicating potential for Pb adsorption onto the pipe surface. Cu concentrations increased by 50%, also consistent with the results from the leaching experiment. Results from these tests, which have not been previously published, are presented in Table 4.1.

Based on these results, the end-fittings used in FD5 had the potential to release Cu into solution, potentially increasing the observed Cu concentrations in these experiments. The impact of these end-fittings on the FD5 results, however, should be limited by their small surface area and size relative to the pipes themselves. The PEX tubing used in the end fittings had an internal diameter of 1.1 cm and a maximum length of 14.5 cm. The volume of water contained within each end-fitting is approximately 13.8 mL, with a total volume for each tested pipe section (which contains two end fittings) of 27.6 mL. By contrast, the lined Pb and Cu pipes had average internal volumes of 254 and 224 mL, respectively (see Physical Lining Characteristics, below). An increase of 6 µg/L Cu in the water held within the end-fitting during the fill and dump experiment due to leaching would correspond to an overall increase of approximately 0.6 µg/L Cu in the bulk solution. This is taken into account in the discussions of the Cu concentrations observed in FD5. The impact of the compression fittings on metal leaching or adsorption in PET-lined pipe sections is expected to be negligible because the lining extended to the end of each compression fitting, where it was then sealed by the ferrule used to connect it to the blue plastic pipe. Calculations similar to those described immediately above show that adsorption onto the plastic pipe would be expected to reduce the bulk Pb concentration in a pipe section by no more than 10%.

Table 4.1
Leaching and adsorption results for end-fittings used in FD5

Sample and Description	Conc, µg/L	
	Pb	Cu
Leaching Samples (after 7 days)		
Leaching Solution	≤0.5	0.6
Sample Vial Control	≤0.5	≤0.5
Glass Beaker Control	≤0.5	0.7
Plastic Pipe, R1*	≤0.5	6.0
Plastic Pipe, R2	≤0.5	5.9
Compression Fitting, R1	≤0.5	1.2
Compression Fitting, R2	≤0.5	4.4
Adsorption Samples (after 7 days)		
Adsorption Solution	8.3	16.4
Sample Vial Control	8.3	16.1
Glass Beaker Control	4.6	14.9
Plastic Pipe, R1	3.4	24.1
Plastic Pipe, R2	3.6	24.9
Compression Fitting, R1	7.8	18.7
Compression Fitting, R2	7.0	18.1

* R# = replicate number

Chlorine Demand

Silicone and HDPE stoppers were tested for free chlorine demand by exposing them to chlorinated pH 8 extraction water (initially 2.03 mg/L free chlorine as Cl_2) held in 600 mL acid-cleaned glass beakers. Six beakers were filled with 400 mL extraction water; two beakers contained one silicone stopper each, two beakers contained one HDPE stopper each, and the remaining two beakers were used as controls. The beakers were covered with sealing film (Parafilm®, Sigma-Aldrich Corp., St. Louis, MO) and stored in the dark. After 24 hours, the average free chlorine concentrations in extraction waters exposed to either a HDPE stopper or a silicone stopper remained within 4% of the average free chlorine concentrations in both the glass-beaker controls (1.96 mg/L as Cl_2) and the 4 L amber glass bottles (with PTFE-lined caps) used to prepare and store the extraction water (1.94 mg/L as Cl_2). Thus, the stoppers did not exert significant chlorine demand.

Leaching and Adsorption of Organic Constituents

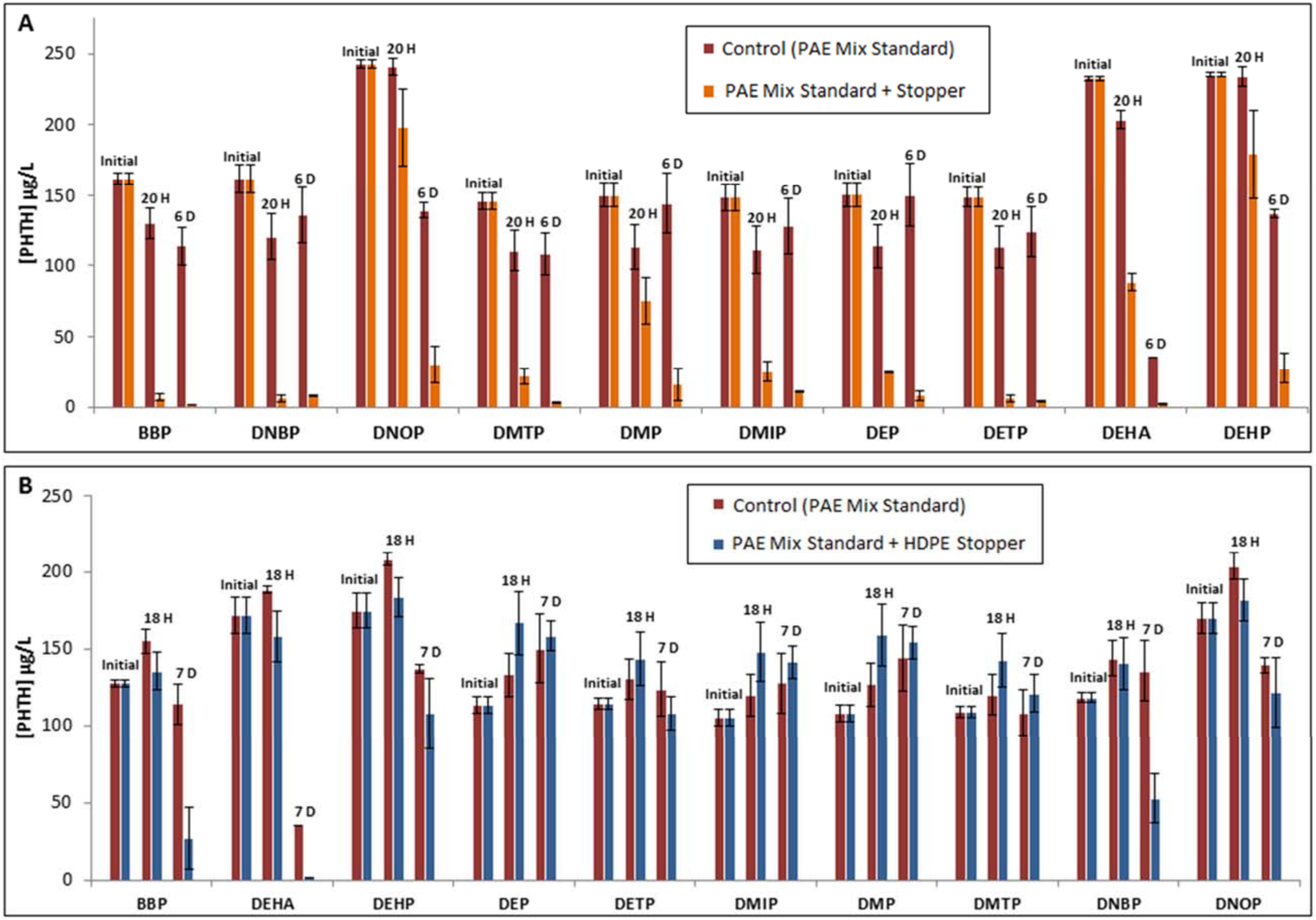
Silicone and HDPE stoppers were tested for TOC leaching by exposing them to chlorinated pH 8 extraction water in 600 mL acid-cleaned glass beakers. Six beakers were filled with 400 mL extraction water; two beakers contained one silicone stopper each, two beakers contained one HDPE stopper each, and the remaining two beakers were used as controls. The beakers were covered with sealing film (Parafilm®, Sigma-Aldrich Corp., St. Louis, MO) and stored in the dark. After 24 hours, the TOC concentrations in extraction water exposed to silicone and HDPE stoppers remained, on average, within 0.06 mg/L of the glass-beaker control samples, a concentration less than the MDL. Thus, both types of stoppers were determined to not leach a significant amount of TOC.

Leaching and adsorption tests for bisphenols, BADGE and BADGE hydrolysis products, phthalate esters, and phthalic acids, were conducted on silicone and HDPE stoppers, SS pipe nipples (both threaded and unthreaded) and HDPE pipe nipples. In addition, two multi-component end-fitting assemblies were tested. One consisted of an SS pipe nipple, a polypropylene compression fitting, and a silicone stopper; the second consisted of an HDPE pipe nipple, a polypropylene compression fitting, and a silicone stopper. A full description of the leaching and adsorption test procedures and results is available in Lane (2015). This section summarizes those results and addresses the most significant findings.

Bisphenol leaching and adsorption studies showed minimal adsorption on silicone stoppers and no leaching or adsorption after 24 hours in the multi-component end-fitting assemblies. Based on these results, all parts were considered acceptable for contact with samples analyzed for bisphenols. No BADGE leaching was observed from end fitting components or assemblies, even after 9.5 d contact time with reagent water. Minimal BADGE adsorption to SS pipe nipples was detected after adjusting for the decay of BADGE by hydrolysis reactions during the adsorption test. Silicone stoppers showed adsorption of BADGE at 6 hours and of BADGE hydrolysis products at longer times at high surface area to volume rations. After retesting with surface-area-to-volume ratios equivalent to those used in the fill and dump experiments, adsorption of both BADGE and BADGE hydrolysis products was still observed. Thus, the use of silicone stoppers during the fill-and-dump experiments on epoxy-coated pipe sections likely resulted in BADGE under-reporting due to adsorption.

No leaching of phthalate esters was observed from any of the individual end fittings. SS pipe nipples showed significant loss of all phthalate esters at 6 days, and loss of three (DNOP, DEHA and DEHP) at 20 h contact time. This may be due to either adsorption or reactive decay of these compounds. Silicone stoppers showed significant adsorption of all tested phthalate esters at 20 h; but HDPE stoppers showed little to no loss at 18 h, and only 3 (BBP, DEHA and DNBP) showed observable loss after 7 d (Figure 4.1). The HDPE stoppers were considered acceptable for use in fill-and-dump experiments with PET-lined pipe sections, while the silicone stoppers were not. The SS pipe nipples were considered adequate for contact with samples analyzed for phthalate esters, despite the adsorption test results, for two reasons: 1) no phthalate esters were found leaching from the pipe nipples; and 2) had any phthalate esters leached from the PET liners they would not have come into contact with the SS pipe nipples, since the lining extended through the pipe nipples.

Phthalic acids were not found to leach from any of the following end-fitting components: threaded and unthreaded SS pipe nipples, silicone stoppers, and HDPE stoppers. In adsorption tests, changes in phthalic acid concentrations were minimal, with no consistent pattern over time. Based on these results, all end fittings used were deemed suitable for use in fill-and-dump tests in which samples were analyzed for phthalic acids.



Source: Lane 2015.
PAEs = phthalate esters; error bars are the standard deviations for n = 3 replicate samples

Figure 4.1 PAE adsorption to stoppers: A) Silicone stoppers; B) HDPE stoppers

FILL-AND-DUMP EXPERIMENTS ON EPOXY-COATED LSLS AND CSLS

Epoxy Analysis

The epoxy used to coat the pipe sections was analyzed for both organic and inorganic constituents. The organic ingredients of the epoxy were considered proprietary and not made available by the manufacturer. To anticipate key epoxy leachates, parts A and part B of the starting materials were dissolved in methanol, diluted, and analyzed using GC/MS in scanning mode. A major key peak in part A was identified as BADGE using the National Institute of Standards and Technology (NIST) spectral library (Lane 2015). Bisphenols (i.e., BPA, BPB, BPD, BPE, BPF, BPS) and BFDGE were not detected.

To determine inorganic constituents, a sample of hardened epoxy was digested in acid as described in Chapter 3. Based on GFAAS analysis of the acid digestate, the epoxy was found to contain approximately 8 mg Cu/kg epoxy. Lead and chromium were not detected above a detection level of 0.1 mg/kg epoxy. ICP-MS analysis of the digested epoxy confirmed the presence of copper and identified no other elements of concern.

Physical Coating Characteristics

Pipe measurements were taken as described in Chapter 3, with the end fittings in place, before and after the epoxy coating was applied. The results are summarized below in Table 4.2. The volumes and thicknesses of the epoxy coating were more variable for the LSLs than for the CSLs, which is attributable to the rougher internal surfaces and more variable IDs of the LSL sections. The average IDs of the uncoated LSLs differed by as much as 2 mm in some cases, whereas the CSLs all had virtually the same ID.

Table 4.2
Physical pipe and coating metrics before and after epoxy coating

Type of Pipe Coated	Parameter	Initial Pipe Volume*	Epoxy Coating Volume	Material Thickness	Coating Surface Area to Water Volume Ratio
		mL	*cm^3*	*mm*	*cm^2/mL*
LSLs	Maximum	306	73.7	1.21	3.01
	Minimum	228	31.7	0.52	2.46
	Mean	257	53.3	0.89	2.82
	SD	±25	±16	±0.28	±0.19
CSLs*	Maximum	287	29.0	0.40	2.51
	Minimum	290	22.3	0.30	2.48
	Mean	289	24.2	0.36	2.49
	SD	±1.6	±2.3	±0.03	±0.01

Source: Breault 2014

* The initial pipe volumes of the CSLs are those of the first three CSLs measured and the mean value was assumed representative of all CSLs since the copper pipe was uniform, with each section cut from the same coil to the same length.

Extraction Water Analysis

Important water quality parameters for the extraction waters used in the fill-and-dump experiments on the epoxy-coated pipe sections are summarized in Table 4.3. All values for dechlorinated tap water parameters, except for initial pH and alkalinity, were measured on samples taken after dechlorination and pH adjustment (to pH 8.0 using 0.1 N HCl). The parameters are within the ranges seen in 2011 in Lawrence, KS tap water except for alkalinity, potassium, hardness, and copper. However, the values measured in the dechlorinated tap water are reasonably close to those reported for 2011 considering the changes in surface water quality that can occur from one year or one season to the next.

Table 4.3
Water quality parameters for extraction waters used in FD1 and FD2

Parameter	Units	pH 6.5 Extraction Water	Chlorinated pH 8 Extraction Water	Dechlorinated pH 8 Tap Water	2011 Lawrence, KS Tap Water*	2012 Rochester, NY Tap Water**
pH	Std.	6.5	8.0	8.4***	8.0 – 9.9	6.6 – 8.5
Alkalinity	mg/L as $CaCO_3$	1.8 – 100	56 – 100	126***	40 – 120	63 – 89
Sodium	mg/L	NA	NA	97	15 – 100	15 – 19
Potassium	mg/L	NA	NA	12	2.9 – 11	1.4 – 1.7
Chloride	mg/L	NA	NA	NA	13 – 100	32 – 35
Sulfate	mg/L	NA	NA	NA	27 – 150	13 – 30
Dissolved Oxygen	mg/L	NA	NA	8.2	NA	NA
Conductivity	µS/cm	NA	NA	706	310 – 1,300	220 – 340
Hardness	mg/L as $CaCO_3$	100	100	96.5	100 – 190	91 – 130
Total Organic Carbon	mg/L	0.29 – 0.35	0.12 – 0.80	3.53	2.93 – 3.75	1.8 – 2.15
Copper	µg/L	≤ 0.25	≤ 0.25	5.7	6.3 – 120	12 – 320
Lead	µg/L	≤ 0.5	≤ 0.5	≤ 0.5	ND – 9.9	ND – 28

Source: Breault 2014
* 2011 Lawrence tap water values taken from the 2012 Lawrence Consumer Confidence Report, Appendix C (City of Lawrence 2012).
** 2012 Rochester, NY tap water values taken from the 2012 Water Quality Report, Supplemental Information (City of Rochester 2012)
***pH and alkalinity measured prior to pH adjustment
NA = Not Analyzed

Lead

Table 4.4 shows the lead concentrations in samples collected from epoxy-coated pipe sections during the first two fill-and-dump experiments, FD1 and FD2. Lead concentrations in all extraction waters were below the detection level of 0.5 µg/L. The lead concentrations in samples drawn from the uncoated LSL section (Pb04) ranged from 1,200 to 25,000 µg/L, three orders of magnitude higher than values seen in 2011 in drinking water from the pipe's native distribution system in Rochester, NY Heavy white particles (most likely PbO) and some lead-colored particles were present in these samples as they were collected. The white particles dissolved when HNO_3 was added for sample preservation, and presumably contributed substantially to the very high Pb levels found in the samples.

The pipe sections were heavily disturbed on both ends, where the pipes were reamed and threaded for SS nipple installation. Two heavy disturbances in a 4 ft long LSL section greatly increases the potential for lead release; and any effects of the end-fittings on water quality would be greatly magnifiied in a pipe section so much shorter than that of a typical full-length service line. In practice, LSLs are not reamed and threaded, but it is well established that disturbing LSLs can cause spikes in lead levels that may largely subside after a month or two (Lewis et al. 2017) but may persist for a year or more (Boyd et al. 2004, Sandvig et al. 2008, EPA 2011). Spikes of the magnitude observed in the control pipe sections in this study would not be expected to occur in practice, but using heavily disturbed pipe sections provided an opportunity to evaluate the effectiveness of lining and coating technologies under conditions far more severe than those typically encountered in practice.

Table 4.4
Lead in samples from epoxy-coated pipe sections in FD1 and FD2

Experiment	Extraction Water	Holding Time, h	Pipe No.		Pb, µg/L	
			LSLs	CSLs	LSLs	CSLs
Fill-and-Dump Experiment 1 (FD1)	Dechlorinated pH 8 Tap Water		Extraction Water		≤ 0.5	
		6	Pb04, Control	Cu10, Control	1,150	0.8
		6	Pb01	Cu01	78.3	≤ 0.5
		6	Pb02	Cu02	1.2	≤ 0.5
		24	Pb05	Cu05	3.8	0.6
		96	Pb07	Cu07	0.9	0.5
		240	Pb05	Cu05	0.8	0.7
	Chlorinated pH 8 Extraction Water		Extraction Water		≤ 0.5	
		6	Pb03	Cu03	≤ 0.5	≤ 0.5
		24	Pb06	Cu06	≤ 0.5	0.6
		96	Pb08	Cu08	1.2	≤ 0.5
		240	Pb06	Cu06	≤ 0.5	≤ 0.5
	pH 6.5 Extraction Water		Extraction Water		≤ 0.5	
		6	Pb04, Control	Cu10, Control	1,800	0.6
		168	Pb04, Control	Cu10, Control	25,000	3.0
		6	Pb01	Cu01	≤ 0.5	≤ 0.5
		6	Pb02	Cu02	≤ 0.5	≤ 0.5
		168	Pb01	Cu01	≤ 0.5	≤ 0.5
		168	Pb02	Cu02	≤ 0.5	≤ 0.5
		6	Pb03	Cu03	≤ 0.5	≤ 0.5
		168	Pb03	Cu03	0.5	≤ 0.5
Seven-Month Wait, then Fill-and-Dump Experiment 2 (FD2)	Chlorinated pH 8 Extraction Water		Extraction Water		≤ 0.5	
		6	Pb04, Control	Cu10, Control	1,700	≤ 0.5
		168	Pb04, Control	Cu10, Control	2,400	≤ 0.5
		6	Pb08	Cu08	≤ 0.5	≤ 0.5
		24	Pb02	Cu02	≤ 0.5	≤ 0.5
		24	Pb05	Cu05	2.11	≤ 0.5
		24	Pb09	Cu09	≤ 0.5	≤ 0.5
		168	Pb02	Cu02	≤ 0.5	≤ 0.5
		168	Pb05	Cu05	1.38	≤ 0.5
		168	Pb09	Cu09	≤ 0.5	≤ 0.5
	Re-Flushed, then Chlorinated pH 8 Extraction Water		Extraction Water		≤ 0.5	
		6	Pb02	Cu02		
		6	Pb05	Cu05	6.2	
		6	Pb08	Cu08		
		6	Pb09	Cu09	≤ 0.5	≤ 0.5
		24	Pb02	Cu02		
		24	Pb05	Cu05	2.0	
		24	Pb08	Cu08		
		24	Pb09	Cu09	≤ 0.5	≤ 0.5
		168	Pb02	Cu02		
		168	Pb05	Cu05	1.3	
		168	Pb08	Cu08		
		168	Pb09	Cu09		

Source: Breault 2014

The data in Table 4.4 demonstrate that epoxy coating of the LSL sections was extremely effective in limiting lead release. Lead was non-detectable (≤0.5 µg/L) in 16 of 27 samples (59%) drawn from epoxy-coated LSLs, and only one had a lead concentration exceeding the AL, i.e., the 6-h sample for Pb01, which had a lead concentration of 78.3 µg/L. When this pipe section was refilled with pH 6.5 extraction water, first for 6 h and later for 168 h, Pb was not detected in either sample. Of the other 10 samples from epoxy-coated LSLs that contained detectable levels of lead, 7 were drawn from the same LSL pipe section (Pb05), which contained a large joint and is discussed in more detail below. The other 3 samples had Pb concentrations of 1.2, 0.9, and 1.2 µg/L. All three were from pipe sections used for the first time; two were reused later in FD1 and the resulting samples contained no detectable lead.

As expected, even better results were obtained for the epoxy-coated CSL sections, which were expected to contain little or no lead. Twenty of the 24 samples (83%) contained no detectable lead, and the maximum concentration detected was only 0.7 µg/L (Table 4.4). Extraction of the uncoated CSL control section (Cu10) with pH 6.5 extraction water for 7 d produced a sample containing only 3 µg/L of lead.

LSL section Pb05 was the only section that consistently produced samples containing detectable levels of lead (3.8, 0.8, 2.1, 1.4, 6.2, 2.0, and 1.3 µg/L), which is why this section was repeatedly tested. As with all coatings, epoxy coatings can potentially have defects, commonly referred to as “holidays” or “discontinuities” by coating specialists. It is possible that there was a defect in the coating applied to LSL section Pb05, perhaps at the large solder joint, which had a diameter approximately twice that of the rest of the pipe section and was located approximately half-way down its length. However, the pipe was carefully inspected with a pipe camera, both initially by the manufacturer (at the time the pipe was coated) and later, following FD2, and no defects were visible near the joint.

In the post-experiment inspection, a possible defect was visible near one end of the pipe. There appeared to be a thin circumferential line of exposed metal at the junction between the SS pipe nipple and the lead pipe. It is possible that too much force was applied in connecting this pipe section to the flushing manifold, such that the epoxy coating was damaged. This could explain the repeated occurrence of detectable lead levels in samples collected from Pb05. Three points are worth noting in this regard: 1) the lead levels detected were still quite low, well below the AL; 2) a defect of this nature would have less relatively less impact on the average lead concentration in a longer pipe section or a full-length water service line; and 3) in practice, a defect of this nature could not occur because the ends of an LSL would be connected to other piping using compression fittings (or equivalent), not threaded SS pipe nipples.

Traces of lead can potentially be incorporated into an epoxy coating as it is being applied. When the interior surface of an LSL is cleaned to prepare it for epoxy coating, loose deposits or lead dust produced by sand blasting can be entrained into the liquid epoxy and may end up close enough to the surface of the hardened epoxy to leach lead into the water, over a period of time, once the line is placed back in service. If so, this could contribute, along with uncoated interior water lines and plumbing fixtures, to detectable levels of lead in tap water after an LSL has been coated. This was recognized decades ago, and companies that apply epoxy coatings to LSLs have developed cleaning and application techniques to minimize such problems.

Copper

Table 4.5 shows the copper concentrations found in samples collected during FD1 and FD2. All 51 extraction water samples collected from CSLs (n = 24) and LSLs (n = 27) contained a detectable level of copper (≥ 0.25 µg/L). Figure 4.2 summarizes the copper concentration increases found in the epoxy-coated pipe sections. To determine the increase in copper concentration, the copper concentration in each dechlorinated tap water sample collected from an epoxy-coated pipe section was corrected by subtracting the initial copper concentration (5.7 µg/L; see Table 4.5). No correction was necessary for the other extraction waters, since they initially contained no detectable copper (≤ 0.25 µg/L).

In samples from the uncoated CSL (control) section, copper increased by 270 to 830 µg/L. Copper increased in 48 of the 51 extraction water samples from epoxy-coated sections, but the increases were relatively small, i.e., one to two orders of magnitude lower than in those in samples from the CSL control section and about two orders of magnitude lower than the AL for copper (1,300 µg/L).

As shown in Table 4.6 and Figure 4.3 lower copper concentration increases were observed with repeated extractions of the pipe sections. The mean increase for all samples (from both LSLs and CSLs for all extraction conditions) was 5.3 µg/L, but the mean increase was only 3.9 µg/L in samples from pipe sections that had been previous extracted (Table 4.6) and less than 3 µg/L in all samples from pipe sections extracted four or more times (Figure 4.3).

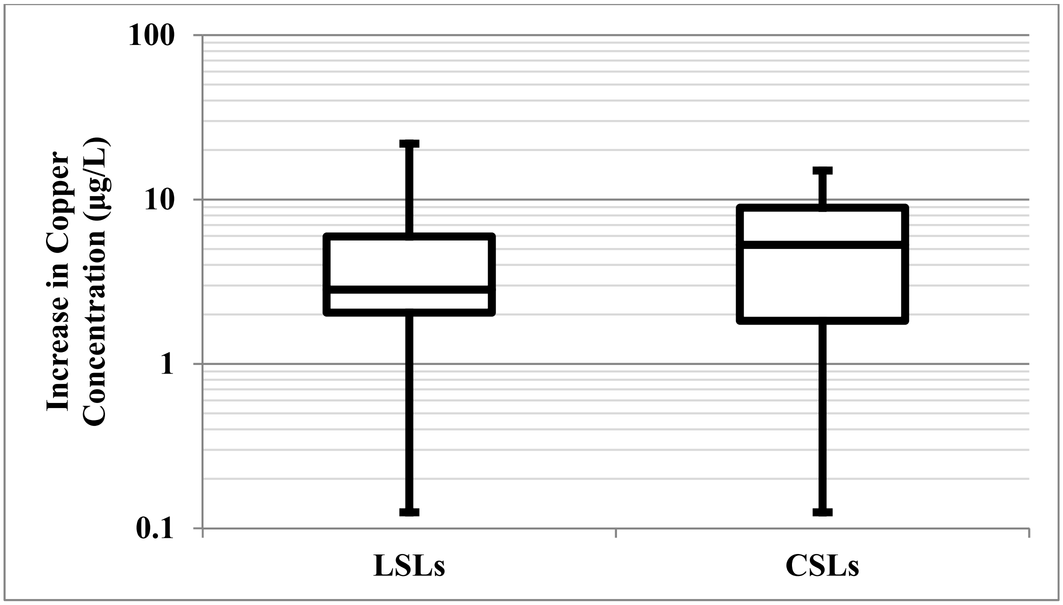
The copper results testify to the effectiveness of the epoxy in controlling lead release, since lead would migrate more slowly than copper through the epoxy; and the traces of copper found in these samples may have come entirely from other sources and not from migration through the epoxy. Some copper may have leached into the samples from the epoxy itself or from the end fittings attached to the pipe sections, and some may have been introduced while collecting and handling the samples, or with the tap water used to flush the pipe sections. As discussed earlier, the epoxy contained approximately 8 mg copper/kg epoxy. Based on the epoxy density and applied volume of epoxy per pipe (Table 4.2), this means there was about 260 – 590 µg copper present in each pipe coating.

Regardless of the mechanism, the amounts of copper found in the epoxy-coated sections were far less than the amounts found in the uncoated control copper pipe section and orders of magnitude less than the current AL for copper (1,300 µg/L). Furthermore, the range of copper increase seen in all samples from epoxy-coated pipes (0.4 – 22 µg/L) is within a lower range than those observed in Lawrence, KS tap water in 2011 (6.3 – 120 µg/L). Since copper concentrations decreased significantly (one-tailed t-test, $\alpha = 0.05$) with repeated extractions, it is reasonable to assume that any copper remaining on the internal surface of an epoxy-coated service line would quickly exhausted when the line is placed back in service. There appears to be no reason for utilities or consumers to be concerned about the copper present in the epoxy.

Table 4.5
Copper in samples from epoxy-coated pipe sections in FD1 and FD2

Experiment	Extraction Water	Holding Time, h	Pipe No.		Cu, µg/L	
			LSLs	CSLs	LSLs	CSLs
Fill-and-Dump Experiment 1 (FD1)	Dechlorinated pH 8 Tap Water		Extraction Water		5.7	
		6	Pb04, Control	Cu10, Control	14	390
		6	Pb01	Cu01	15	15
		6	Pb02	Cu02	9.1	20.0
		24	Pb05	Cu05	9.3	7.6
		96	Pb07	Cu07	5.0	7.3
		240	Pb05	Cu05	5.5	3.1
	Chlorinated pH 8 Extraction Water		Extraction Water		≤ 0.25	
		6	Pb03	Cu03	6.8	7
		24	Pb06	Cu06	5.6	8.9
		96	Pb08	Cu08	10	15
		240	Pb06	Cu06	2.8	7.4
	pH 6.5 Extraction Water		Extraction Water		≤ 0.25	
		6	Pb04, Control	Cu10, Control	5.5	830
		168	Pb04, Control	Cu10, Control	10	400
		6	Pb01	Cu01	2.6	6.3
		6	Pb02	Cu02	4.0	4.3
		168	Pb01	Cu01	7.1	15
		168	Pb02	Cu02	10	8.9
		6	Pb03	Cu03	2.1	1.9
		168	Pb03	Cu03	6.3	11
Seven-Month Wait, then Fill-and-Dump Experiment 2 (FD2)	Chlorinated pH 8 Extraction Water		Extraction Water		≤ 0.25	
		6	Pb04, Control	Cu10, Control	3.7	270
		168	Pb04, Control	Cu10, Control	4.5	85
		6	Pb08	Cu08	2.7	3.3
		24	Pb02	Cu02	0.37	0.38
		24	Pb05	Cu05	2.6	1.3
		24	Pb09	Cu09	22	14
		168	Pb02	Cu02	1.1	1.0
		168	Pb05	Cu05	2.8	0.67
		168	Pb09	Cu09	4.1	3.8
	Re-Flushed, then Chlorinated pH 8 Extraction Water		Extraction Water		≤ 0.25	
		6	Pb02	Cu02		
		6	Pb05	Cu05	2.2	
		6	Pb08	Cu08		
		6	Pb09	Cu09	2.8	8.7
		24	Pb02	Cu02		
		24	Pb05	Cu05	1.6	
		24	Pb08	Cu08		
		24	Pb09	Cu09	1.8	2.7
		168	Pb02	Cu02		
		168	Pb05	Cu05	2.0	
		168	Pb08	Cu08		
		168	Pb09	Cu09		

Source: Breault 2014



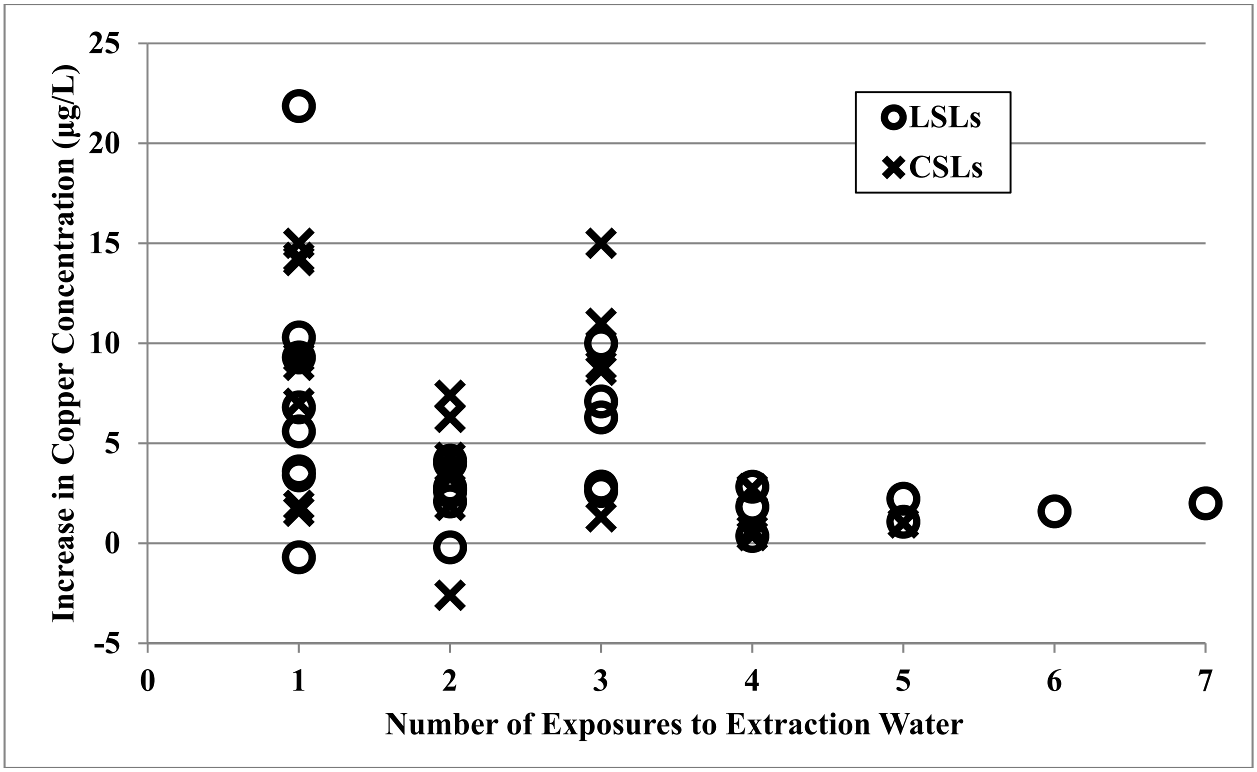
Source: Breault 2014.

Figure 4.2 Increase in copper in samples from epoxy-coated pipe sections

Table 4.6
Mean copper increases in samples from epoxy-coated pipe sections

Sample Subset	Mean Copper Concentration Increase (µg/L)	±SD (µg/L)	Number of Samples
All Samples	5.3	4.8	51
Samples from Sections Extracted for the First Time	8.3	5.8	16
Samples from Previously Extracted Sections	3.9	3.5	35

Source: Breault 2014



Source: Breault 2014.

Figure 4.3 Increase in copper in samples from epoxy-coated pipe sections after sequential fill-and-dump tests

Total Organic Carbon (TOC)

Table 4.7 shows the TOC concentrations found in the extraction waters for FD1 and FD2. Three values were omitted from statistical analysis performed for the discussion below: one for pipe section Pb08 (13.1 mg/L) when exposed to chlorinated pH 8 water for 4 days, and two for pipe section Cu02 (4.78 mg/L and 4.36 mg/L) when exposed to dechlorinated tap water for 6 hours and pH 6.5 extraction water for 7 days, respectively. All three values were determined to be statistical outliers (Grubb's test, α = 0.05). Other values with excessively high %RSDs (3.06 ± 4.2%, 1.38 mg/L ± 6.3%, 0.78 mg/L ± 5.4%, and 0.51 mg/L ± 11.3%) were included in data analysis because they were not statistical outliers (Grubb's test, α = 0.05) and the results from sequential injections were not trending strongly enough to suggest that the TOC analyzer was experiencing a membrane equilibration issue.

As shown in Table 4.8 and Figure 4.4, the dechlorinated pH 8 tap water, chlorinated pH 8 extraction water, and pH 6.5 extraction water had average initial TOC concentrations of 3.53 mg/L, 0.39 mg/L, and 0.32 mg/L, respectively. Following extraction, the mean TOC concentrations for the three extraction waters were 3.48 ± 0.27 mg/L (n = 9), 0.87 ± 0.50 mg/L (n = 33), and 1.19 ± 0.79 mg/L (n = 11). The mean TOC increases in the extraction waters (based on the increases observed in each individual sample of each type of extraction water) were −0.05 mg/L, +0.48 mg/L, and +0.87 mg/L, respectively. The difference in TOC concentration before and after exposure to the epoxy was not statistically significant for the dechlorinated pH 8 tap water (two-tailed t-test, α = 0.05), but the increases were statistically significant (one-tailed t-test, α = 0.05) for the chlorinated pH 8 extraction water and the pH 6.5 extraction water. The small but measurable increases in two of the extraction waters are consistent with previous research (Heim and Dietrich 2007).

A previous study (Jackson et al. 2007) addressed the longer-term leaching of TOC and individual organic constituents from epoxies used to rehabilitate water mains. Five distinct epoxy formulations were tested in-situ at times ranging from 1-10 years after installation. None of the epoxies showed detectable TOC leaching relative to field blanks. GC-MS analysis found no epoxy-specific compounds resulting from four of the five epoxies. The fifth epoxy showed evidence of leaching of 4-t-butyl phenol (4-TBP), and the presence of halogenated 4-TBP products, in some samples, with a maximum concentration of 2.2 µg/L; but this was the only epoxy containing 4-TBP. Overall, the authors found little evidence of long-term leaching of TOC or individual constituents from epoxy.

Since at least one typical epoxy component (polyamines) can potentially bind copper and might therefore help draw it into solution, the data were examined to determine if the increases in TOC and copper were correlated. As reported by Breault (2014), increases in copper concentration were not significantly correlated ($\alpha = 0.05$) with TOC increases for either CSL or LSL pipe sections.

Table 4.7
TOC in samples from epoxy-coated pipe sections

Experiment	Extraction Water	Holding Time, h	Pipe No.		TOC, mg/L	
			LSLs	CSLs	LSLs	CSLs
Fill-and-Dump Experiment 1 (FD1)	Dechlorinated pH 8 Tap Water		Extraction Water		3.53	
		6	Pb04, Control	Cu10, Control	3.62	3.62
		6	Pb01	Cu01	3.28	3.46
		6	Pb02	Cu02	3.36	4.78**
		24	Pb05	Cu05	3.65	3.48
		96	Pb07	Cu07	3.76	3.99
		240	Pb05	Cu05	3.18	3.19
	Chlorinated pH 8 Extraction Water		Extraction Water		0.80/0.45*	
		6	Pb03	Cu03	0.96	1.36
		24	Pb06	Cu06	0.92	1.10
		96	Pb08	Cu08	13.10**	1.72
		240	Pb06	Cu06	0.77	1.11
	pH 6.5 Extraction Water		Extraction Water		0.35/0.29*	
		6	Pb04, Control	Cu10, Control	0.50	0.31
		168	Pb04, Control	Cu10, Control	1.00	0.28
		6	Pb01	Cu01	0.52	1.38 ± 6.3%†
		6	Pb02	Cu02	0.73	1.48
		168	Pb01	Cu01	0.78 ± 5.4%†	3.06 ± 4.2%†
		168	Pb02	Cu02	1.68	4.36 ± 2.8%†**
		6	Pb03	Cu03	0.39	0.86
		168	Pb03	Cu03	0.49	1.71
Seven-Month Wait, then Fill-and-Dump Experiment 2 (FD2)	Chlorinated pH 8 Extraction Water		Extraction Water		0.19/0.20*	
		6	Pb04, Control	Cu10, Control	1.87	0.41
		168	Pb04, Control	Cu10, Control	1.02	0.25
		6	Pb08	Cu08	1.46	0.91
		24	Pb02	Cu02	0.36	0.34
		24	Pb05	Cu05	0.81	1.01
		24	Pb09	Cu09	0.95	2.66
		168	Pb02	Cu02	0.51	0.54
		168	Pb05	Cu05	0.58	0.80
		168	Pb09	Cu09	0.88	1.46
	Re-Flushed, then Chlorinated pH 8 Extraction Water		Extraction Water		0.51 ± 11.3%†/0.17*	
		6	Pb02	Cu02		
		6	Pb05	Cu05		
		6	Pb08	Cu08		
		6	Pb09	Cu09	0.49	0.43
		24	Pb02	Cu02		
		24	Pb05	Cu05		
		24	Pb08	Cu08		
		24	Pb09	Cu09	0.46	0.46
		168	Pb02	Cu02	0.44	0.43
		168	Pb05	Cu05	0.48	0.52
		168	Pb08	Cu08	1.75	0.73
		168	Pb09	Cu09	0.69	0.71

Source: Breault 2014

* Values for batches of extraction water used for holding times of 6 – 24 hours and 7 days, respectively

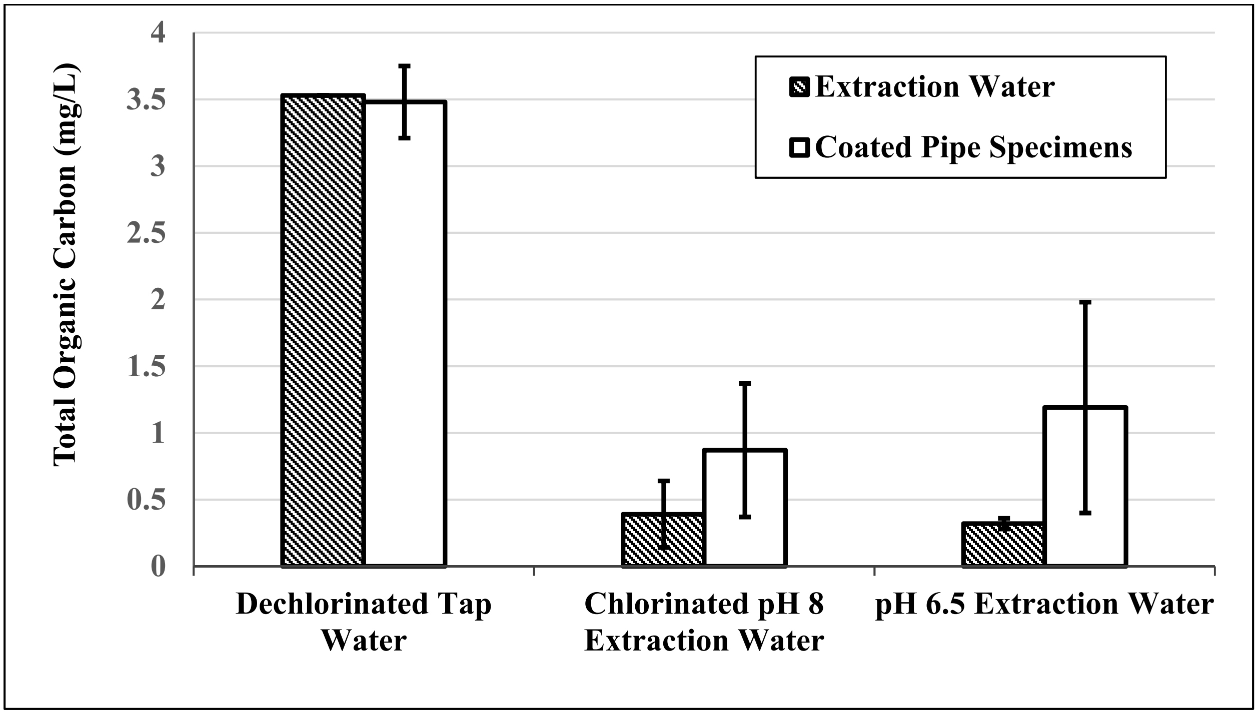
** Omitted from data analysis as an outlier

† %RSD values are shown where they exceeded the applicable QC criterion.

Table 4.8
TOC in extraction waters and samples from epoxy-coated pipes

Extraction Water	Sample Subset	Mean TOC Concentration (mg/L)	±SD (mg/L)	Number of Samples
Dechlorinated Tap Water	Initial	3.53	N/A	1
	Exposed to Coated Pipe Section	3.48	0.27	9
Chlorinated pH 8 Extraction Water	Initial	0.39	0.25	6
	Exposed to Coated Pipe Section	0.87	0.50	33
pH 6.5 Extraction Water	Initial	0.32	0.04	2
	Exposed to Coated Pipe Section	1.19	0.79	11

Source: Breault 2014



Source: Breault 2014.
Note: Error bars represent one SD.

Figure 4.4 TOC in extraction waters and in samples from epoxy-coated pipe sections

Residual Chlorine

The chlorinated pH 8 extraction water samples for FD1 and FD2 were analyzed for total chlorine to determine residual free chlorine. Some of the samples were also analyzed for monochloramine, even though they initially contained only free chlorine, to verify that the total chlorine measured was free chlorine and not combined chlorine formed by the reaction of chlorine with the epoxy, which contains organic amines. The measured monochloramine concentrations in samples initially containing only free chlorine were ≤ 8% of the total chlorine measured. The traces of monochloramine found in these samples may have resulted from “carryover” (reactions of free chlorine with the reagents for monochloramine analysis) or from organic chloramines formed by the reaction of chlorine with amines present in the epoxy. The latter possibility is explored in more detail in a later section of this report (see Reactivity of Chlorine with Triethylenetetramine [TETA]). It is assumed in the following discussion that all total chlorine measured was actually free chlorine unless the samples initially contained combined chlorine. Chlorine demand was determined by subtracting the chlorine residual measured in a sample from the chlorine residual in a sample of the extraction water stored in an amber glass bottle.

The free chlorine residuals in samples of chlorinated pH 8 extraction water drawn from the uncoated control pipes (Pb04 and CU10) are shown in Table 4.9. Only traces of residual free chlorine were found in the 24 h samples, and no detectable amount in either of the 168 h samples. Very similar results were found for samples of chlorinated pH 8 extraction water drawn from epoxy-coated LSL and CSL sections (Table 4.10). Thus, both coated and uncoated LSL and CSL pipe sections exerted a very significant free chlorine demand, approaching 2 mg/L in 24 hours, with most of the demand being exerted in the first 6 hours in the epoxy-coated pipe sections.

Table 4.9
Free chlorine in samples from uncoated control pipe sections

Sample*	Holding Time (h)	Free Chlorine Residual (mg/L as Cl_2)
Control	0	1.94
Pb04	24	0.05
Cu10	24	0.20
Pb04	168	≤0.02
Cu10	168	≤0.02

Source: Breault 2014
* All were chlorinated pH 8 extraction water.

Table 4.10
Free chlorine in samples from epoxy-coated pipe sections

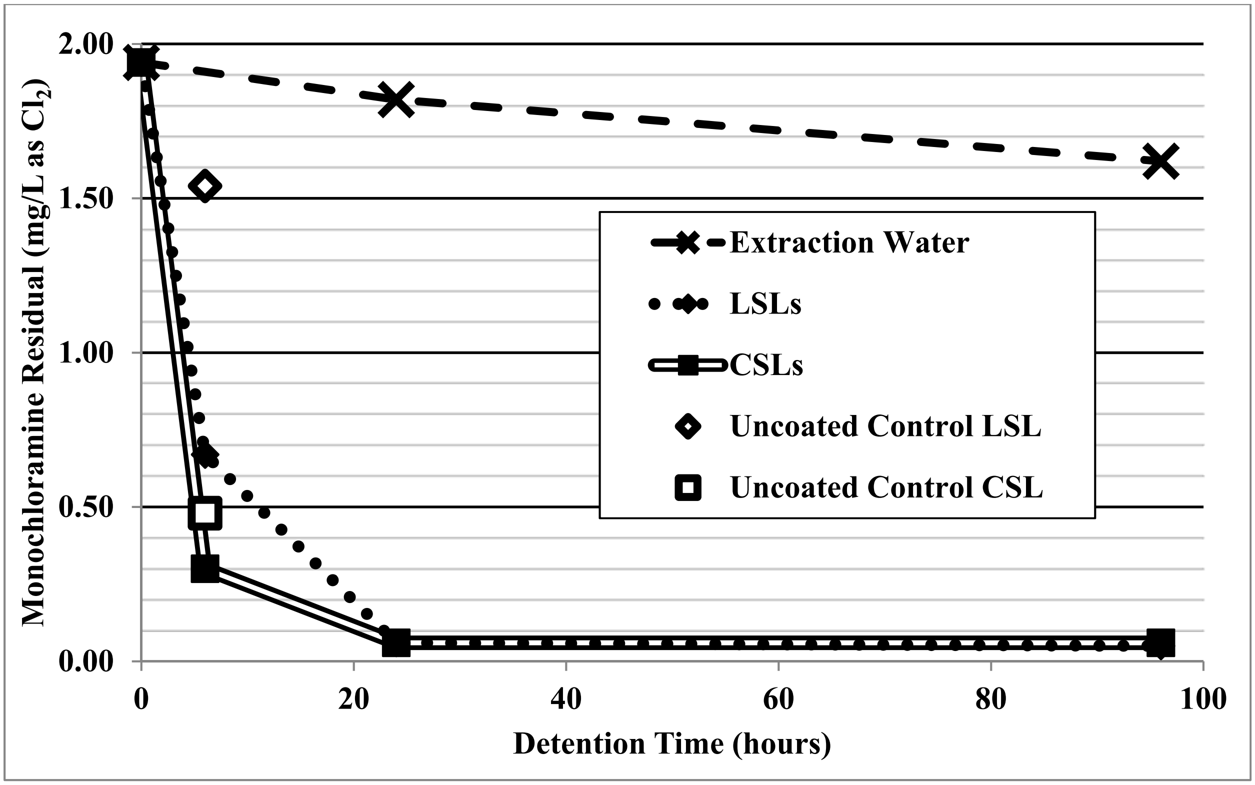
Sample*	Holding Time (h)	Free Chlorine Residual (mg/L as Cl_2)
Control	0	2.00
Pb03	6	0.17
Cu03	6	0.33
Pb06	24	0.08
Cu06	24	0.12
Pb08	96	≤ 0.02
Cu08	96	≤ 0.02
Pb06	240	≤ 0.02
Cu06	240	≤ 0.02

Source: Breault 2014

* All were chlorinated pH 8 extraction water

To examine the reactivity of combined chlorine with coated and uncoated pipe sections, a similar experiment was conducted using pH 8 extraction water spiked with an initial combined chlorine concentration of about 1.94 mg/L as Cl_2. The results are shown in Figure 4.5. The monochloramine concentration in the control water (chlorinated pH 8 extraction water stored in a 4 L amber glass bottle) decreased by 0.34 mg/L as Cl_2 over 4 d, a typical autodecomposition rate in relatively pure solution. After 6 hours, combined chlorine residuals in the epoxy-coated pipe sections averaged 0.52 mg/L as Cl_2, versus 0.26 mg/L as Cl_2 with free chlorine. After 24 h, the combined chlorine residuals averaged 0.06 mg/L as Cl_2, versus ≤ 0.02 mg/L as Cl_2 with free chlorine. After 6 h, the uncoated (control) LSL section exhibited a much lower combined chlorine demand than the other pipe sections, which is attributable to its exposure to low levels of residual free chlorine over the course of its many years in service. The CSL control section was made from virgin copper pipe, and the copper is assumed to have either reacted with combined chlorine or catalyzed its autodecomposition.

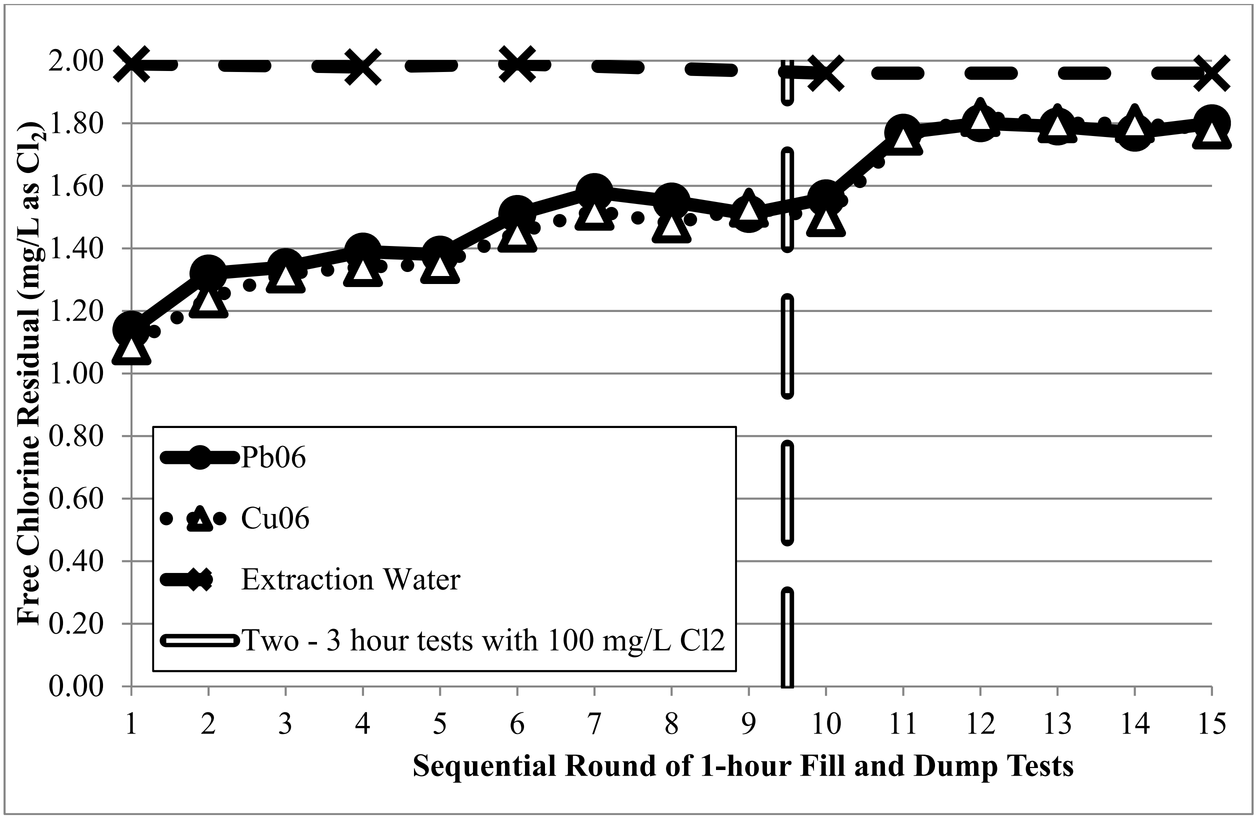
To determine whether the chlorine demand associated with the epoxy coatings could be gradually satisfied, additional fill-and-dump testing was conducted. Two epoxy-coated pipe sections, one LSL and one CSL (Pb06 and Cu06, respectively) were sequentially exposed to chlorinated pH 8 extraction water, starting with nine 1-h exposures with an initial free chlorine concentration of 2 mg/L as Cl_2. Over the course of these nine exposures, the residual free chlorine concentration remaining after 1 h gradually rose from 1.0 to 1.2 mg/L as Cl_2 to between 1.4 and 1.6 mg/L as Cl_2 (Figure 4.6).



Source: Breault 2014.

Note: The pipe sections were extracted with chlorinated pH 8.0 extraction water having an initial combined chlorine concentration of 1.94 mg/L as Cl_2.

Figure 4.5 Monochloramine versus time in samples from epoxy-coated pipe sections

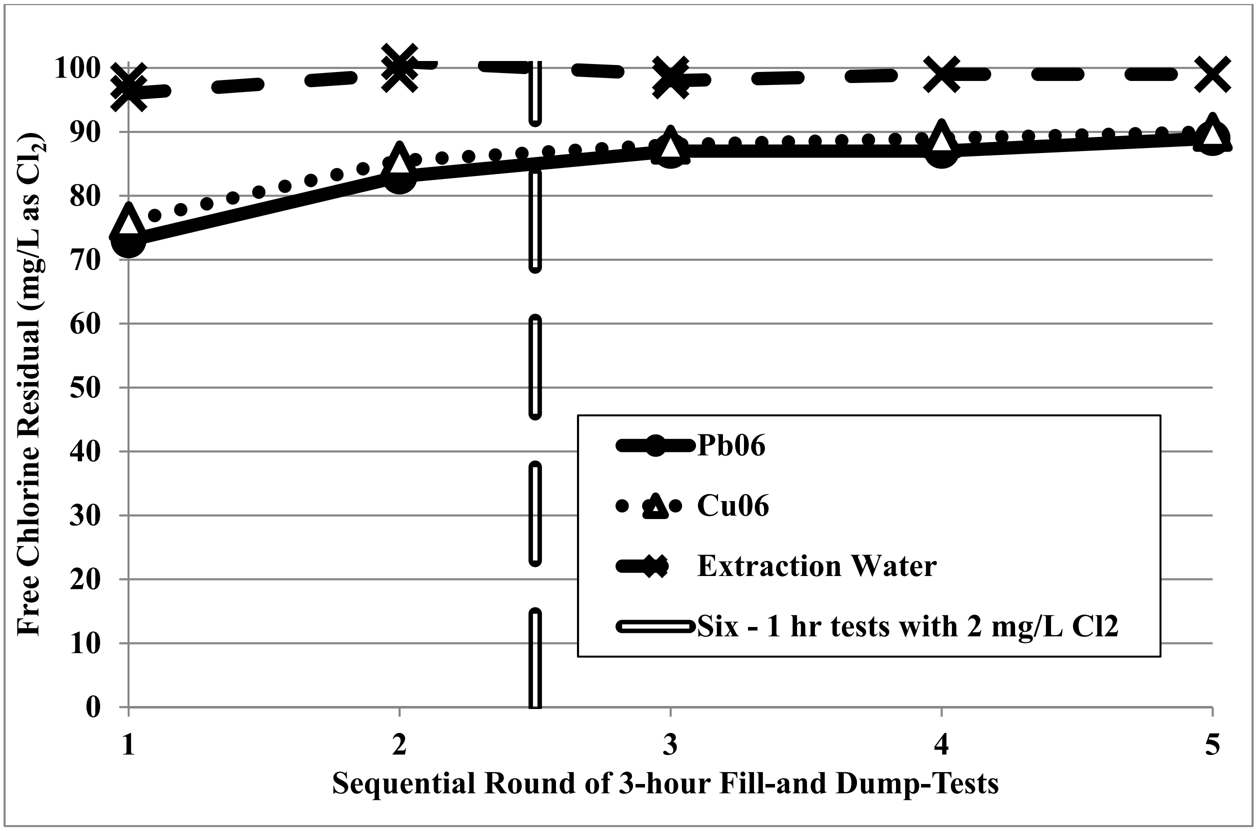


Source: Breault 2014.

Note: The pipe sections were extracted with chlorinated pH 8.0 extraction water having an initial free chlorine concentration of 2.00 mg/L as Cl_2.

Figure 4.6 Free chlorine remaining after sequential 1-h fill-and-dump tests on epoxy-coated pipe sections

After the ninth 1-h test, two 3-h tests were performed in which each pipe section was exposed to a free chlorine concentration of 100 mg/L as Cl_2 for 3 h. This was followed by 6 more 1-h tests with 2 mg/L of free chlorine as Cl_2 followed by 3 more 3-h tests with 100 mg/L of free chlorine as Cl_2. As shown in Figure 4.6, the residual free chlorine levels in the 1-hr test samples rose to about 1.8 mg/L as Cl_2 following the first two 3-h exposures to 100 mg/L of free chlorine as Cl_2. The free residual chlorine concentrations measured after the 3-h tests using 100 mg/L of chlorine as Cl_2 are shown in Figure 4.7. For both chlorine dosages used, 2 and 100 mg/L as Cl_2, the chlorine demand was about the same when expressed as a percentage, i.e., about 10%, though the holding times differed (1 h versus 3 h).



Source: Breault 2014.
Note: The pipe sections were extracted with chlorinated pH 8.0 extraction water having an initial free chlorine concentration of 100 mg/L as Cl_2.

Figure 4.7 Free chlorine remaining after sequential 3-hour fill-and-dump tests on epoxy-coated pipe sections

It is unclear from these results just how long it would take for chlorine demand associated with the epoxy to be fully satisfied. It evidently would not be fully satisfied under conditions similar to those specified in AWWA Standard C651-05 (AWWA 2005) for disinfecting water mains, i.e., conditions similar to those of a 3-h test with an initial free chlorine concentration of 100 mg/L as Cl_2. If the chlorine were reacting with only the surface of the epoxy coating, it would be reasonable to expect the chlorine demand to be rapidly satisfied; but that is not what was observed.

The persistence of the chlorine demand indicates that chlorine is diffusing into or through the epoxy and reacting with the epoxy throughout its depth and/or with the underlying pipe surface or, for the LSL sections, with deposits on the pipe surface. If the demand were being exerted primarily by the underlying pipe surfaces and deposits, the rate of reaction should have been much slower in the epoxy-coated pipe sections, since diffusion of chlorine to the pipe surface would have been impeded; but that was not what was observed. Thus, it appears that the epoxy coating itself is exerting a strong chlorine demand. A representative of an epoxy manufacturing company (one that does not make products for coating LSLs) informed a member of the project team that it is well known within the industry that epoxy reacts with chlorine, and that in some cases this can cause problems, for example, high concentrations of chlorine in swimming pool water can shorten the service life of epoxy-based paints used in swimming pools.

It is also unclear which component(s) of the epoxy the chlorine is reacting with. Both free and combined chlorine are expected to react quickly with polyamine compounds, and this possibility is explored in more detail below (see Reactivity of Chlorine with Triethylenetetramine [TETA]). Both would also be expected to react with reduced forms of iron, such as the iron oxide listed as a component of the epoxy used in this study; but the reaction rate would likely be much faster for free chlorine than for combined chlorine, based on the reaction rates typically observed in aqueous solution. Both free and combined chlorine were found to be unreactive with BADGE, as discussed below (see Chapter 4, Chlorination of BPA, BPF, and BADGE) and as reported in greater detail by Lane (2015) and Lane et al. (2015b); but it is conceivable they are reactive with other components of the epoxy unknown to the investigators.

Potential secondary effects of the chlorine demand associated with epoxy coatings include: 1) reduced formation of disinfection byproducts such as THMs and HAAs; 2) formation of new, unregulated DBPs (if they are able to leach out of the epoxy after they form); 3) increased biofilm growth in the service lines and household plumbing (due to reduced concentrations of residual chlorine); 4) reduced biofilm growth in the service lines (if the reactions cause the surface of the epoxy to inhibit bacterial growth); 5) reduced residual chlorine concentrations in tap water samples; 6) increased heterotrophic bacteria in tap water samples, which could potential lead to excessive heterotrophic plate counts; and 7) reduced service life. As part of this project, a concerted effort was made to identify chlorinated byproducts leaching from epoxy exposed to chlorine, as detailed elsewhere in this report; but further investigations of the other potential secondary effects listed above was beyond the scope of this project. It should be noted however, that the internal surface of any pipe material used in a water distribution system can potentially react with residual disinfectants (creating what is commonly referred to as “pipe wall demand”), or support biofilm growths or accumulate deposits that react with residual chlorine. Thus, epoxy coatings are not unique in the regard.

Bisphenols and BADGE

The samples from FD1 were analyzed for bisphenols, including tetrachloro-BPA (BPA-4Cl), and BADGE. The FD2 samples were analyzed for these same constituents, plus BADGE and three of its hydrolysis products, i.e., BADGE-H_2O, BADGE-$2H_2O$, and BADGE-H_2O-HCl. Halfway through FD2, BADGE-2HCl was added to the analysis but was not reported, since there was not a complete data set; but it was never detected in any of the samples. The method(s) needed to analyze these additional constituents were still being developed when FD1 was conducted.

Fill-and-Dump Experiment 1 (FD1)

Results from the first fill-and-dump experiment (FD1) on the epoxy-coated pipe sections are shown in Table 4.11. BADGE was detected in 9 of the 36 samples at concentrations ranging from 13 to 340 μg/L. Interestingly, BADGE was detected only in samples having holding times of 24 h or less. The lack of BADGE at longer holding times was attributed primarily to hydrolysis, though some may have been lost to adsorption on the silicone stoppers (see Leaching and Adsorption of Constituents by End-Fittings). BADGE hydrolysis is discussed in greater detail below (see Chapter 4, Hydrolysis of Bisphenol Diglycidyl Ethers [BDGEs] and BPA).

The samples were also analyzed for BPA, BPB, BPD, BPE, BPF, and BPA-4Cl, all of which were undetected except for BPA. BPA was detected in only 5 of the 36 samples, and only at trace levels, i.e., 0.25 to 1.7 µg/L. Other compounds, referred to herein as "BPA-like" compounds also appeared to be present in the samples. These compounds are referred to as BPA-like because they had the same MS/MS quantitation and confirmation ions as BPA but different retention times. BPA-like compounds having retention times of 6.0 – 6.4 minutes were detected in 31 of the 36 samples in FD1 (Table 4.11). Assuming a response factor equivalent to BPA, their concentrations were estimated to range from 0.94 to 94 µg/L.

To eliminate the possibility that sample matrix affects were shifting the retention time of BPA, selected samples were spiked with a BPA standard, but the retention time of BPA (6.5 min.) was unchanged (Lane 2015). It was later determined that the observed BPA-like compounds were most likely attributable an MS electrospray in-source conversion, i.e., they were produced as larger molecules (including BADGE hydrolysis products and other compounds) were broken (fragmented) into smaller pieces by the MS/MS as they passed through the instrument. They were not initially present in the samples, they were not BPA, and they were not formed through physical, chemical, or biological degradation processes that could potentially occur in a water distribution system. This is discussed in greater detail below (see Identification of "BPA-Like" Compounds) and by Lane (2015).

Table 4.11
BADGE, BPA, and BPA-like compounds in samples from epoxy-coated pipe sections in FD1

Extraction Water and Holding Time	**BADGE, µg/L**		**BPA, µg/L**		**BPA-like, µg/L* 6.0 min RT**		**BPA-like, µg/L* 6.4 min RT**	
	LSLs	**CSLs**	**LSLs**	**CSLs**	**LSLs**	**CSLs**	**LSLs**	**CSLs**
Dechlorinated pH 8 Tap Water	≤7.0	≤7.0	≤0.057	≤0.057	ND†	ND	ND	ND
Control (unlined) – 6 h	≤7.0	≤7.0	≤0.057	≤0.057	0.94	ND	ND	ND
6 h (A)	340	32	≤0.057	≤0.057	36	52	ND	ND
6 h (B)	214	36	≤0.057	≤0.057	49	62	ND	ND
24 h	241	≤7.0	≤0.057	≤0.057	34	46	ND	ND
4 d	≤7.0	≤7.0	≤0.057	≤0.057	68	54	5.6	6.3
24 h, then 10 d	≤7.0	≤7.0	≤0.057	≤0.057	10	14	3.3	11
Chlorinated pH 8 Extraction Water	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
6 h	236	76	≤0.057	≤0.057	37	7.4	9.4	ND
24 h	101	≤7.0	≤0.057	≤0.057	51	59	12	13
4 d	≤7.0	≤7.0	≤0.057	≤0.057	94	20	20	11
24 h, then 10 d	≤7.0	≤7.0	≤0.057	1.7	ND	11	51	23
pH 6.5 Extraction Water	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
Control (unlined) initially filled with dechlorinated pH 8 tap water, held for 6 h, then								
6 h	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
6 h, then 7 d	≤7.0	≤7.0	≤0.057	≤0.057	ND	ND	ND	ND
Pipes initially filled with dechlorinated pH 8 tap water, held 6 h, then:								
6 h (A)	≤7.0	≤7.0	≤0.057	≤0.057	11	14	ND	ND
6 h (B)	≤7.0	≤7.0	0.82	≤0.057	7.4	11	2.5	1.7
6 h, then 7 d (A)	≤7.0	≤7.0	0.25	≤0.057	16	8.8	11	10
6 h, then 7 d (B)	≤7.0	≤7.0	≤0.057	≤0.057	15	13	7.8	6.3
Pipes initially filled with chlorinated pH 8 extraction water, held 6 h, then:								
6 h	13	≤7.0	1.3	≤0.057	9.0	8.2	4.0	5.1
6 h, then 7 d	≤7.0	≤7.0	1.6	≤0.057	ND	11	12	13

Source: Lane 2015

* Assuming a response factor equivalent to BPA

† ND = not detected

Although the BPA concentrations found in five FD1 samples exceeded the MDL for BPA, the conclusion of the investigators, after carefully examining the totality of the data, is that BPA was not significantly detected in these sample. The basis for this conclusion is that: 1) no BPA was found in the starting products, so there was no monomeric BPA present to leach out of the epoxy; 2) although BPA was not found in control (unexposed) samples of the extraction waters, the possibility that trace contamination had been introduced into some samples during the experiment or during sample handling and collection could not be ruled out; 3) one or more BPA-like compounds was found in every sample in which a trace level of BPA was detected, and the observed BPA could very well have been the result of an MS electrospray in-source conversion associated with one or more BADGE degradation products or similar compounds present in epoxy; and 4) BPA reacts readily with chlorine to form a series of chlorinated byproducts, as discussed below (see Chapter 4, Chlorination of BPA, BPF, and BADGE), yet no BP-4Cl was found in any of the FD1 or FD2 samples extracted with chlorinated pH 8 reagent water.

Fill-and-Dump Experiment 2 (FD2)

One objective of FD2 was to examine the effect of storage time and conditions (Table 3.5) on leaching of key organic constituents. The concentrations of BADGE and its hydrolysis by-products found in the FD2 samples are shown in Table 4.12. BADGE was not detected in any of the samples, including those from the pipe sections not previously employed in FD1 (Pb09 and Cu09). Thus, in seven months' time, leaching of BADGE diminished to below the detection level regardless of the storage conditions (wet or dry).

BADGE-H2O was detected in only 2 of the 38 samples, at concentrations of 3.2 and 4.6 µg/L, and it was not found in any of the 24 samples collected after the pipe sections were reflushed. BADGE-2H2O was found in 23 of the 38 samples, in concentrations ranging from 0.83 to 91 µg/L. Thus, it appears that BADGE hydrolysis continued to progress over time, gradually forming BADGE-2H2O, the end-product of BADGE hydrolysis in solution, as discussed below (see Chapter 4, Hydrolysis of Bisphenol Diglycidyl Ethers [BDGEs] and BPA).

Based on the results for the pipe sections stored wet (Pb02 and Cu02), with the water replaced every 7 days, the concentrations of extractable BADGE hydrolysis products decreased over time, eventually dropping below the detection level. BADGE-H2O was not detected in any of the samples from these pipe sections, and BADGE-2H2O was detected in only a single sample, the first 24-h sample, at a concentration of 1.8 µg/L, slightly above the MDL of 1.0 µg/L. BADGE-2H2O was not detected in any of the samples when these pipe sections were held for 7 d, nor in any samples collected after these pipe sections were reflushed.

An unknown compound having quantitation and confirmation ion intensities inverted compared to those of BADGE-H2O was detected in 32 of the 38 samples (Lane 2015). Thus, other reactions may be occurring, on or within the epoxy-coatings, that were not observed in aqueous solution in the experiments on BADGE hydrolysis.

BPA appeared to have been detected in 35 of the 38 FD2 samples at concentrations ranging from 0.22 to 12 µg/L (Lane 2015). Only 3 samples had a concentration exceeding the NSF 61 single product limit of 0.010 mg/L and all three were collected from pipe sections held for 7 d. In addition to the BPA-like compounds detected in FD1, which had retention times of 6.0 and 6.4 min and which were detected in all of the samples collected in FD2, additional BPA-like compounds were detected at 4.4, 5.7, 5.9, and 7.4 min., and some were present in all of the samples (Lane 2015). Given the presence of so many compounds known to be causing artifacts, and following the same line of reasoning described above for the FD1 samples, it is not reasonable to conclude that BPA was actually detected in the FD2 samples.

Table 4.12
BADGE and BADGE hydrolysis products in samples from epoxy-coated pipe sections in FD2

Extraction Water, Pipe Section No. and Holding Time*	BADGE, µg/L		BADGE-H_2O, µg/L		BADGE-$2H_2O$, µg/L	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Chlorinated pH 8 Extraction Water (0h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe08: 6 h	≤ 7.0	≤ 7.0	4.6	≤ 1.0	91	2.2
Pipe02: 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	1.8	≤ 1.0
Pipe05: 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	3.5	11
Pipe09: 24 h	≤ 7.0	≤ 7.0	3.2	≤ 1.0	231	≤ 1.0
Chlorinated pH 8 Extraction Water (0h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe02: 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe05: 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	2.5	6.3
Pipe09: 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	66	46
Reflushed, then:						
Chlorinated pH 8 Extraction Water (0h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe02: 6 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe05: 6 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe08: 6 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	38	6.7
Pipe09: 6 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	2.8
Chlorinated pH 8 Extraction Water (0h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe02: 6 h, then 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe05: 6 h, then 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe08: 6 h, then 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	19	2.0
Pipe09: 6 h, then 24 h	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	1.9	≤ 1.0
Chlorinated pH 8 Extraction Water (0h)	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe02: 6 h, then 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0
Pipe05: 6 h, then 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	1.1	1.5
Pipe08: 6 h, then 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	21	5.4
Pipe09: 6 h, then 24 h, then 7d	≤ 7.0	≤ 7.0	≤ 1.0	≤ 1.0	6.5	5.8

Source: Lane 2015

* Pipe05 and Pipe08 (for both LSLs and CSLs) were used in FD1, exposed to chlorinated extraction water, and stored dry; Pipe02 was stored wet; and Pipe09 was not used in FD1.

FILL-AND-DUMP EXPERIMENTS ON PET-LINED LSLS AND CSLS

PET Liner Analysis

An unexpanded PET liner representative of those used to line the pipe sections in this study, obtained from the manufacturer, was analyzed for both inorganic constituents and extractable organic constituents. The results for extractable organic constituents are presented below (see Phthalate Esters and Phthalic Acids).

Laser ablation and ICP-MS revealed the presence of antimony (Breault 2014) and non-detectable levels of other constituents of interest, including chromium. Antimony was not quantifiable using laser ablation since the amount of liner drawn from the PET liner into the ICP-

MS instrument was unknown. To obtain quantitative results, a known mass of liner was digested, and the digestate was analyzed using ICP-MS. The average acid-extractable antimony concentration in subsamples of the PET liner was found to be 130 mg Sb/kg PET. This result is only slightly below the range of 190 – 300 mg/kg reported by Duh (2002).

ICP-MS analysis of digested PET liner solutions indicated the presence of chromium, which was inconsistent with the ICP-MS results using laser ablation. When testing lower-molecular-weight elements, the ICP-MS technique has the potential to pick up compounds of similar molecular weight. In this case, ClO^- present in the plasma (formed by oxidation of chloride in the sample) could be mistaken as chromium. To confirm the ICP-MS results, the same samples were analyzed for chromium using GFAAS. The GFAAS technique should not confuse similarly weighted compounds for chromium, as this analysis is based on light absorbance at an element-specific wavelength. Using GFAAS, the chromium concentration was found to be non-detectable, i.e., less than 0.5 mg Cr/kg PET. Thus, both laser-ablation ICP-MS and GFAAS tests indicate that there was no measureable amount of chromium in the PET liner, and that the results of the quantitative ICP-MS analysis of the acid digested sample were due to interference.

Physical Lining Characteristics

Measurements of the PET-lined pipe sections were taken as described in Chapter 3, with the end fittings in place, before and after liner installation, to determine physical characteristics of the pipes and liners. The results are shown in Table 4.13. The CSL sections had a slightly larger ID than the LSLs (1.58 ± 0.01 cm versus 1.48 ± 0.05 cm, respectively), but the same size liner was installed in both. Therefore, surface-area-to-volume ratios of the LSLs were slightly higher than those of the CSLs (2.7 versus 2.5 cm^2/L on average).

Table 4.13
Physical PET liner and pipe characteristics

	Parameter	Initial Pipe Volume*	Lining Volume	Lining Thickness	Lining Surface Area to Water Volume Ratio
		mL	*cm^3*	*mm*	*cm^2/mL*
LSLs	Maximum	276	37.9	0.61	2.8
	Minimum	239	32.8	0.50	2.6
	Mean	259	35.3	0.56	2.7
	SD	±12.9	±1.7	±0.03	±0.09
CSLs	Maximum	294	39.6	0.59	2.5
	Minimum	291	33.8	0.50	2.5
	Mean	292	37.6	0.56	2.5
	SD	±2.0	±1.8	±0.03	±0.01

Source: Breault 2014

* The initial pipe volumes of the CSLs are those of the first three CSLs measured and the mean value was assumed representative of all CSLs since the copper pipe was uniform, from the same coil, with each section cut to the same length.

Extraction Water Analysis

As shown in Table 4.14, the water quality parameters for the dechlorinated tap water were within the ranges reported in 2011 for Lawrence, KS tap water, except for alkalinity. However, considering the variance in surface water quality from year to year (and season to season), the alkalinity measured in the dechlorinated tap water was not unreasonable. All values for dechlorinated tap water measurements listed in Table 4.14 were measured after dechlorination and pH adjustment, except pH and alkalinity. The pH was lowered to 8.0 using 0.1 N HCl, which also lowered the alkalinity. The lead and copper concentrations in pH 6.5 and pH 8.0 chlorinated extraction waters were non-detectable (≤ 0.5 µg/L Pb and ≤ 0.25 µg/L Cu, respectively). The lead concentration in the dechlorinated tap water was also below the MDL, while the copper concentration (23 µg/L) was within the levels seen in 2011 in Lawrence, KS drinking water (6.3–120 µg/L).

Table 4.14
Water quality parameters for extraction waters used in FD3

Parameter	Units	pH 6.5 Extraction Water	Chlorinated pH 8.0 Extraction Water	Dechlorinated Tap Water	2011 Lawrence, KS Tap Water*	2012 Rochester, NY Tap Water**
pH	Std.	6.5	8.0	8.3***	8.0 – 9.9	6.6 – 8.5
Alkalinity	mg/L as $CaCO_3$	1.8	56	122***	40 – 120	63 – 89
Sodium	mg/L	NA	NA	18	15 – 100	15 – 19
Potassium	mg/L	NA	NA	3.8	2.9 – 11	1.4 – 1.7
Chloride	mg/L	NA	NA	NA	13 – 100	32 – 35
Sulfate	mg/L	NA	NA	NA	27 – 150	13 – 30
Dissolved Oxygen	mg/L	N/A	N/A	8.5	N/A	N/A
Conductivity	µS/cm	NA	NA	390	310 – 1,300	220 – 340
Hardness	mg/L as $CaCO_3$	100	100	118	100 – 190	91 – 130
Total Organic Carbon	mg/L	0.08	0.15	3.34	2.93 – 3.75	1.8 – 2.15
Copper	µg/L	≤ 0.25	≤ 0.25	23	6.3 – 120	12 – 320
Lead	µg/L	≤ 0.5	≤ 0.5	≤ 0.5	ND – 9.9	ND – 28
Antimony	µg/L	≤ 0.06	≤ 0.06	0.19	N/A	ND

Source: Breault 2014

* 2011 Lawrence tap water values taken from the 2012 Lawrence Consumer Confidence Report, Appendix C (City of Lawrence 2012).

** 2012 Rochester, NY tap water values taken from the 2012 Water Quality Report, Supplemental Information (City of Rochester 2012)

***pH and alkalinity measured before pH adjustment

NA = Not Analyzed

Lead and Copper

Very high concentrations of lead and copper were found in the extraction water samples drawn from the unlined LSL and CSL control sections for FD3. Lead increased by 1,400–21,000 µg/L, and copper by 310–910 µg/L, respectively. Unfortunately, as noted in Chapter 3, when the pipe sections were flushed with tap water at the beginning of FD3, water evidently infiltrated the space between the PET liner and pipe wall in at least some of the pipe sections, and this water undoubtedly became highly contaminated with lead or copper, depending on type of the pipe section (LSL or CSL); but the significance of this was not immediately recognized.

When the lead and copper data for FD3 were reviewed, 5 of 21 samples from PET-lined LSL sections were found to have a Pb concentration exceeding 5 µg/L; and 4 of these were associated with the same pipe section. Unexpectedly high levels of Cu were detected in samples from 3 PET-lined LSLs and 3 PET-lined CSLs. Although the Cu levels were higher than expected, there were still one to two orders of magnitude below the AL (1,300 µg/L). The research team evaluated possible explanations for these results and concluded that there was no evidence they were caused by random contamination of reagents, sample vials, glassware, etc., since Pb was below the MDL (≤0.5 µg/L) in 13 of the 21 CSL samples and exceeded 1 µg/L in only 2 of the other 8 samples, with a maximum concentration of 1.2 µg/L. It also seemed highly unlikely that Pb or Cu could have permeated through the PET liners, which were visually inspected using a miniature video camera and found to be completely intact.

The only reasonable explanation the research team could come up with for the high Pb and Cu concentrations found in some of the FD3 samples was that water passed behind the liners in some of the pipe sections, became contaminated with very high levels of Pb and Cu (similar to those found in the unlined control sections), and then either dripped into the extraction water as samples were dumped or was drawn in by capillary action as the extraction water flowed over the unsealed ends of some of the liners.

When the end-fittings used in FD3 were removed to inspect them, droplets of water were observed on the outer surfaces of the ends of some of the PET liners, confirming that water had passed behind some of the liners. Based on lead concentrations seen in unlined LSL control sections, only 10–1,000 µL of infiltrated water would be needed to produce the elevated lead levels measured in samples collected from the PET-lined LSLs in FD3. Therefore, the research team decided that the lead and copper results for FD3 had been compromised and that the testing should be repeated for these analytes. Using similar lines of reasoning, the research determined that the results for other analytes discussed below (e.g., antimony and TOC) had not been compromised because the analyte concentrations in water passing behind the liner would have been too low to be detected or because no evidence of contamination was observed.

Based on discussions with the manufacturer, it became clear that the end-fittings provided and used by the research team in FD3 (specifically the SS pipe nipples) were incompatible with proper installation of PET liners. When using nipples, the liner and pipe wall are parallel throughout the length of the pipe, and the end of the liner is not sealed. When water flows through the pipe, as was the case during the flushing procedure, there is nothing keeping the water from flowing behind the liner. When liners are installed in the field, a flanged end fitting is used, and the expanded liner is molded onto it, as shown in Figure 4.8, creating a physical barrier to stop water from flowing between the liner and pipe wall. Effective and efficient lining and coating methods have been carefully developed by manufacturers and installers based on many years of practical experience and research. The high Pb levels observed in FD3 were directly attributable to the use of improper end-fittings, underscoring the importance of proper installation.

Source: Photo by Zachary A. Breault.

Figure 4.8 Image depicting the difference in PET-lined pipes with: SS nipple used in the fill-and-dump experiments (top) and flanged fitting designed to seal liner (bottom)

FD4 was conducted to retest the PET-lined pipe sections after the end-fittings were removed, including the threaded SS pipe nipples screwed into the ends of the PET-lined LSLs, and after the exposed ends of the PET-liners were cleaned as described in Chapter 3. The Pb and Cu concentrations found in the FD4 samples are shown in Tables 4.15 and 4.16, respectively. Only trace amounts of Pb were found in the samples from the PET-lined pipe sections; the maximum concentration found was only 2.9 µg/L, and that result was for a PET-lined CSL. The average Pb concentration found in samples from PET-lined LSLs was 1.2 µg/L, and the average found in samples from PET-lined CSLs was 1.3 µg/L. These levels, though statistically significant, are only slightly higher than the MDL (0.5 μg/L) and an order of magnitude lower than the AL for Pb (15 μg/L).

Table 4.15
Lead in samples from PET-lined pipe sections in FD4

Extraction Water and Holding Time	Section Nos.	Pb, μg/L	
		LSLs	CSLs
Dechlorinated pH 8 Tap Water		≤0.5	
6 h	Pb15/Cu15	1.2	2.4
24 h	Pb16/Cu16	2.5	1.5
4 d	Pb17/Cu17	1.1	1.9
Chlorinated pH 8 Extraction Water		≤0.5	
6 h	Pb13/Cu13	0.7	1.3
pH 6.5 Extraction Water		≤0.5	
6 h (A)	Pb13/Cu13	1.5	≤0.5
6 h (B)	Pb15/Cu15	<0.5	0.6
24 h	Pb16/Cu16	≤0.5	≤0.5
4 d (A)	Pb13/Cu13	1.1	0.6
4 d (B)	Pb15/Cu15	2.4	2.9
	Avg., PET-Lined*	1.2	1.3
Acid Bath, 0.5% HCl		182	

* Average calculated using one-half the value of the MDL for values ≤MDL

Table 4.16
Copper in samples from PET-lined pipe sections in FD4

Extraction Water and Holding Time		Cu, µg/L	
	Section Nos.	LSLs	CSLs
Dechlorinated pH 8 Tap Water		20.2	
6 h	Pb15/Cu15	43.1	72.4
24 h	Pb16/Cu16	42.0	50.7
4 d	Pb17/Cu17	54.3	88.6
Chlorinated pH 8 Extraction Water		≤0.7	
6 h	Pb13/Cu13	64.9	196.4
pH 6.5 Extraction Water		≤0.7	
6 h (A)	Pb13/Cu13	6.4	12.0
6 h (B)	Pb15/Cu15	10.5	18.6
24 h	Pb16/Cu16	2.9	7.0
4 d (A)	Pb13/Cu13	5.4	7.9
4 d (B)	Pb15/Cu15	5.5	64.0
Acid Bath, 0.5% HCl		3.5	

The investigators believe it is highly unlikely that any of the traces of Pb found in the FD4 samples entered the extraction water by migrating through the PET liner. The fact that the average was virtually the same for both LSLs and CSLs suggests that the source of the Pb was contamination associated with disturbance of the end-fittings, handling of the pipe sections, and/or sample collection and handling. Given the short length of the pipe sections, any contribution of lead or other substances by the end fittings would be accentuated relative to what would be observed in a full-scale service line. It is also conceivable that glassware contamination contributed to the observed Pb levels, but the research team believes this is unlikely. Following FD3, the acid bath (0.5% HCl) used to clean the glassware was found to have a Pb concentration of 182 µg/L. However, this level is not exceptionally high for a cleaning bath, and all items soaked in the acid bath were subsequently triple rinsed in deionized (RO) water and then triple rinsed with reagent water. Furthermore, acid-cleaned glassware was also used to prepare the extraction waters and analytical standards, none of which showed any evidence of Pb contamination.

Knowing of the contamination issues the research team encountered during FD3, the manufacturer graciously offered to reline a set of pipe sections – four LSLs and four CSLs – using end-fittings that would effectively seal the PET-liners and prevent water from passing behind them. The Pb and Cu results for FD5, conducted to test the relined pipe sections, are shown in Tables 4.17 and 4.18, respectively. Overall, the results were similar to those for FD4, with only traces amounts of Pb found in samples from the PET-lined pipe sections. Only one sample had a Pb concentration greater than 3 µg/L. The average Pb concentration found in samples from PET-lined LSLs was 1.9 µg/L, and the average found in samples from PET-lined CSLs was 1.0 µg/L. These levels, like those found in FD4, though statistically significant, are only slightly higher than the MDL (0.5 µg/L) and much lower than the AL for Pb (15 µg/L).

Table 4.17
Lead in samples from PET-lined pipe sections in FD5

Extraction Water and Holding Time	Section Nos.	Pb, µg/L LSLs	Pb, µg/L CSLs
Dechlorinated pH 8 Tap Water		≤0.59*	
6 h (A)	Pb13/Cu13	1.3	0.9
6 h (B)	Pb15/Cu15	2.7	1.4
24 h	Pb16/Cu16	2.2	0.7
4 d	Pb17/Cu17	1.0	0.8
Chlorinated pH 8 Extraction Water		≤0.59	
6 h (A)	Pb13/Cu13	0.6	≤0.59
6 h (B)	Pb15/Cu15	1.3	0.8
pH 6.5 Extraction Water		≤0.59	
6 h (A)	Pb13/Cu13	0.8	0.6
6 h (B)	Pb15/Cu15	1.6	1.2
24 h	Pb16/Cu16	1.7	0.7
4 d (A)	Pb13/Cu13	2.5	1.0
4 d (B)	Pb15/Cu15	5.4	2.5
	Avg., PET-Lined†	1.9	1.0
Acid Bath, 0.5% HCl			
5/10/14		68	
5/13/14		79	
Tech. Grade HCl, 0.5% in reagent water		≤0.59	

* The MDL was 0.59 µg/L FD5.

† Average calculated using one-half the value of the MDL for values ≤MDL

The investigators believe the traces of Pb found in the FD5 samples are attributable in part to handling of the pipe sections and to sample collection and handling. The factory-applied compression fittings should have prevented water from passing behind the PET liners, and the research team observed nothing during or after the experiment, or in the results, to suggest otherwise. However, the distant end of each end-fitting, the end away from the pipe section, was connected to plastic (PEX) tubing suitable for connecting the pipe sections to the flushing apparatus. Although the connections between the end-fittings and the plastic tubing appeared to be reasonably snug, they did not appear to be absolutely water-tight, as would have been the case had they been connected to an actual water service line. It appeared as if it were possible for water to pass from inside the PEX tubing into the threads of the compression fittings; and a few drops of water were observed leaking from both end-fittings on two different pipe sections, indicating that water had indeed comes into contact with the threads of at least four compression fittings. Prior to FD5, the end-fittings were flushed at the same time the pipe sections were flushed, but they were not disassembled and scrupulously cleaned in the same manner as the end-fittings used in other tests. Therefore, it is possible that any Pb-bearing residues on or in the compression fittings, especially on the threads, could potentially have contributed to sample contamination.

In any event, the traces of lead found in the FD4 and FD5 samples are inconsequential relative to the levels typically found in tap water following field installation of linings and coatings (or when LSLs are partially or fully replaced). Traces of lead may be released from encrusted plumbing materials upstream from a lined or coated LSL, especially after the material have been disturbed; but much higher concentrations of lead can potentially be (and often are) released into tap water from downstream Pb-bearing deposits that have accumulated over many years in the interior water lines and plumbing fixtures, especially in interior lines made of galvanized iron pipe. Pb levels as low as those observed in FD4 and FD5 would be a welcome relief in locations where the AL was previously being exceeded, and even lower levels would be expected to be found over time, since the primary source of the lead (the LSL) would be cut off by an impermeable barrier.

Copper was detected in all of the FD5 samples. Samples from pipes exposed to dechlorinated tap water had the highest consistent Cu concentrations due to the presence of Cu in the tap water used to prepare the extraction water. All samples obtained using dechlorinated tap water were within + 16% of the initial measured Cu concentrations in the tap water. Samples from the extraction waters were all below 10 µg/L, with three exceptions. Possible sources of Cu in these lined pipes include the plastic end fittings (as described earlier in this chapter), which are estimated to have contributed less than 1 µg/L Cu to the sample water, and Cu residues on the end-fittings that were not removed prior to the experiment. Cu concentrations in samples from the Pb and Cu pipes were similar within each type of extraction water, making it highly unlikely that the Cu present in the samples was due to direct leaching from the pipe material through the liner.

Table 4.18
Copper in samples from PET-lined pipe sections in FD5

Extraction Water and Holding Time	Section Nos.	Cu, µg/L	
		LSLs	CSLs
Dechlorinated pH 8 Tap Water		33.5, 40.1*	
6 h (A)	Pb13/Cu13	28.3	30.9
6 h (B)	Pb15/Cu15	32.3	36.5
24 h	Pb16/Cu16	30.8	32.1
4 d	Pb17/Cu17	33.7	35.6
Chlorinated pH 8 Extraction Water		0.31	
6 h (A)	Pb13/Cu13	4.7	4.7
6 h (B)	Pb15/Cu15	40.9	13.5
pH 6.5 Extraction Water		0.56, 0.37*	
6 h (A)	Pb13/Cu13	3.2	3.2
6 h (B)	Pb15/Cu15	8.5	9.6
24 h	Pb16/Cu16	6.7	5.5
4 d (A)	Pb13/Cu13	2.1	4.1
4 d (B)	Pb15/Cu15	3.6	12.2
Acid Bath, 0.5% HCl			
5/10/14		10.2	
5/13/14		0.41	
Tech. Grade HCl, 0.5% in reagent water		≤0.25†	

* Two batches were prepared, the first for the 6 and 24 h holding times, the second for the 4-d holding time.
† The MDL for Cu was 0.25 µg/L for FD5.

Antimony (Sb)

The antimony (Sb) concentrations found in the samples from FD3 are shown in Table 4.19 and summarized in Table 4.20. All but two samples collected from PET-lined LSLs and all samples collected from the PET-lined CSLs contained detectable Sb (>0.06 µg/L), although the measured concentrations were all quite low. As shown in Table 4.20, the average Sb concentration in samples extracted using dechlorinated pH 8 tap water was 0.28 ± 0.04 µg/L (n = 8), but since the dechlorinated tap water initially contained 0.19 µg/L Sb, the increase was only 0.09 µg/L. The average Sb concentrations found in samples obtained using chlorinated pH 8 extraction water and the pH 6.5 extraction water were 0.09 ± 0.06 µg/L (n = 6), and 0.29 ± 0.18 µg/L (n = 12), respectively. These increases were statistically significant (one-tailed t-test, α = 0.05). The mean Sb increase for all 26 samples was 0.18 ± 0.16 µg/L. In comparison, the Sb concentration increases in samples collected from the unlined LSL and CSL control sections were 0.42–3.94 µg/L and 0.00–0.13 µg/L, respectively.

Table 4.19
Antimony in samples from PET-lined pipe sections

Extraction Water	Holding Time, h	Pipe No.		Sb, µg/L	
		LSLs	CSLs	LSLs	CSLs
Dechlorinated pH 8 Tap Water	0	Extraction Water		0.19	
	6	Pb11, Control	Cu11, Control	4.13	0.19
	6	Pb12	Cu12	0.24	0.31
	6	Pb13	Cu13	0.24	0.28
	24	Pb15	Cu15	0.25	0.25
	96	Pb17	Cu17	0.34	0.34
Chlorinated pH 8 Extraction Water	0	Extraction Water		≤ 0.06	
	6	Pb14	Cu14	≤ 0.06	0.08
	24	Pb16	Cu16	≤ 0.06	0.13
	96	Pb18	Cu18	0.09	0.18
pH 6.5 Extraction Water	0	Extraction Water		≤ 0.06	
	6	Pb11, Control	Cu11, Control	1.32	≤ 0.06
	96	Pb11, Control	Cu11, Control	0.42	0.13
	6	Pb12	Cu12	0.14	0.13
	6	Pb13	Cu13	0.14	0.12
	96	Pb12	Cu12	0.40	0.44
	96	Pb13	Cu13	0.46	0.43
	6	Pb14	Cu14	0.09	0.09
	96	Pb14	Cu14	0.43	0.55

Source: Breault 2014

Table 4.20
Mean antimony (Sb) in samples from PET-lined pipe sections

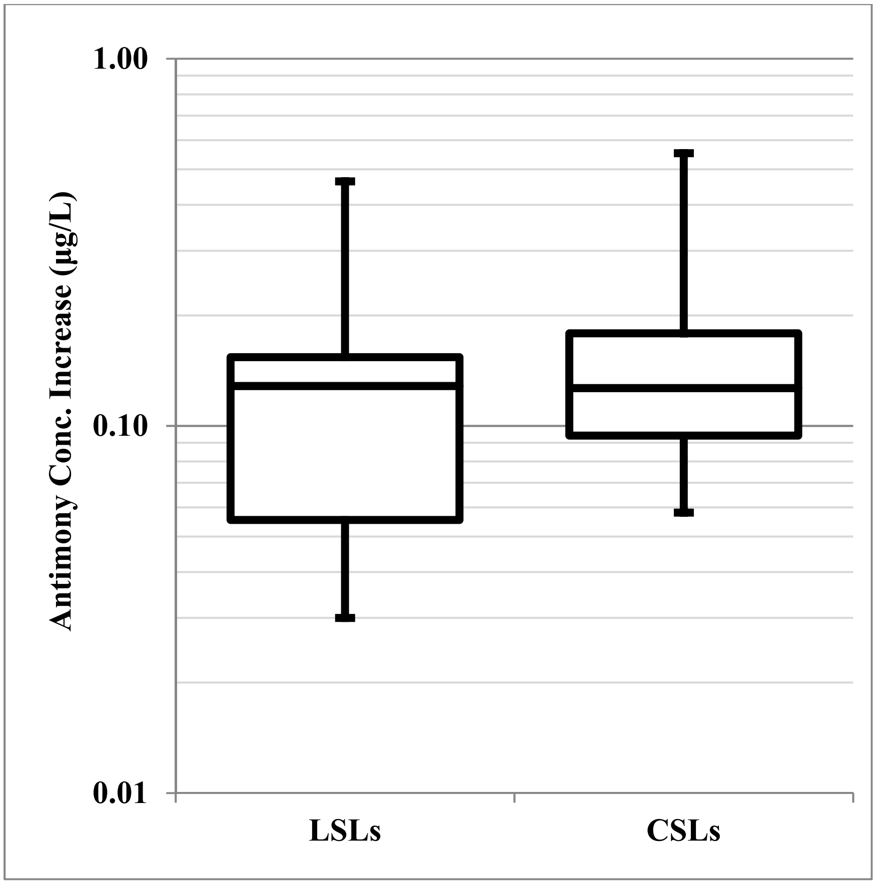
Extraction Water	Sample Subset	Mean Sb Concentration (µg/L)	±SD (µg/L)	Number of Samples
Dechlorinated pH 8 Tap Water	Initial Extraction Water	0.19	N/A	1
	PET-Lined Pipe Section Samples	0.28	0.04	8
Chlorinated pH 8 Extraction Water	Initial Extraction Water	≤ 0.06	N/A	1
	PET-Lined Pipe Section Samples	0.09	0.06	6
pH 6.5 Extraction Water	Initial Extraction Water	≤ 0.06	N/A	1
	PET-Lined Pipe Section Samples	0.29	0.18	12

Source: Breault 2014

Figure 4.9 summarizes the Sb concentration increases in the LSL and CSL samples. The increases were determined by subtracting the Sb concentration initially present in the extraction water, i.e., 0.19 µg/L for the dechlorinated pH 8 tap water, with no corrections needed for the other two extraction waters. The median increase, 0.13 µg/L, was the same for both LSLs and CSLs. The average increase was slightly lower in the LSLs (0.17 µg/L) than in the CSLs (0.20 µg/L), the opposite of what might be expected based on the slight difference in the average surface-area-to-volume ratios of the LSLs and CSLs (Table 4.13).

Antimony concentrations in water in PET bottles have been found to increase over time (Cheng et al. 2010, Reimann et al. 2010). A similar relationship can be seen in Figure 4.10, which compares the increases in samples associated with shorter holding times (6–24 h) to those with longer times (4 d). The mean Sb increase in samples associated with shorter holding times was 0.09 ± 0.04 µg/L (n = 16), which is statistically significant (one-tailed t-test, α = 0.05) relative to the levels initially present in the extraction waters (prior to exposure). The mean Sb increase in the samples associated with longer holding times (4 d) was 0.33 ± 0.17 µg/L (n = 10), which is significantly greater (one-tailed t-test, α = 0.05) than the mean for the samples associated with shorter holding times. However, a larger proportion of the samples with longer holding times were extracted with pH 6.5 extraction water, which also yielded high antimony concentrations, so it is unclear whether a longer holding time or a lower pH exerted a greater influence on the antimony concentrations.

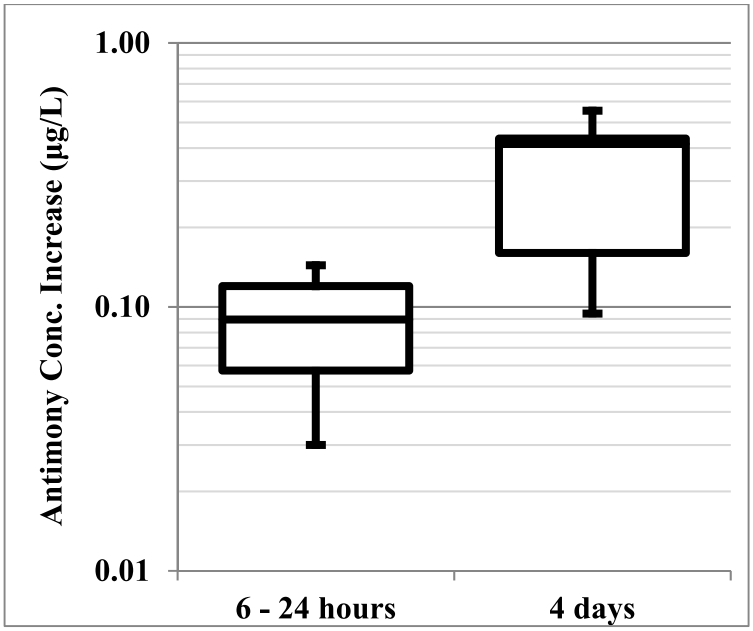
Careful inspection of the Sb data shows that the samples analyzed for Sb were not contaminated with Sb by water that leaked behind the liners as the pipes were flushed. The median Sb increase in the samples exposed to PET-lined LSLs is approximately the same as the median increase in samples collected from PET-lined CSLs (0.13 µg/L for both). Had water passing behind or through the PET liner leached a significant amount of antimony from the pipe walls and then passed into the samples, the antimony concentrations in samples from the PET-lined LSLs would have been higher than those in samples from the PET-lined CSLs, since there was a significant amount of antimony present in the unlined and uncoated LSLs, but not in the unlined and uncoated CSLs. Furthermore, if 10–1,000 µL of water (the volume cited above in discussing contamination of the samples with Pb) containing the highest Sb concentration increase observed in the unlined LSL control section (i.e., 3.94 µg/L) had circumvented a PET liner and contaminated a sample, the resulting antimony concentration increase would have been undetectable (≤ 0.06 µg/L).



Source: Breault 2014.

Figure 4.9 Antimony concentration increases in extraction water samples from PET-lined LSL (n = 13) and CSL (n = 13) pipe sections

It is important to note that although the PET liners leached small amounts of Sb into the extraction waters, the concentrations found were significantly lower (one-tailed t-test, $\alpha = 0.05$) than those in samples from the unlined (control) LSL section. This demonstrates that PET liners can significantly reduce Sb concentrations in drinking water by providing a barrier between Sb-containing deposits and drinking water. PET liners would also serve as an effective barrier against numerous other traces constituents found in pipe deposits, such as those identified by Schock et al. (2008).



Source: Breault 2014.

Figure 4.10 Antimony concentration increases in extraction waters exposed to PET-lined pipe sections for 6–24 hours (n = 16) and 4 days (n = 10)

Total Organic Carbon (TOC)

The TOC concentrations found in the FD3 samples are shown in Table 4.21 and summarized in Table 4.22 and Figure 4.11. The mean TOC concentration in the dechlorinated pH 8 tap water samples was 3.37 ± 0.03 mg/L (n = 8), not significantly different (one-tailed t-test, α = 0.05) from the TOC concentration in the extraction water (3.34 mg/L). The mean TOC concentration in the chlorinated pH 8 extraction water samples, 0.30 ± 0.08 mg/L (n = 6), was only slightly higher than the TOC found in the pH 8 extraction water (0.15 mg/L). Although the difference was statistically significant (one-tailed test, α = 0.05), at TOC concentrations this low it is quite possible that the difference was caused by sample handling or small variations in instrument response rather than leaching. The measured TOC concentration was below the detection limit in the pH 6.5 extraction water and in 10 of the 12 samples of pH 6.5 extraction water drawn from PET-lined pipe sections; and the other two samples contained only 0.11 mg/L of TOC. Overall, based on the results for all 26 samples, it is reasonable to conclude that leaching of TOC from the PET-lined pipe sections was negligible.

The TOC data are deemed to be valid despite the fact water may have passed behind the liners as the lined sections were flushed. The maximum TOC increase in a sample from an unlined (control) section was only 1.09 mg/L. Had even 1,000 µL of water having this TOC concentration leaked from behind a liner into an extraction water sample, the resulting increase in the TOC concentration would not have been detectable. Furthermore, there was no detectable TOC increase observed in samples obtained using dechlorinated pH 8 tap water and pH 6.5 extraction water, whereas all but one sample collected from each unlined control pipe (LSL and CSL) exhibited an increase in TOC concentration. These results indicate that the samples collected from lined pipes were not affected by water that may have passed behind the liners.

Table 4.21
TOC in samples from PET-lined pipe sections

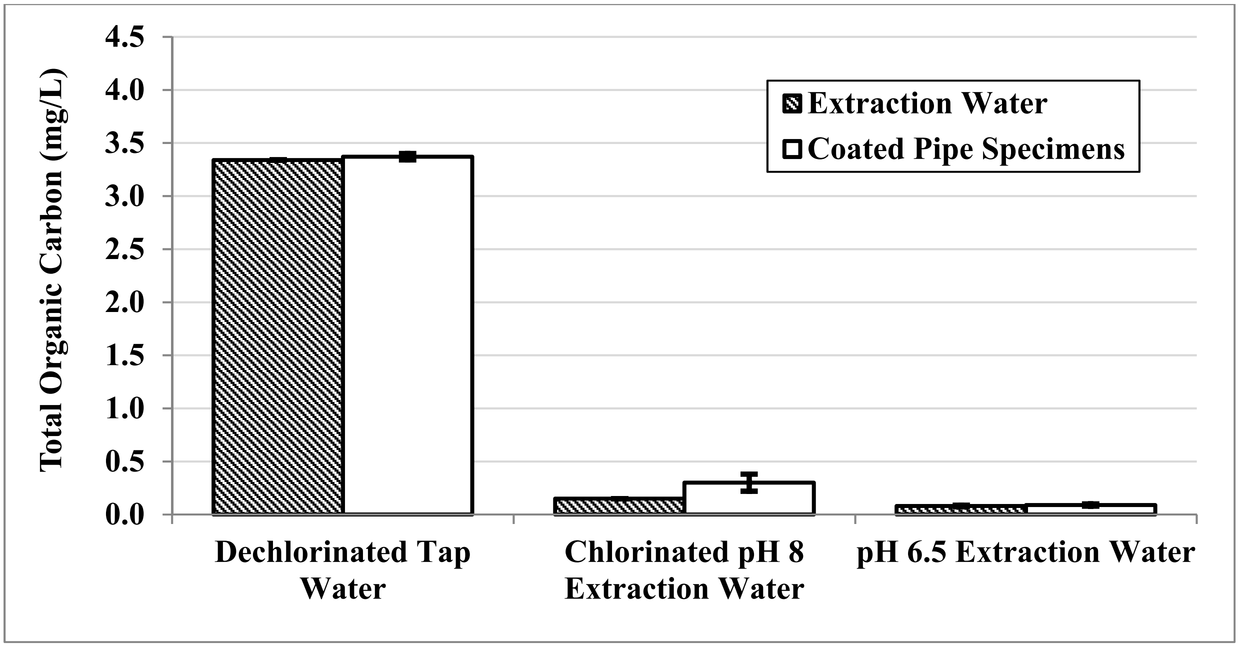
Extraction Water	Holding Time, h	Pipe No.		TOC, mg/L	
		LSLs	CSLs	LSLs	CSLs
Dechlorinated pH 8 Tap Water	0	Extraction Water		3.34	
	6	Pb11, Control	Cu11, Control	3.34	3.21
	6	Pb12	Cu12	3.35	3.36
	6	Pb13	Cu13	3.36	3.34
	24	Pb15	Cu15	3.45	3.36
	96	Pb17	Cu17	3.37	3.38
Chlorinated pH 8 Extraction Water	0	Extraction Water		0.15	
	6	Pb14	Cu14	0.22	0.19
	24	Pb16	Cu16	0.36	0.27
	96	Pb18	Cu18	0.39	0.35
pH 6.5 Extraction Water	0	Extraction Water		≤ 0.10/≤ 0.10*	
	6	Pb11, Control	Cu11, Control	0.38	0.16
	96	Pb11, Control	Cu11, Control	1.09	0.18
	6	Pb12	Cu12	≤ 0.10	≤ 0.10
	6	Pb13	Cu13	0.11	≤ 0.10
	96	Pb12	Cu12	0.11	≤ 0.10
	96	Pb13	Cu13	≤ 0.10	≤ 0.10
	6	Pb14	Cu14	≤ 0.10	≤ 0.10
	96	Pb14	Cu14	≤ 0.10	≤ 0.10

Source: Breault 2014
* The FD3 pH 6.5 extraction waters used in the 6 hour and 4 day experiments each contained ≤ 0.10 mg/L TOC

Table 4.22
Mean TOC concentrations in samples from PET-lined pipe sections

Extraction Water	Sample Subset	Mean TOC Concentration (mg/L)	±SD (mg/L)	Number of Samples
Dechlorinated pH 8 Tap Water	Initial Extraction Water	3.34	N/A	1
	PET-Lined Pipe Section Samples	3.37	0.03	8
Chlorinated pH 8 Extraction Water	Initial Extraction Water	0.15	N/A	1
	PET-Lined Pipe Section Samples	0.30	0.08	6
pH 6.5 Extraction Water	Initial Extraction Water	≤ 0.10	0.01	2
	PET-Lined Pipe Section Samples	≤ 0.10	0.02	12

Source: Breault 2014

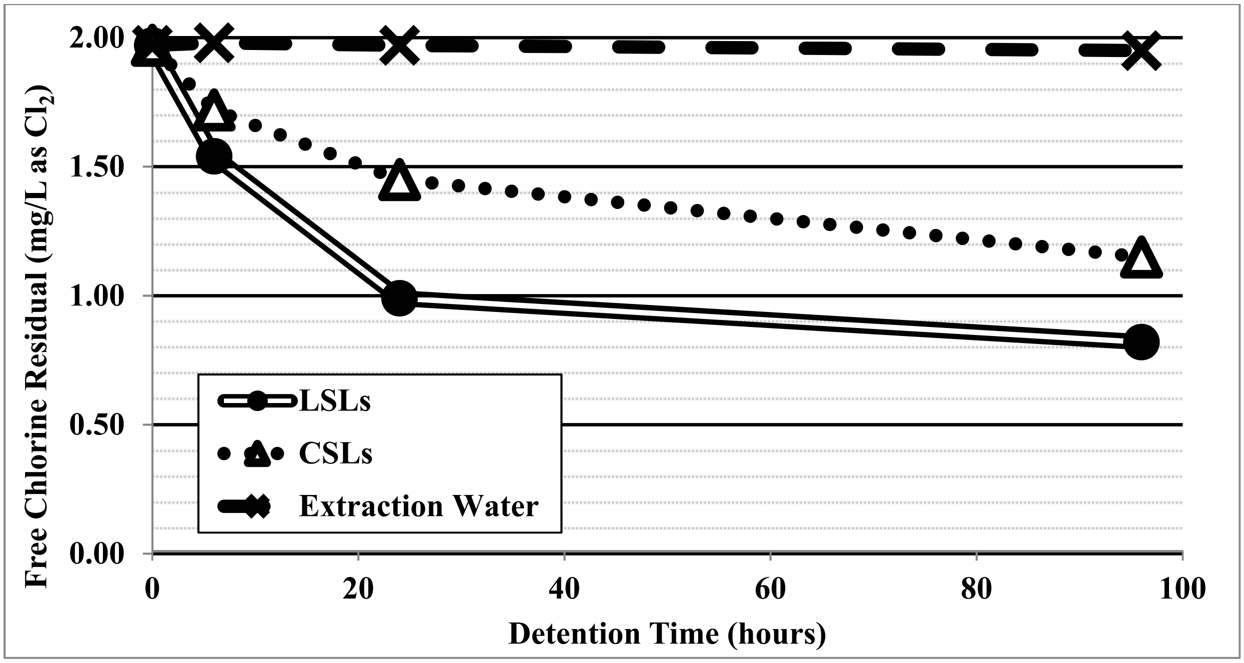


Source: Breault 2014.
Note: Error bars represent SD.

Figure 4.11 TOC in extraction waters and in samples from PET-lined pipe sections

Residual Chlorine

The residual free chlorine concentrations found in PET-lined LSL and CSL pipe sections extracted with chlorinated pH 8 extraction water are shown in Figure 4.12 as a function of holding time. On average, the residual free chlorine concentration dropped only about 1 mg/L, or half of the initial concentration, after 96 hours.

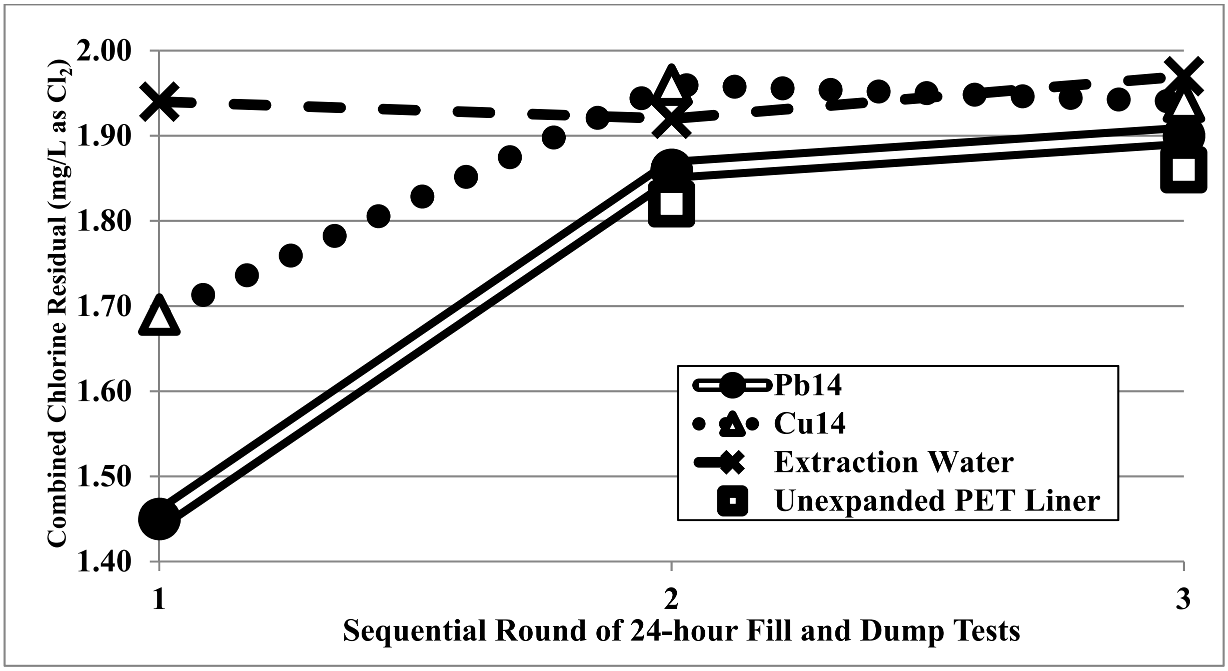


Source: Breault 2014.

Note: The pipe sections were extracted with chlorinated pH 8.0 extraction water having an initial free chlorine concentration of 1.97 mg/L as Cl_2.

Figure 4.12 Free chlorine versus time in samples from PET-lined pipe sections

To further evaluate the chlorine demand associated with PET liners, a series of three fill-and-dump tests was performed on two PET-lined pipe sections used in FD3 (one LSL and one CSL, Pb14 and Cu 14, respectively). Each test involved filling the pipe sections with chlorinated pH 8 extraction water having an initial free chlorine concentration of 2 mg/L, holding them for 24 h, then dumping out the extraction water and analyzing it for free chlorine. During the second and third tests, a previously unused and unexpanded piece of PET liner was also tested in similar fashion. As shown in Figure 4.13, the free chlorine demand decreased with each exposure and averaged about 0.1 mg/L (or 5% of the available concentration) in the third and final 24-h test.



Source: Breault 2014.
Note: The pipe sections were extracted with chlorinated pH 8.0 extraction water having an initial free chlorine concentration of approximately 2.0 mg/L as Cl_2.

Figure 4.13 Free chlorine residuals in PET-lined pipe sections, a PET liner, and extraction water after sequential 24-hour fill-and-dump tests

PET liners are not expected to exert a significant chlorine demand, as was the case for the results presented in Figure 4.13. The small chlorine demand associated with the PET liners during FD3 may have been associated with substances adsorbed onto the liner as it was expanded or later, as it was flushed with tap water. The chlorine demand exerted by the PET liners in this study was much lower than that observed in the control pipe sections and, in general, one would expect a PET lining to significantly reduce the chlorine demand in any service line whether the demand is associated with oxidation of lead or copper, oxidation of other substances (organic or inorganic) present in deposits inside the pipe, or biofilm. Thus, higher residual chlorine concentrations are expected to be present in service lines lined with PET. As discussed above in regard to epoxy coatings, this may have secondary impacts on DBP formation and biofilm growths, not only in the service lines themselves but also in subsequent piping and plumbing fixtures. Further investigation and evaluation of such impacts was beyond the scope of this study.

Phthalate Esters and Phthalic Acids (PAs)

No phthalate esters or phthalic acids were detected in any of the FD3 extraction waters, as shown in Tables 4.23 and 4.24. To investigate if leaching of these compounds from the PET liner could be induced under more extreme conditions, pieces of the liner were extracted with a 50:50 mixture of hexane and chloroform, with acetonitrile, and with a 10:90 mixture of methanol and water (10:90). These extractions also yielded no detection of phthalate esters or phthalic acids. The lack of leaching is likely attributable to the purity of the PET used in the liners. Products made from virgin PET leach very few phthalates, but products made with recycled PET have been found to leach phthalates (Safa and Bourelle 1999, Nerin et al. 2003, Sax 2010). The PET liners used in this study were made from virgin PET.

Table 4.23
Phthalate esters in samples from PET-lined pipe sections in FD3

Extraction Water and Holding Time	BBP, µg/L		DEHP, µg/L		DEP, µg/L		DETP, µg/L		DMIP, µg/L		DMP, µg/L		DMTP, µg/L	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Dechlorinated Tap Water, pH 8	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
Control (unlined) – 6 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h (A)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h (B)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
24 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
4 d	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
Chlorinated pH 8 Extraction Water	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
24 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
4 d	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
Low-pH Extraction Water, pH 6.5	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
Control (unlined, 6 h dechlorinated tap water)														
6 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h, then 4 d	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h dechlorinated tap water														
6 h (A)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h (B)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h, then 4 d (A)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h, then 4 d (B)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h chlorinated pH 8 reagent water														
6 h	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1
6 h, then 4 d	≤ 10	≤ 10	≤ 10	≤ 10	≤ 25	≤ 25	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1	≤ 1

Source: Lane 2015

Table 4.24
Phthalate esters and phthalic acids in samples from FD3

Extraction Water and Holding Time	DNBP, µg/L		DNOP, µg/L		DEHA, µg/L		PA, µg/L		IPA, µg/L		TPA, µg/L	
	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs	LSLs	CSLs
Dechlorinated Tap Water, pH 8	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
Control (unlined) – 6 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
6 h (A)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
6 h (B)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
24 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
4 d	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 4	≤ 4	≤ 2	≤ 2	≤ 3	≤ 3
Chlorinated pH 8 Extraction Water	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
24 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
4 d	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
Low-pH Extraction Water, pH 6.5	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
Control (unlined, 6 h dechlorinated tap water)												
6 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h, then 4 d	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h dechlorinated tap water												
6 h (A)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h (B)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h, then 4 d (A)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h, then 4 d (B)	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h chlorinated pH 8 reagent water												
6 h	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7
6 h, then 4 d	≤ 1	≤ 1	≤ 10	≤ 10	≤ 10	≤ 10	≤ 1	≤ 1	≤ 0.5	≤ 0.5	≤ 0.7	≤ 0.7

Source: Lane 2015

HYDROLYSIS OF BISPHENOL DIGLYCIDYL ETHERS (BDGES) AND BPA

An important question regarding constituents that might conceivably leach from epoxy coatings is whether they are able to react with water (i.e., hydrolyze) or with chlorine (discussed in the next section of this report) under conditions representative of those encountered in water service lines. If so, such compounds might not be detected, even if initially present, and any byproducts formed might need to first be identified and then evaluated for potential health or aesthetic impacts on drinking water. For these reasons, experiments were conducted to study hydrolysis and chlorination of BADGE, BFDGE, and BPA, all common base constituents of epoxies. Many contain either BADGE or BFDGE, and those certified for use with potable water must be BPA-free as defined in practice in the U.S. and Canada by NSF 61 compliance. No BFDGE or BPA was found in the epoxy used in this study.

Hydrolysis of BADGE was studied as a function of pH (2–12) and temperature (15–40 °C). Hydrolysis of BFDGE was studied as a function of pH (2-12) at a single temperature (25 °C) for comparison with the BADGE results. BPA hydrolysis was studied only at 25 and 40 °C, but not at lower temperatures, since no hydrolysis or decay of BPA was observed at higher temperatures. Each experiment was designed using a pseudo-first-order kinetic approach, with all conditions held constant except the concentration of the analyte of interest, such that its decay could be expressed in terms of a first-order decay constant. Once the hydrolysis rates were known for a broad range of pH and temperature values, the acid, neutral, and base hydrolysis constants were determined for each temperature, using non-linear, least-squares regression. An Arrhenius approach was used to model the effect of temperature.

The results and model development have been previously described in detail by Lane (2015) and Lane et al. (2015a) and are summarized here for the convenience of the reader. The experimentally determined acid, neutral, and base hydrolysis rate constants are listed in Table 4.25, and the data and model results for BADGE and BFDGE hydrolysis are summarized in Figures 4.14 and 4.15. In the BADGE hydrolysis model, BADGE hydrolysis is expressed as a function of the acid, neutral and base hydrolysis constants as follows (Lane 2015, Lane et al. 2015a):

$$\frac{d[\mathrm{BADGE}]}{dt} = -k_A[\mathrm{BADGE}][\mathrm{H^+}] - k_N[\mathrm{BADGE}] - k_B[\mathrm{BADGE}][\mathrm{OH^-}] \quad (3.1)$$

where k_A = acid hydrolysis rate constant ($M^{-1}s^{-1}$)
k_N = neutral hydrolysis rate constant (s^{-1})
k_B = basic hydrolysis rate constant ($M^{-1}s^{-1}$)
t = reaction time

The three hydrolysis rate constants in Equation 3.1 can be incorporated into a single pseudo-first-order rate constant:

$$\mathrm{k}'_{\mathrm{Hyd}} = k_A[\mathrm{H^+}] + k_N + k_B[\mathrm{OH^-}] \quad (3.2)$$

where $\mathrm{k}'_{\mathrm{Hyd}}$ = pseudo-first-order hydrolysis rate constant (s^{-1}).

Rearranging, substituting Equation 3.2 into Equation 3.1, and integrating yields the following equation:

$$\ln\left(\frac{[\mathrm{BADGE}]}{[\mathrm{BADGE}]_0}\right) = -k'_{\mathrm{Hyd}}t \quad (3.3)$$

For a given pH, k'_{Hyd} can be calculated as a function of temperature using Equation 3.2 in concert with the following relationships:

$$k_A = e^{(-8{,}547 \cdot (1/T(K)) + 23.16)} \qquad (3.4)$$

$$k_N = e^{(-7{,}547 \cdot (1/T(K)) + 12.05)} \qquad (3.5)$$

$$k_B = e^{(-10{,}358 \cdot (1/T(K)) + 27.05)} \qquad (3.6)$$

$$[OH^-] = K_w / (10^{-pH}) \qquad (3.7)$$

$$\log(K_W) = -\left(\frac{4470.99}{T(K)}\right) + 6.0875 - (0.01706 \times T(K)) \qquad (3.8)$$

where K = degrees Kelvin.

The same approach was used to develop and experimentally calibrate a model for hydrolysis of BFDGE at 25 °C. This effort was complicated by the fact that BFDGE was only commercially available as an isomeric mix (i.e., *o,o'*-BFDGE, *o,p'*-BFDGE, *p,p'*-BFDGE). Therefore, pseudo-first-order rates constants for BFDGE were determined for each isomer as a function of pH, then combined to develop a model based on the overall rate of BFDGE hydrolysis.

As shown in Figure 4.14, experimentally measured rates of BADGE and BFDGE hydrolysis agreed well with modeled rates. Thus, the BADGE and BFDGE hydrolysis models can be used to estimate the hydrolytic degradation and/or stability of BADGE in water systems, once leached, and the BADGE and BFDGE concentrations remaining in the water over time. This information will facilitate assessments, by others, of human exposure to BADGE, BFDGE, and BADGE hydrolysis products under varied conditions.

The half-life of BADGE or BFDGE can be calculated using Equation 3.9.

$$\text{Half life (days)} = \frac{-\ln(0.5)}{k'_{\mathrm{Hyd}}} \qquad (3.9)$$

Modeled half-lives of BADGE and BFDGE are illustrated in Figure 4.15. The half-lives of BADGE at pH 7 and 15, 25, 35, and 40 °C were found to be 11, 4.6, 2.0, and 1.4 days, respectively. The half-life of BFDGE was 5 days at pH 7 and 25 °C. As illustrated in Figure 4.14, the model appears to effectively match the experimental results. The hydrolysis rates of BADGE and BFDGE were nearly identical, as might be expected based on their structural similarity (Figure 2.4).

As described in more detail by Lane (2015) and Lane et al. (2015a), the two identified BADGE hydrolysis products were BADGE-H_2O and BADGE-$2H_2O$. BADGE-H_2O hydrolyzed to BADGE-$2H_2O$, with BADGE-$2H_2O$ being the final end product under the conditions studied. The molar sum of BADGE, BADGE-H_2O and BADGE-$2H_2O$ remained relatively constant, indicating that no other major byproducts were being formed.

As reported by Lane (2015) and Lane et al. (2015a), BPA did not hydrolyze or decay at reaction times up to 30 days at temperatures of 25 and 40 °C and over a pH range of 2–12. This was expected, as BPA does not have readily hydrolysable groups as do BADGE and BFDGE, which contain hydrolysable epoxide functional groups. Similar results would be expected for other bisphenols, including BFP, but this was not experimentally verified as part of this project.

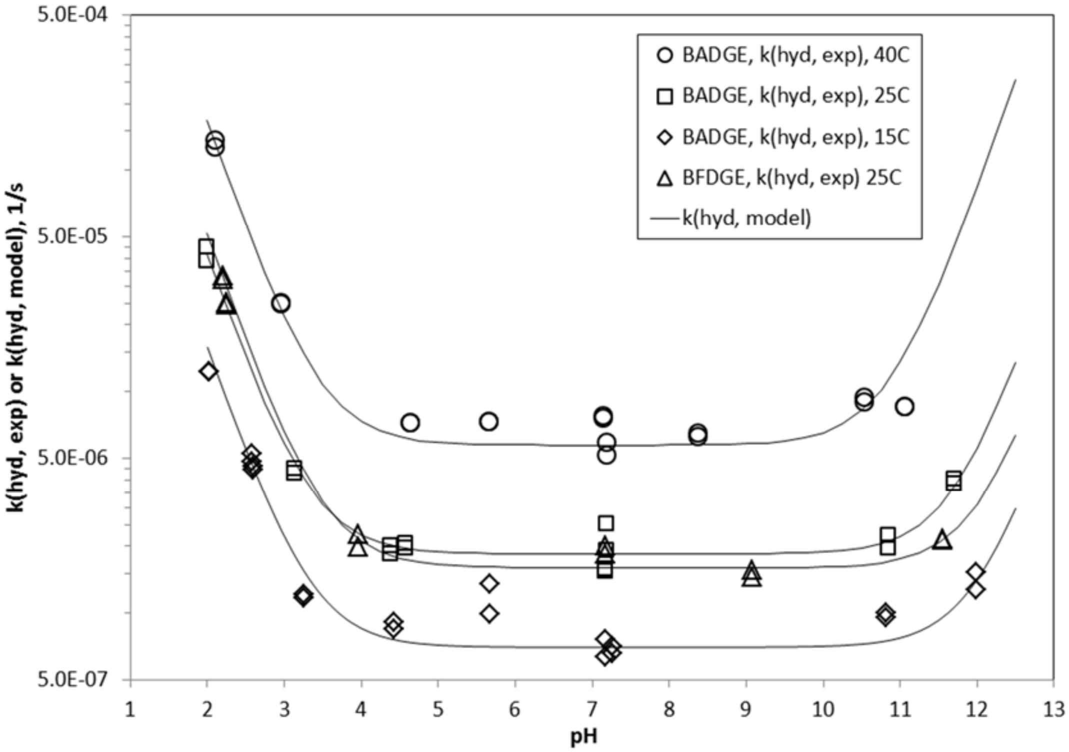
Table 4.25

Experimentally determined rate constants for hydrolysis of BADGE and BFDGE

Analyte	Temperature	k_A ($s^{-1}M^{-1}$)	k_N (s^{-1})	k_B ($s^{-1}M^{-1}$)
BADGE	15 °C	1.52E-03	7.02E-07	1.57E-04
BADGE	25 °C	3.99E-03	1.85E-06	3.64E-04
BADGE	40 °C	1.61E-02	5.73E-06	2.67E-03
BFDGE*	25 °C	5.03E-03	1.60E-06	1.47E-04

Source: Reprinted from *Water Research*, vol. 72, Lane, R.F., Adams, C.D., Randtke, S.J., and Carter, Jr., R.E., Bisphenol Diglycidyl Ethers and Bisphenol A and Their Hydrolysis in Drinking Water, Copyright 2015, with permission from Elsevier.

* Rate constants shown for BFDGE are averages for three isomers.



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Note: BADGE was modeled at 15–40 °C, and BFGDE at 25 °C, for comparison.

Figure 4.14 Plot comparing the experimental kinetic rates (data points) and model results (black lines) for hydrolysis of BADGE and BFDGE

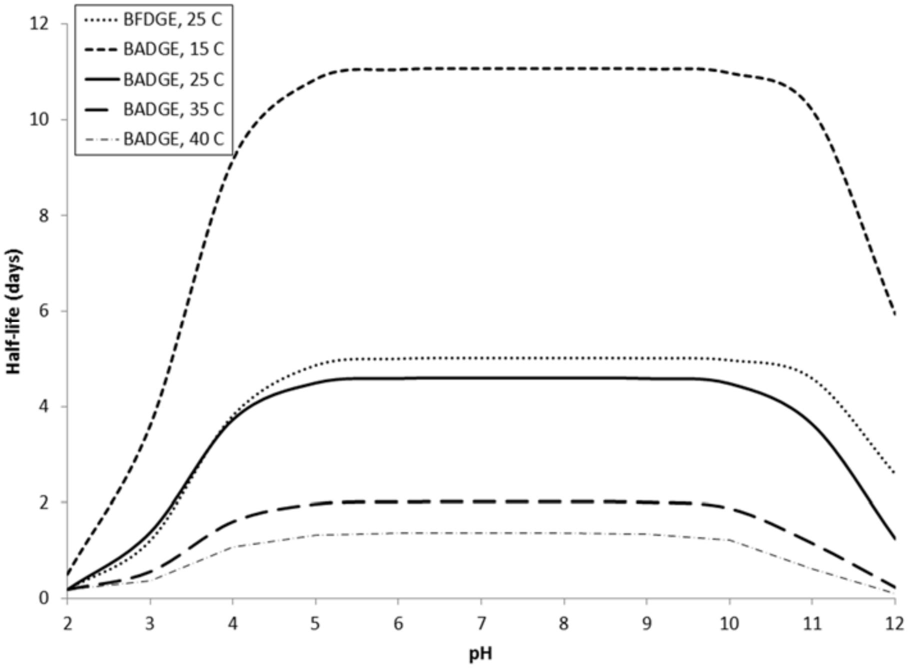

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Figure 4.15 Modeled half-lives of BADGE and BFDGE at 15, 25, 35, and 40 °C in phosphate-buffered waters

CHLORINATION OF BPA, BPF, AND BADGE

As a companion study to the investigation of BDGEs and BPA described in the previous section of this report, experiments were conducted to examine the reaction kinetics of BPA, BPF, and BADGE with free and combined chlorine and to identify and quantity byproducts thereby formed. The methods used, model development, and results were described in detail by Lane (2015) and Lane et al. (2015b), and summarized here for the convenience of the reader.

Reaction Kinetics

Using a pseudo first-order kinetic approach similar to the one used for the hydrolysis experiments, all conditions were kept constant except for the concentration of the analyte of interest, such that its decay rate could be determined, by linear regression, under a fixed set of conditions of pH and temperature, which also controlled both bisphenol and chlorine speciation. Unlike BADGE, BPA and BPF are diprotic acids, so each is present as a mixture of three species depending on pH and temperature. For example, for BPA:

$$\text{BPA} \leftrightarrow \text{BPA}^- + \text{H}^+ \qquad (\text{p}K_{a1,\text{BPA}} = 10.05\ (10\ °\text{C}),\ 9.78\ (25\ °\text{C})) \qquad (3.10)$$

$$\text{BPA}^- \leftrightarrow \text{BPA}^{2-} + \text{H}^+ \qquad (\text{p}K_{a2,\text{BPA}} = 10.81\ (10\ °\text{C}),\ 10.53\ (25\ °\text{C})) \qquad (3.11)$$

where $pK_{a1,BPA}$ and $pK_{a2,BPA}$ and the first and second acid dissociation constants of BPA.

Once the rate of reaction of the analyte of interest was determined under a range of pH and temperature values, a non-linear regression model was used to determine the rate of reaction of HOCl with each of the three BPA or BPF species present, assuming that the rate of reaction with OCl^- was negligible relative to the rate of reaction with HOCl. The amount of HOCl present under any condition was calculated from the total chlorine concentration, $[HOCl]_T$, based on the dissociation of HOCl as a function of pH and temperature. Since the rate of reaction of HOCl with BPA or BPF can be acid catalyzed (Gallard et al. 2004), this was also incorporated into the model. In the model, the overall reaction of BPA with free chlorine is described as follows:

$$-d[BPA]_T / dt = [HOCl] \cdot (k_1 \cdot [BPA] \cdot [H^+] + k_2 \cdot [BPA] + k_3 \cdot [BPA^-] + k_4 \cdot [BPA^{2-}])$$

$$= [HOCl]_T \cdot [BPA]_T \cdot (\alpha_{HOCl} \cdot (k_1 \cdot \alpha_1 \cdot [H^+] + k_2 \cdot \alpha_2 + k_3 \cdot \alpha_3 + k_4 \cdot \alpha_4))$$

$$= [HOCl]_T \cdot [BPA]_T \cdot k_{eff} \qquad (3.12)$$

where:

α_1, α_2, α_3 and α_4 are the ionization fractions of the total concentration of BPA, $[BPA]_T$ in the acid catalyzed, neutral, mono-anionic and di-anionic forms at a given pH, respectively

k_1, k_2, k_3, and k_4 are the rates of reaction of HOCl with each of these forms, respectively

k_{eff} is the effective second-order rate constant, based on the total concentrations of HOCl and BPA at a given pH and temperature

Bisphenols (BPA and BPF) reacted with both free chlorine and monochloramine but BADGE did not react with either free chlorine or monochloramine under the conditions studied. The rate constants determined in this study for BPA and BPF at temperatures of 10 and 25 °C are listed in Table 4.26 along with those determined by Gallard et al. (2004) at 20 °C. The experimental results for BPA and BPF are compared with modelled values in Figures 4.16 and 4.17. In both cases, it can be seen that bisphenols reacted relatively rapidly with free chlorine at pH values around 3 and 9, and more slowly at pH values of approximately 6 and 12. Under all conditions relevant to water service lines, the half-life of BPA would be quite short (3 to 35 min.) in the presence of a free chlorine concentration of 1 mg/L as Cl_2, as shown in Figure 4.18.

BPA and BPF reacted much more slowly with monochloramine than with free chlorine, but still rapidly enough to be relevant to holding times in water distribution systems, including water service lines with overnight or longer stagnation times. Estimated half-lives for BPA and BPF under selected conditions in the presence of a monochloramine concentration of 3.5 mg/L as chlorine are listed in Table 4.27; they ranged from about 1 to 10 days under conditions commonly encountered in water service lines.

Byproduct Formation

Formation of chlorinated byproducts of BPA was also studied. The concentrations of mono-, di-, tri-, and tetrachloro BPA formed at pH 7.6 and 9.1, at temperatures of 10 and 25 °C are shown in Figure 4.19. At the higher temperature, BPA reacted more rapidly and formed byproducts more quickly; but sum of the BPA species declined more rapidly, indicating that other byproducts were also being formed, perhaps via ring cleavage. At pH 9.1 BPA reacted more rapidly than at pH 7.6. Figure 4.20 tracks the loss of BPA and the gradually increasing concentrations of four of its chlorinated byproducts over 2.5 hours, with an initial free chlorine concentration of 0.8 mg/L as Cl_2.

Relevance to Epoxy Coatings

The relevance of these results to epoxy coatings is that if BPA leaches out of a BPA-based epoxy coating, it will react relatively rapidly with free chlorine and more slowly with monochloramine to forms various byproducts, including chlorinated derivatives of BPA. The model developed as part of this project can be used to facilitate estimates of human exposure for health risk assessments, or estimates of the environmental fate of BPA and its byproducts. Modern epoxy coatings must effectively be BPA-free, as determined on the basis of leaching tests, and any traces of BPA that do leach into chlorinated drinking water can be expected to undergo oxidation. BADGE is unreactive with either free or combined chlorine but, as noted in the previous section of this report, it will promptly begin to hydrolyze.

Table 4.26
Rate and dissociation constants for BPA and BPF oxidation by free chlorine

	BPA			**BPF**	
Constants	**10 °C (this study)**	**25 °C (this study)**	**20 °C (Gallard)***	**10 °C (this study)**	**25 °C (this study)**
k_1	8.9E+05	2.0E+06	3.8E+04	4.2E+05	7.6E+05
k_2	1.9E+01	2.1E+01	1.8E+00	2.0E+01	2.0E+01
k_3	5.9E+04	6.0E+04	3.1E+04	3.9E+04	4.0E+04
k_4	2.0E+05	2.7E+05	6.6E+04	2.3E+05	2.4E+05
pK_{aHOCl}	7.69	7.54	7.54	7.69	7.54
pK_{a1BP}	10.05	9.78	9.60	10.05	9.78
pK_{a2BP}	10.81	10.53	10.20	10.81	10.53

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*Gallard et al. (2004)

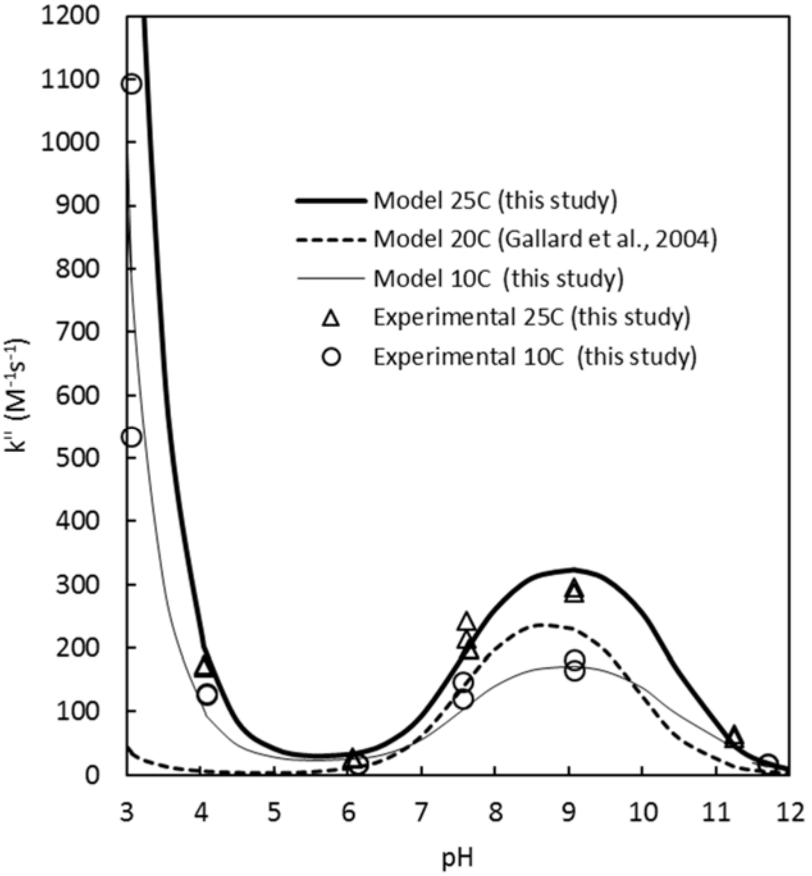

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Figure 4.16 Experimental, modeled, and previously published second-order rate constants for BPA oxidation by free chlorine

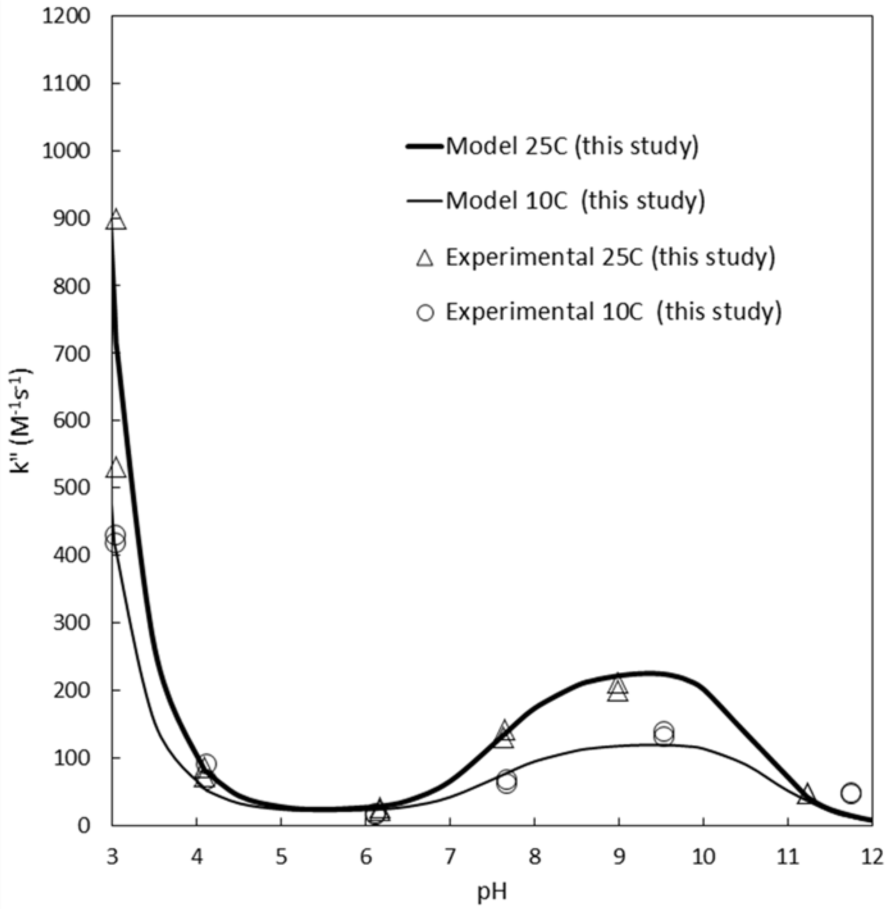

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Figure 4.17 Experimental and modeled second-order rate constants for oxidation of BPF with free chlorine

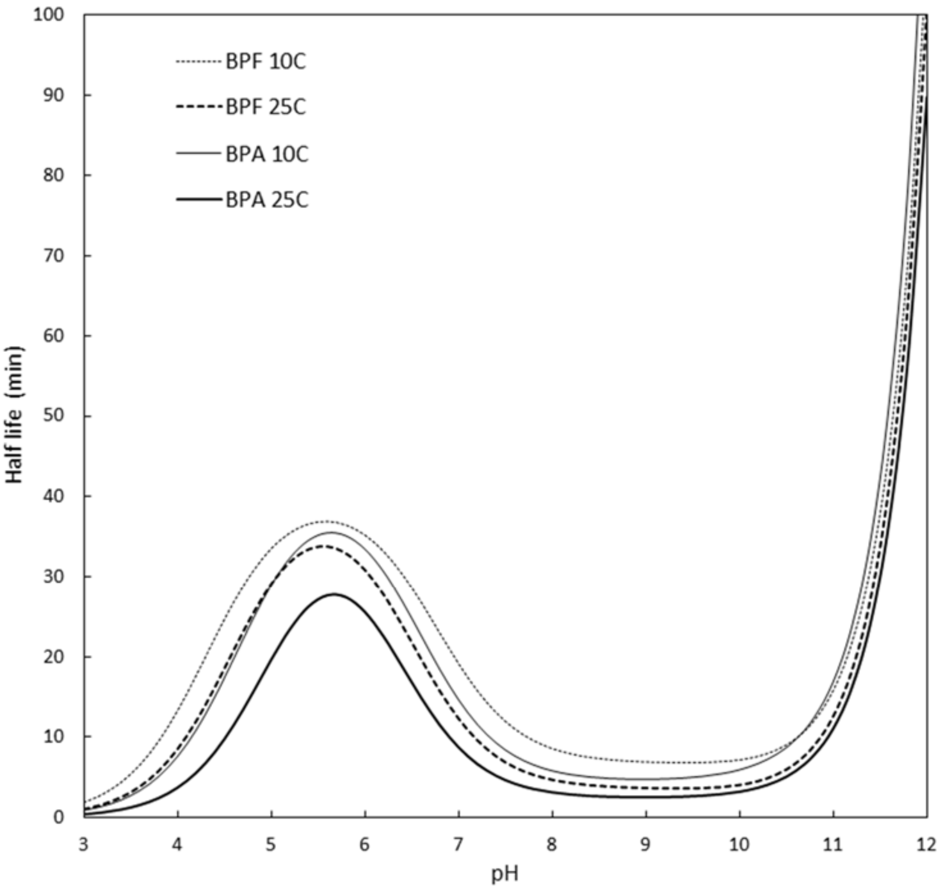

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Figure 4.18 Half-lives (min.) for BPA and BPF as a function of pH when exposed to 1 mg/L Cl_2 at 10 °C and 25 °C

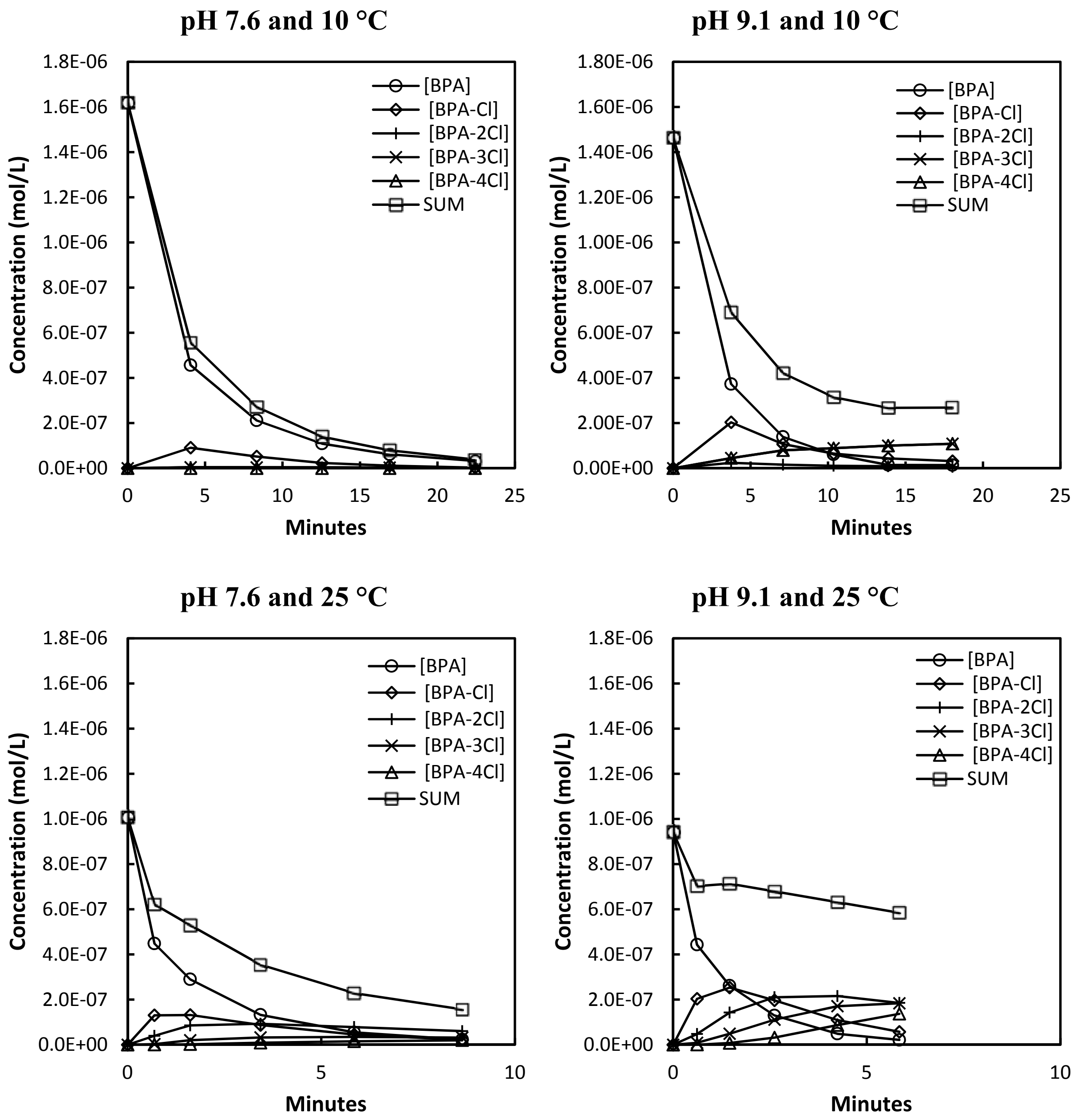
Table 4.27

Approximate half-lives for oxidation of BPA and BPF with monochloramine

	Approximate Half Life*			
	25 °C		**10 °C**	
	pH 7.6	**pH 8.9**	**pH 7.6**	**pH 8.9**
BPA	17 hours	1.8 days	2.6 days	8.8 days
BPF	19 hours	23 hours	2.0 days	1.5 days

Source: Lane 2015

* For a monochloramine concentration of 3.5 mg/L as Cl_2



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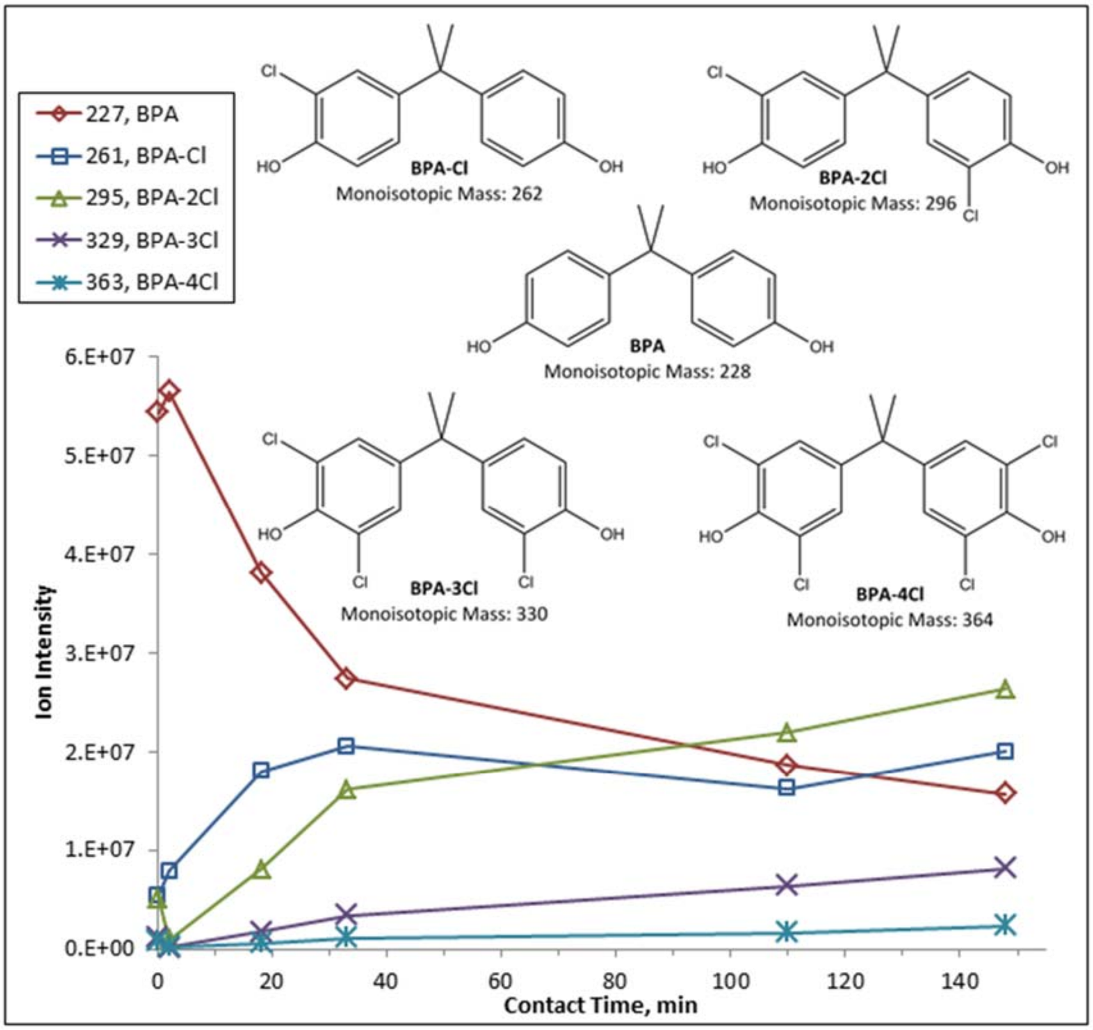
Note: The free chlorine concentration averaged 2.1 mg/L as Cl_2 at pH 7.6 and 2.4 mg/L as Cl_2 at pH 9.1. All experiments were run in duplicate, with averaged values shown.

Figure 4.19 BPA decay and formation of chlorinated by-products during oxidation of BPA with free chlorine at pH 7.6 and 9.1 at 10 °C and 25 °C

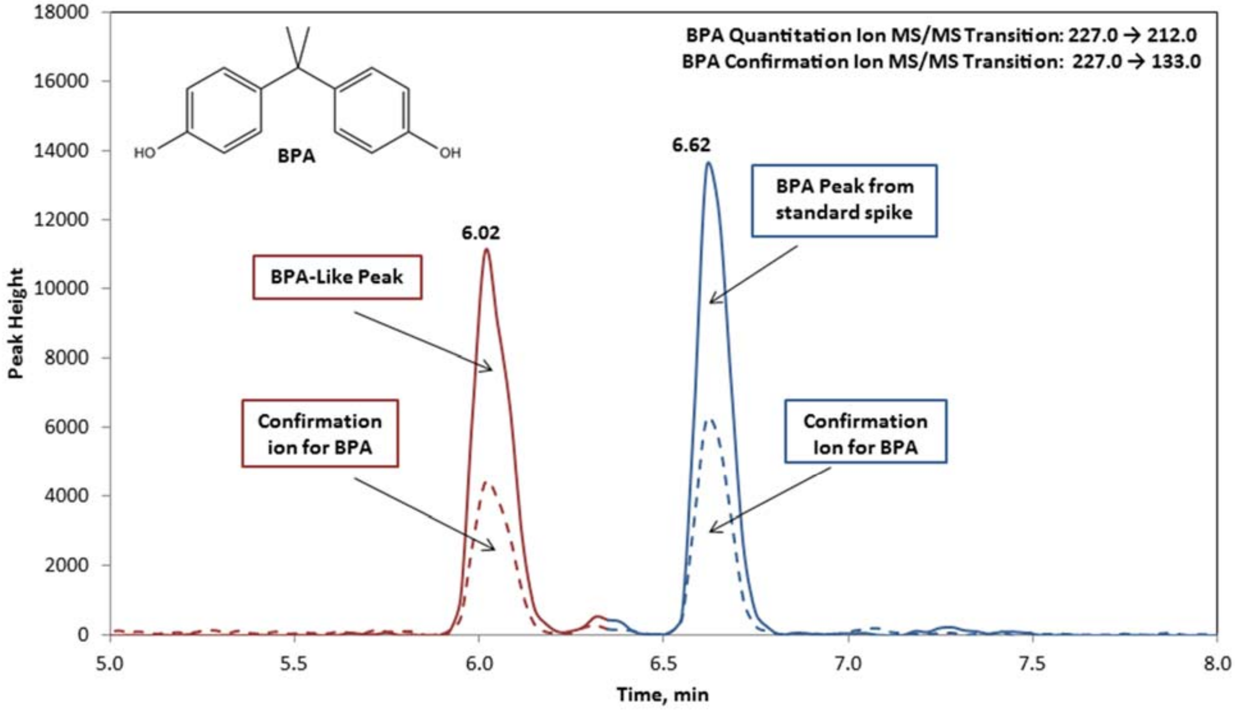


Source: Lane 2015.

Figure 4.20 MS ion scans tracking of BPA and chlorinated BPA by-products for an initial BPA concentration of 500 µg/L (2.2 µM) and an initial free chlorine concentration of 0.8 mg/L as Cl_2 (2.2µM)

IDENTIFICATION OF "BPA-LIKE" COMPOUNDS

When samples from the epoxy-coated pipe sections in FD1 were analyzed for bisphenols using LC/MS/MS, additional peaks were observed at retention times shorter than that of BPA (6.6 min.). A major peak at 6.0 min, attributed to BPA-like compound A, was found in 28 of 30 FD1 samples; a second, minor peak at 6.3 min, attributed to BPA-like compound B, was found in 21 of the 30 FD1 samples. The compounds responsible for these two peaks are referred to as "BPA-like" compounds because they produced MS MRM transitions identical to those of BPA (quantitation transition: 227.0 → 212.0 and confirmation transition: 227.0 → 133.0) and the same quantitation-to-confirmation-ion ratio, as illustrated in Figure 4.21. This result was reproduced for BPA-like compound A using a different instrument at KU's Mass Spectrometry & Analytical Proteomics Laboratory, demonstrating that it was not an artifact associated with a particular instrument. Matrix spikes were analyzed to confirm that the retention time of BPA had not shifted due to matrix effects associated with the composition of the extraction waters.



Source: Lane 2015.
Note: Sample DT-Pb-6H was collected from an epoxy-coated lead pipe filled with dechlorinated pH 8 tap water and held for 6 hours.

Figure 4.21 LC/MS/MS chromatogram from FD1 sample DT-Pb-6H spiked with a 40 µg/L BPA standard

When the samples from FD2 were analyzed, BPA-like compounds were observed in all of the samples. In addition to BPA-like compounds A and B, other minor peaks were observed having approximate elution times of 4.4, 5.7, 5.9, and 7.4 min. The shapes of these minor peaks were not as well defined as those of BPA-like compounds A and B, and their quantitation-to-confirmation-ion ratios did not always match those of BPA.

Observing additional peaks, especially those similar to BPA but having different retention times was considered by the research team to be potentially very significant. Analytical methods used to detect trace contaminants in environmental samples often look for them only within a specific time window; thus, it is possible that the compounds observed in the FD1 and FD2 samples had been, and continued to be, overlooked or misidentified in studies of BPA in various matrices, including drinking water, foods, and beverages in contact with epoxy coatings. Therefore, a concerted effort was made to identify and characterize these compounds. This effort, described in detail by Lane (2015), is summarized in the following paragraphs.

One possibility considered was that some of the BPA-like compounds were isomers of BPA. The most commonly manufactured and sold form of BPA is the para, para isomer, *p,p'*-BPA, but other, less common isomers exist. Standards for the isomers considered most likely to be present, *o,p'*-BPA and *o,o'*-BPA, were not commercially available, but experimental results for commercially available isomers combined with previously published results for similar compounds indicated that ortho ring substitution would cause later longer retention times, not earlier times. All of the BPA-like compounds observed had shorter retention times than BPA except one occasionally observed at 7.4 min. This compound's peak was usually small and irregularly shaped, and its confirmation-to-quantitation-ion ratio often failed to match that of BPA. On this basis, it was concluded that none of the observed BPA-like compounds was *o,p'*-BPA, *m,p'*-BPA, or *o,o'*-BPA.

Another possibility considered was that one of the BPA-like compounds could have been formed by methylation of the hydroxyl groups or phenol rings (ortho position) of BPF. This would also require BPF or methylated BPF to be present as an impurity in one of the starting materials. Adding two methyl groups to BPF would yield a compound having the same molecular weight as BPA and a similar MS fragmentation pattern. LC/MS/MS analysis of the methylated form of BPF (*p,p'*-BPF-2CH_3) showed that it had the same retention time as BPA. BPF with ortho methylated phenol rings was not commercially available but BPA with ortho methylated phenol rings (*p,p'*-BPA-2CH_3) was available and had a retention time essentially the same as BPA. Since methylation of the hydroxyl groups and phenol rings did not yield the earlier retention times in the range of those observed for the BPA-like compounds, these results indicated that none of the observed BPA-like compounds was a methylated form of BPF or BPA.

As reported in more detail by Lane (2015), additional efforts to identify and characterize the BPA-like compounds included: 1) GC/MS, LC/MS/MS, and TOF-MS analyses to more closely compare the fragmentation patterns of *p,p'*-BPA and BPA-like compound A, which were found to be identical to within the limits of the instruments employed; 2) experiments exploring the possibility that adduct (complex) formation, between BPA and components of the epoxy and the extraction waters was responsible for one or more BPA-like compounds, which identified only one possible adduct (BPA plus TETA) able to produce a small BPA-like peak that did not adequately explain the presence of any of the BPA-like peaks observed in FD1 and FD2; and 3) a study of the stability of BPA-like compound A and related analytes to look for clues that could explain the sequence in which compounds were forming and decaying, which demonstrated that BPA-like compound A was not degrading to BPA. The possibility of using nuclear magnetic resonance (NMR) to identify BPA-like compound A was explored, but this option was ruled out because NMR requires a large quantity of relatively pure material, which was not available.

The one possibility that was supported, at least in part, by the results of this study, is that one or more of the BPA-like peaks may be attributable to BADGE hydrolysis products. Ackerman et al. (2010) observed two earlier-eluting BPA-like compounds leaching from a can lining for infant formulas. One of these compounds was identified as BADGE-2H_2O, which was found to fragment in negative mode electrospray to generate ions that mimicked BPA MS/MS ions (Ackerman et al. 2011). Thus, BADGE hydrolysis products could explain some of the BPA-like peaks observed during FD1 and FD2. However, only two BADGE hydrolysis products were found in the samples, and in some samples, more than two BPA-like peaks were observed.

There were some indications that BPA-like compound A might actually be the result of an MS electrospray in-source conversion associated with the fragmentation of BADGE-2H2O as it passed through the MS/MS. If BPA-like compound A came from the electrospray fragmentation of BADGE-2H_2O, both compounds should be detected and there should be some correlation between the two observed concentrations. Of the 38 samples from FD2, 5 samples had BADGE-2H_2O with no observed BPA-like compound A, while 15 samples had BPA-like compound A with no observed BADGE-$2H_2O$. In the 18 samples with both BADGE-$2H_2O$ and BPA-like compound A, there was no correlation between the two concentrations.

Although the compounds responsible for the BPA-like peaks could not be specifically identified, it is clear from the results reported by Lane (2015) that they are most likely the result of MS electro-spray conversions, i.e., the peaks were produced as larger molecules (perhaps including BADGE hydrolysis products and other compounds of a similar nature) were broken (fragmented) into smaller pieces by the MS/MS as they passed through the instrument. The compounds associated with the peaks were not initially present in the samples, were not BPA, and if they resulted from electrospray conversions they were not formed through physical, chemical, or biological degradation processes that could potentially occur in a water distribution system.

REACTIVITY OF CHLORINE WITH TRIETHYLENETETRAMINE (TETA)

The reactivity of chlorine with triethylenetetramine (TETA) was studied to determine if the presence of TETA or similar compounds provided a reasonable explanation for the reactivity of chlorine with epoxy coatings observed in the fill-and-dump experiments. TETA is a major component of some epoxies, and is representative of the amines used in other amine-based epoxies. Primary amines are expected to readily react with chlorine, and TETA has a primary amine group on each of its terminal ends, as shown in Figure 3.11. BADGE had been found to be relatively unreactive with chlorine as noted earlier (see Chapter 4, Chlorination of BPA, BPF, and BADGE), leading the investigators to believe that the chlorine demand associated with the epoxy was most likely related to amines present in the hardener.

As shown in Figure 4.22, free chlorine reacted rapidly with TETA and the free chlorine residual was non-detectable after only two hours. Monochloramine (MCA) was also undetectable, as expected, but the total chlorine concentration dissipated much more gradually, presumably due to the formation of organic chloramines able to react with DPD and to be detected as chlorine.

As shown in Figure 4.22B, MCA decayed more slowly than free chlorine, but nevertheless decayed rather rapidly, decreasing from 3.67 mg/L as Cl_2 to an average of less than 0.5 mg/L as Cl_2 after 5 hours and below the method detection limit (MDL) after 24 hours. Only trace amounts of free chlorine were observed, which are attributable to “bleed through” from combined chlorine. Total chlorine decayed just slightly more slowly than MCA, again suggesting that organic chloramines were being formed. The ammonia-N results appeared to follow logical trends, but the concentrations were not consistent with those expected from simple mass balances. It was subsequently determined that TETA was interfering with the free ammonia-N analysis.

The chlorine-decay results shown in Figure 4.22 are consistent with those observed in FD1 and FD2 and associated follow-up tests reported above. That is, free chlorine decayed more rapidly than combined chlorine and both decayed to low or non-detectable concentrations within 24 hours. However, in the fill-and-dump experiments on epoxy-coated pipe sections described earlier in this report, only one form of chlorine was normally measured (free, total, or MCA), sometimes using spot tests on selected samples to verify the presence or absence of free or combined chlorine. Therefore, additional fill-and-dump experiments were conducted to more closely examine the chlorine demand associated with epoxy-coated LSL sections, this time measuring three forms of chlorine as well as free ammonia N.

The results of the additional chlorine demand tests conducted using epoxy-coated pipe sections are shown in Figure 4.23. Free chlorine decayed very rapidly, as observed in previous chlorine demand tests, averaging only about 0.34 mg/L as Cl_2 after 2 hours and falling below the MDL at 5.9 hours. MCA decayed more slowly than free chlorine, but was still largely dissipated within 24 hours. Although it is tempting to directly compare the decay rates of free and combined chlorine shown in Figure 4.23 with those shown in Figure 4.22, it must be recognized that the similarity of the decays rates is almost entirely coincidental, since the results shown in Figure 4.22 were undoubtedly heavily influenced by the concentration of TETA.

What does merit attention in comparing the results of Figure 4.23 to those in Figure 4.22 is that in both cases: 1) free chlorine decayed much more rapidly than MCA; and 2) total chlorine decayed less rapidly than free chlorine or MCA, although the difference was very small on average, and variable, for the epoxy-coated pipe sections (Figure 4.23). The latter result is as expected since, if organic chloramines formed as free or combined chlorine reacted with the epoxy coating, most of them would be expected to be associated with the solid phase (whether bound or trapped in the epoxy) and not with the aqueous phase from which the samples were drawn for analysis.

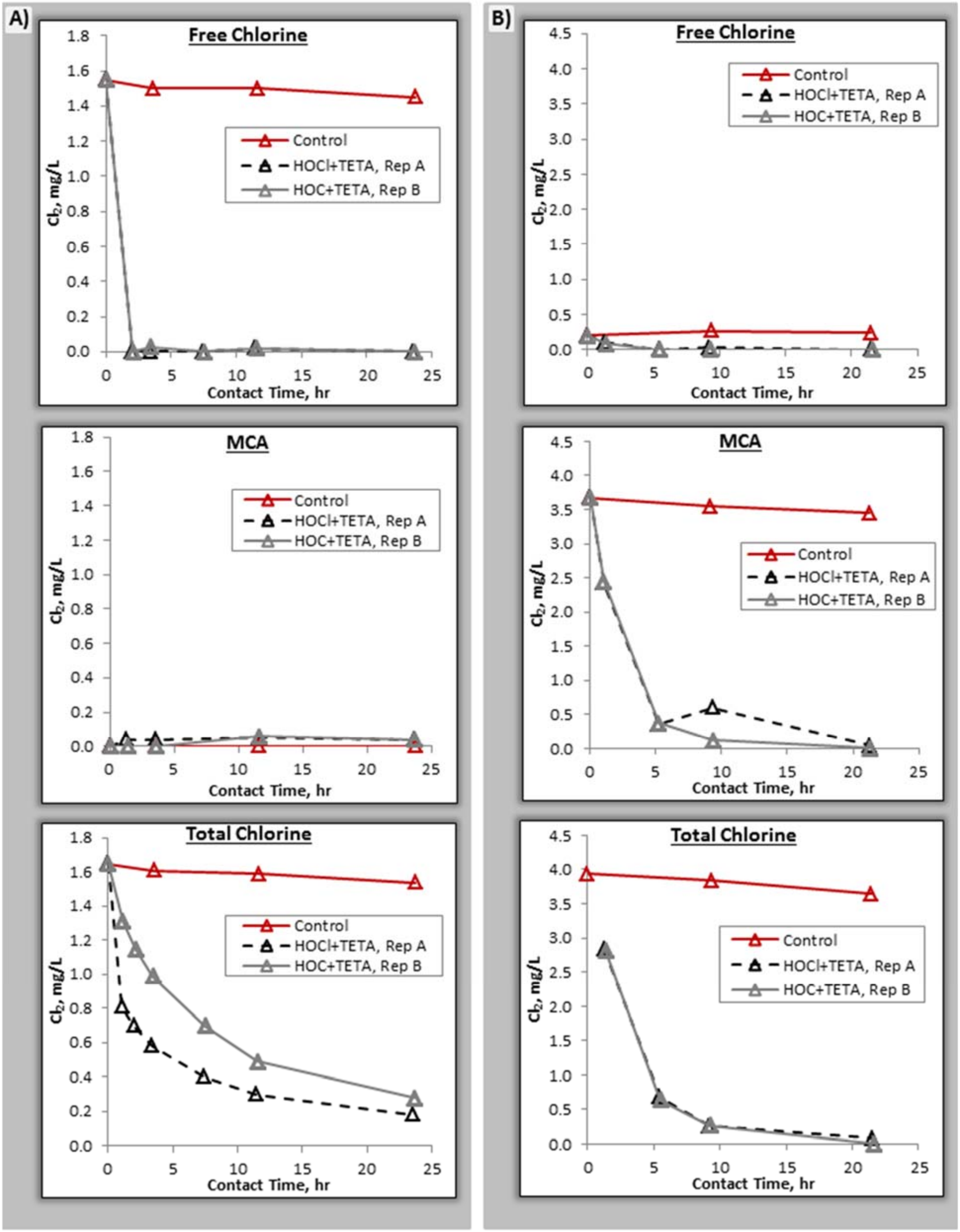


Figure 4.22 Concentrations of free chlorine, monochloramine (MCA), and total chlorine (all in mg/L as Cl_2) over time in solutions containing: A) TETA and free chlorine; and B) TETA and MCA

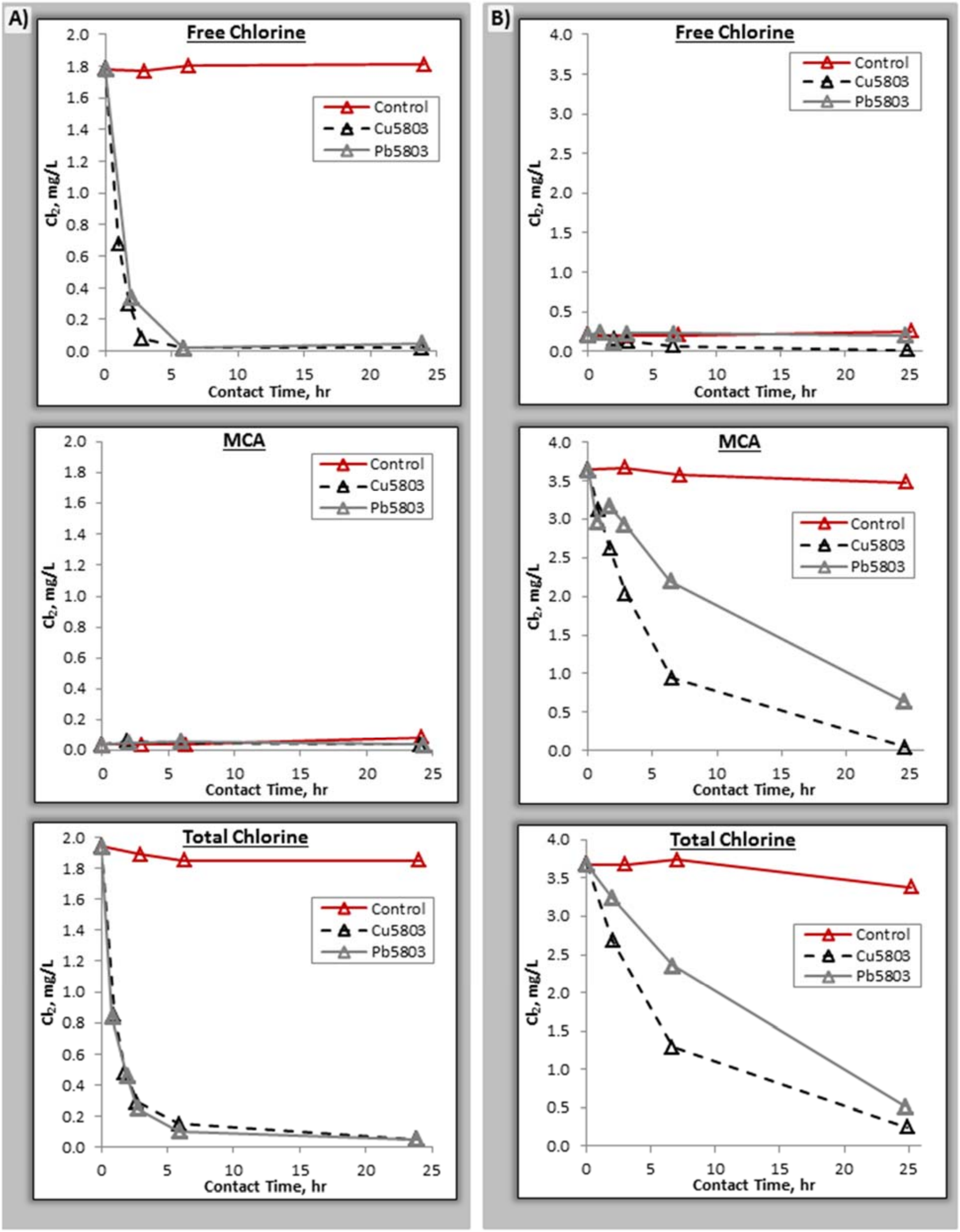


Figure 4.23 Concentrations of free chlorine, monochloramine (MCA), and total chlorine (all in mg/L as Cl_2) over time in epoxy-coated lead and copper pipe sections filled with extraction water initially containing: A) free chlorine; and B) monochloramine (MCA)

Based on the results shown in Figures 4.22 and 4.23, it appears entirely plausible that the chlorine demand associated with the BADGE-based epoxy coatings we studied is being exerted by TETA. However, the possibility that other ingredients in the epoxy are exerting a chlorine demand cannot be ruled out, nor can the possibility that some of the chlorine demand is associated with reactions with the underlying pipe surface. Epoxies are slightly porous and the uncoated LSL and copper service line (CSL) sections used as controls also exerted a very high chlorine demand. However, it is very unlikely that free or combined chlorine can diffuse quickly enough through a relatively thick layer of epoxy for this to have had a measurable effect on the results.

MCA and total chlorine decayed more slowly in the epoxy-coated LSL than in the epoxy-coated CSL (Figure 4.23), but no special significance should be attached to this since it was most likely related not to the chemical nature of underlying surface but to differences between the two separate batches of epoxy used to coat the LSL and CSL pipe sections and perhaps to different curing rates caused by the great difference in thermal properties between the two pipe materials (very thick lead versus very thin copper).

SOURCE OF ANTIMONY (Sb) IN THE LSL CONTROL SAMPLES

After noting the unexpectedly high Sb concentrations in the unlined LSL control section, the research team decided to look into this further, i.e., to attempt to determine whether the Sb was associated with the deposits in the LSL section or with the pipe itself, and whether the results were unique to this particular section. This effort involved both a quick online search and a set of additional laboratory tests. The laboratory test procedures are described in Chapter 3 and the results are presented below.

The online search revealed that antimonial lead, or 'hard lead,' a lead alloy containing 1-6% antimony, has historically been used for lead pipes (Total Materia 2001). The LSLs themselves are therefore a potential source for some or all of the antimony found in the control (unlined and uncoated) LSL sections in the initial fill-and-dump experiments. Solders containing antimony have been widely recommended for use as replacements for lead solder since use of lead solder was banned by the Clean Water Act Amendments of 1986. Tin-antimony solders usually contain 5% antimony, with other formulations (such as Sn-Ag-Cu-Sb) containing 0.5-2% antimony (Siewert et al. 2002). Thus, both LSLs and solders can potentially contribute to antimony concentrations found in tap water.

The laboratory tests consisted of four successive fill-and-dump experiments (or rounds) with LSL pipe sections. In the first two rounds of testing, LSL sections obtained from the City of Rochester (NY) Bureau of Water (2 replicates of LSLs from two different locations) and from Providence Water (two replicates from one LSL) were filled with pH 6.5 extraction water and held for 24 h. In the third and fourth rounds of testing, the same LSL sections were filled with water acidified with HNO_3 to a pH of about 3 and again held for 24 h. The results for the pH 6.5 and pH 3 extraction waters are shown in Tables 4.28 and 4.29, respectively. As noted in these tables, many of the samples collected from the Rochester pipe sections in the four rounds of this experiment were observed to contain particulate matter, primarily white solids with occasional darker particles. These solids were dissolved before analysis by the addition of 0.3 mL concentrated HNO_3 per 10 mL of sample.

As shown in Table 4.28, the samples from the first two rounds of testing (using pH 6.5 extraction water) all contained measurable concentrations of Sb, but the Sb concentrations found in the samples from the Providence LSLs (which ranged from 19.6 to 24.7 µg/L) were about an order of magnitude higher than those in the samples from the Rochester LSLs (which ranged from 0.69 to 3.31 µg/L). High (mg/L) levels of lead were found in all samples except one, with the levels significantly higher in the LSLs from Rochester. The pH of the extraction water increased considerably during the experiment, rising from ~6.5 to between 8.8 and 11.1, presumably because the deposits within the LSLs were primarily composed of carbonates or metal oxides. The pH values of control samples of the extraction water fell slightly, to about 6.0, for reasons that are unclear. The results obtained in the second round of testing were similar to those obtained in the first round, indicating that the first exposure had not dramatically changed the nature of the scale deposits.

As shown in Table 4.29, the Pb and Sb results for the samples obtained using the dilute nitric acid solution showed similar rank-order trends to those obtained using pH 6.5 extraction water, except that the Pb concentrations for the Providence section in the fourth-round test exceeded those for the pipe section 2 from Rochester. All of the samples extracted with the pH 3 water had higher Pb concentrations than those obtained using pH 6.5 extraction water, as would be expected; but all of the samples had lower Sb concentrations, suggesting that the readily extractable Sb had already been removed by the pH 6.5 extraction water and/or that the Pb and Sb were present in separate mineral phases having different solubilities in dilute nitric acid. It would be difficult to distinguish between these mechanisms without knowing more about the mineral composition and acid solubility of the deposits. The pH values once again increased, to values ranging from 8.64 to 9.94, surprisingly high, but not as high as the values observed using the pH 6.5 extraction water.

The average Pb concentrations found in the extraction waters from each pipe section, during each round of testing, are shown in Figure 4.24, with error bars used to indicate one standard deviation (SD) of the measured values. The Pb concentrations in the samples from the first two rounds of testing, using pH 6.5 extraction water, were relatively low (all less than 1 mg/L) for the LSL pipe sections from Providence; and all of the samples were relatively clear, i.e., they contained few or no visible particles. In contrast, the samples from the first two rounds of testing on the LSL pipe sections from Rochester had much higher Pb concentrations; but they also contained noticeable amounts of particles prior to sample acidification, such that much of the Pb in these samples was initially extracted in the form of particulate lead. In rounds 3 and 4, using dilute nitric acid as the extraction water, even higher lead concentrations were found in the samples from all three pipe sections, with the greatest increase found in the samples from the LSL section from Providence. Since fewer particles were observed in in the samples collected in rounds 3 and 4, much of this increase is presumably due to lead leaching into solution directly from the wall of the lead pipe or from deposits more resistant to dissolution.

The Sb concentrations in the extraction water samples followed a different pattern, as shown in Figure 4.25. High Sb concentrations were observed in the samples from the LSL pipe section from Providence during the first two rounds, using pH 6.5 extraction water. Lower concentrations were found in the later rounds (3 and 4), when using dilute nitric acid as the extraction solution. This pattern suggests that, in the Providence LSLs, a limited amount of Sb was initially present, likely in easily dissolved scale material. Both Rochester pipes yielded much lower Sb concentrations (<1 to 3 µg/L) throughout the extraction experiments. Especially noteworthy is that increases in dissolved lead were not accompanied by increases in Sb concentrations. Based on these results, the most likely source for antimony in these pipes is low levels of Sb in the source water that were trapped in scale deposits over time.

Scale materials removed from LSL sections directly adjacent to the sections used in the extraction tests were obtained and digested as described in Chapter 3; and filtered samples of the digestates were analyzed for Pb and Sb, yielding the results shown in Table 4.30. For both of the LSL sections from Rochester, acid-extractable Pb concentrations in the scale deposits obtained using a nylon brush were higher than those in scale deposits subsequently obtained using a round file, while acid-extractable Sb concentrations showed the opposite trend. (Only a filed sample was available for digestion from the Providence pipe, as brushing removed much less scale material from this pipe section.) While the acid-extractable Pb concentrations in the scale deposits were similar for the two LSL sections from Rochester, the acid-extractable Sb concentrations were much lower in pipe section R-1. The filed scale deposits from the Providence LSL contained more acid-extractable Pb than those from the Rochester LSLs, but more acid-extractable Sb than any of the scale deposits in the Rochester LSL sections. The higher acid-extractable Sb level in the deposits in the Providence LSL section is consistent with the higher Sb concentrations found in the extraction water samples from the Providence LSL sections (Tables 4.28 and 4.29). Despite the high lead concentrations in the scale, however, the Providence pipe sections released little Pb into the pH 6.5 extraction water; higher levels were not observed until dilute nitric acid was used as the extraction water. This suggests that the Sb and Pb in the scale deposits were present in separate phases, which is further reinforced by the varying Sb/Pb ratios among the different samples of scale deposits. Overall, the results suggest no consistent relationship between Pb and Sb in the scale materials, which indicates that Sb in these pipe sections likely comes not from the pipe itself, but from trapping of influent aqueous Sb in the scale material. The research team initially planned to analyze clean cuttings from inside the walls of the LSL pipe sections using the ablation technique described in Chapter 3; but the owner of the ICP-MS was unwilling to risk analyzing virtually pure lead for fear of contaminating it and reducing its sensitivity for its normal purpose of analyzing trace metals in aqueous samples. The samples have been stored for later analysis by alternative methods and possible publication in future journal article.

Table 4.28
Pb and Sb in pH 6.5 extraction water from unlined LSL pipe sections

LSL Section	Section No.	Final pH	Pb (mg/L)	Sb (µg/L)	Notes†
Round 1, pH 6.5 Extraction Water (initial pH = 6.49)					
Rochester Pipe Section 1	R1-1*	11.01	68.7	1.08	Opaque white particles present
	R1-2	10.84	59.3	1.22	Opaque white particles present
Rochester Pipe Section 2	R2-1	10.02	1.95	3.41	A few particles present
	R2-2	9.23	4.47	2.03	A few particles present
Providence Pipe Section 1	P1-1	8.80	0.56	24.6	
	P1-2	8.79	0.44	20.1	
pH 6.5 Extraction Water	Control	6.07	BDL§	BDL	
Round 2, pH 6.5 Extraction Water (initial pH = 6.54)					
Rochester Pipe Section 1	R1-1	11.07	39.1	0.71	A few white particles present
	R1-2	10.80	12.2	0.78	A few white particles present
Rochester Pipe Section 2	R2-1	10.47	1.99	1.97	A few particles present
	R2-2	9.96	1.49	2.77	A few particles present
Providence Pipe Section 1	P1-1	9.38	0.47	25.4	
	P1-2	9.26	BDL	21.7	
pH 6.5 Extraction Water	Control	6.01	BDL	BDL	

* R = Rochester, P = Providence, and #-# = section-replicate numbers

† Particles initially present in the samples dissolved when HNO_3 was added prior to sample analysis.

§ Below detection limit (0.21 mg/L for Pb; 0.03 µg/L for Sb)

Table 4.29
Pb and Sb in pH 3 extraction water from unlined LSL pipe sections

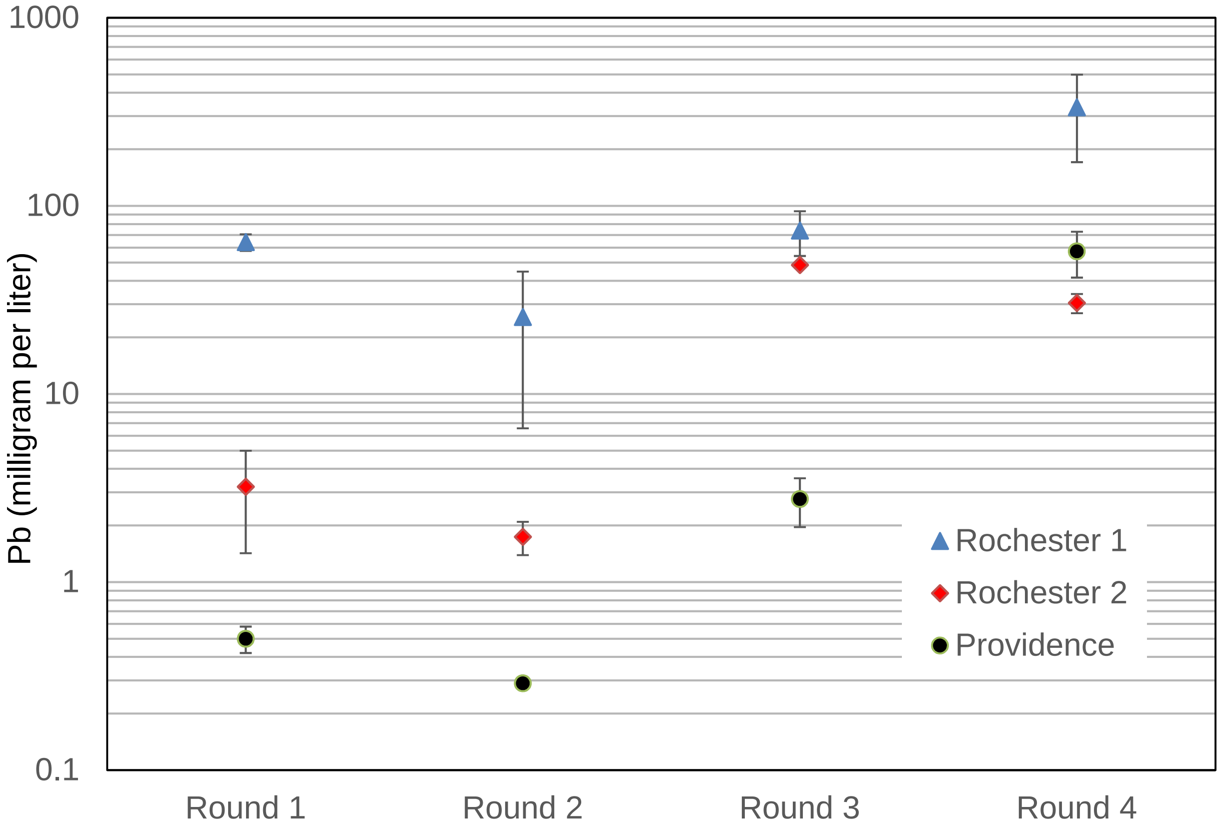
LSL Section	Section No.	Results			
		End pH	Lead (mg/L)	Antimony (µg/L)	Notes†
Round 3, HNO3 solution (initial pH = 2.92)					
Rochester Pipe Section 1	R1-1*	9.23	87.6	0.62	
	R1-2	9.62	59.9	0.72	
Rochester Pipe Section 2	R2-1	9.94	49.5	1.40	A few white particles present
	R2-2	9.76	47.4	1.65	A few white particles present
Providence Pipe Section 1	P1-1	8.84	2.19	6.91	
	P1-2	8.64	3.33	3.88	
HNO_3 Solution	Control	2.84	BDL§	BDL	
Round 4, HNO3 solution (initial pH = 2.83)					
Rochester Pipe Section 1	R1-1	9.23	450	BDL‡	Particles present
	R1-2	9.62	219	BDL‡	Particles present
Rochester Pipe Section 2	R2-1	9.94	27.9	0.94	
	R2-2	9.76	32.9	1.30	Particles present
Providence Pipe Section 1	P1-1	8.84	46.1	1.53	
	P1-2	8.64	68.3	1.71	
HNO_3 Solution	Control	2.88	BDL	BDL	

* R = Rochester, P = Providence, and #-# = section-replicate numbers

† Particles initially present in the samples dissolved when HNO_3 was added prior to sample analysis.

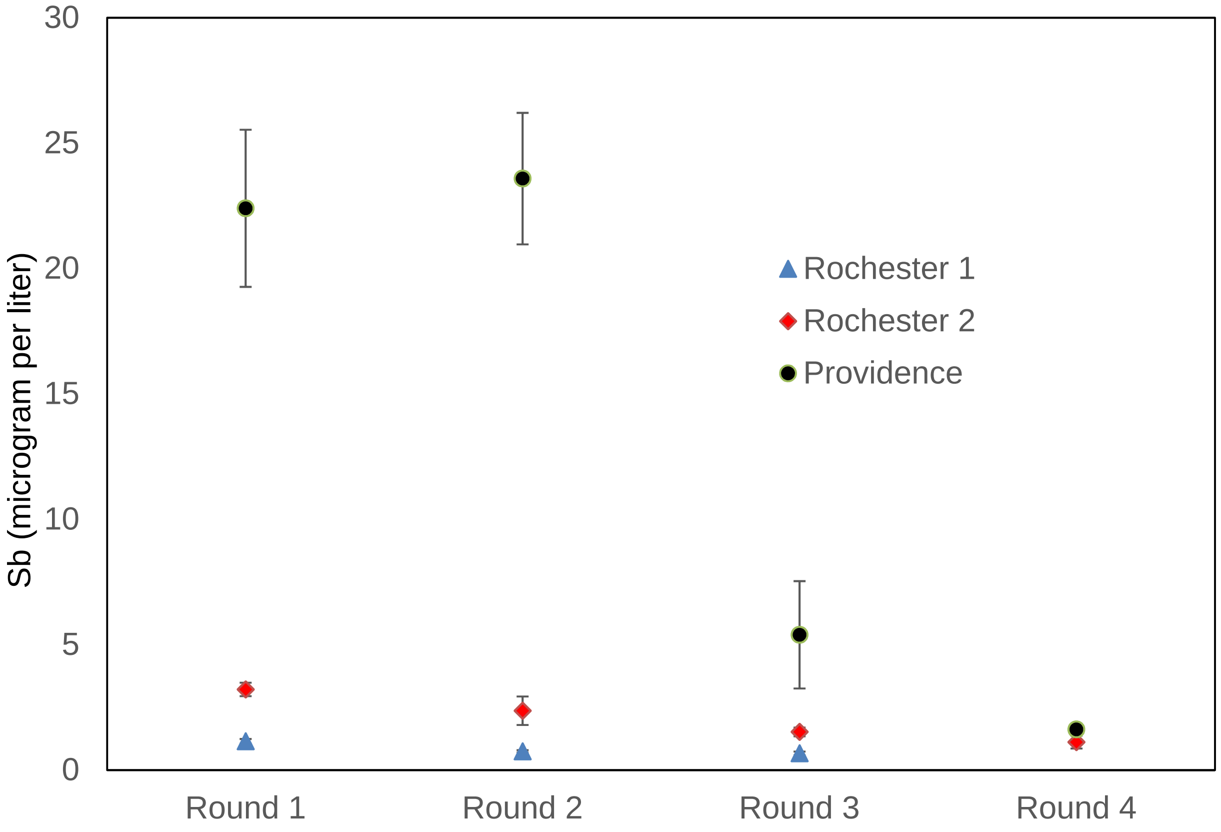
§ Below detection limit (0.21 mg/L for Pb; and 0.03 µg/L for Sb, except as noted)

‡ Detection limit = 0.6 µg/L; samples diluted 20-fold because of high Pb concentration



Note: Error bars indicate 1 SD.

Figure 4.24 Pb in extraction waters from unlined LSL pipe sections



Note: Error bars indicate 1 SD; Sb concentrations in the Rochester 1 samples were below detection limit in round 4, but see the note in Table 4.29.

Figure 4.25 Sb in extraction waters from unlined LSL pipe sections

Table 4.30
Acid-extractable Pb and Sb in LSL scales

Pipe Section	Scale Material*	Pb (mg/kg)	Sb (mg/kg)	Sb/Pb (%)
Rochester 1	Brushed	5708	5.15	0.09
Rochester 1	Filed	3410	11.9	0.35
Rochester 2	Brushed	7004	39.2	0.56
Rochester 2†	Filed	2598	55.7	2.14
Providence†	Filed	6678	~380‡	5.69

* Brushed solids were removed first, using a stiff nylon brush; filed solids were obtained using a round file on the deposits remaining after brushing. See Chapter 3 for details.

† Results shown are the average of duplicate samples.

‡ Sample concentration was five times the highest standard, so this value is only an estimate.

CHAPTER 5
PRACTICES AND EXPERIENCES IN THE UNITED STATES, CANADA, AND ELSEWHERE

UTILITY CASE STUDIES IN THE UNITED STATES AND CANADA

When evaluating new technologies, or when developing or revising a program to address a complex and important challenge, it is often helpful to consider the experiences of others – what they have tried, what worked well and what did not, what could be done differently or better in the future, and what aspects or program elements are most applicable to the local situation being addressed. In that vein, to give some food for thought to utilities interested in linings and coatings as alternatives to LSL replacement, the research team developed a series of brief case studies, presented below, that illustrate the thoughts and experiences of eight utilities in the U.S. and Canada. These were:

- City of Calgary, Alberta
- DC Water, Washington, D.C.
- Denver Water, Denver, Colorado
- EPCOR, Edmonton, Alberta
- Louisville Water Company, Louisville, Kentucky
- Madison Water Utility, Madison, Wisconsin
- Providence Water, Providence, Rhode Island
- City of Rochester Water Bureau, Rochester, New York

Two of these utilities (the City of Calgary and EPCOR in Edmonton) conducted trials with PET liners; one (DC Water) conducted a trial with epoxy coatings; and two (Louisville Water Company and Providence Water) conducted trials with both PET liners and epoxy coatings. Two others, Denver Water and the City of Rochester (NY) Water Bureau, are interested in the possible use of lining and coating technologies to help meet the challenges they face. Denver's situation is qualitatively similar to other large cities in the U.S. and Canada, though some face even greater challenges; the City of Chicago, IL, for example, has an estimated 400,000 LSLs and more congested urban areas to contend with (Stark and Putz 2015). Madison (WI) Water Utility did not consider lining or coating LSLs, but developed and successfully implemented a full LSL replacement program that eliminated virtually all of the LSLs in the city, and serves as an excellent model for other utilities to consider, whether or not they are considering including linings or coatings in their LSL program.

There are other good examples to consider, not included in the case studies below, of utilities that have implemented LSLR or broader programs to reduce tap water lead levels. For example, the American Water Works Association recently published a series of brief case studies in its monthly magazine, *Opflow*, featuring programs adopted by:

- The Lansing (MI) Board of Water and Light (Roost 2016), which established a goal of removing all of the city's LSLs within 10 years and has been relying on trenchless technologies in striving toward that goal – a difficult goal to be sure, but one easier to accomplish than in many cities because the utility owns the water services lines all the way from the main to the water meter inside the home

- Halifax Water (Krkosek 2016), which after many years of partial LSL replacements is now recommending full LSL replacements and has developed a proactive, integrated plan involving strong engagement with its customers
- Greater Cincinnati Water Works (Arnette et al. 2016), which is working to further to goal of full LSL replacement and researching ways to incentivize customer participation

Also exemplary are the LSL replacement programs of Saskatoon, SK (AWWA 2010, Francis 2016, City of Saskatoon 2016), which requires full LSL replacement when an LSL is worked on or develops a leak (otherwise, replacement remaining voluntarily); and Saint Paul (MN) Regional Water Services (Benson 2016), which is working to replace all utility-owned LSLs (seeing no sense in delaying the inevitable) and encouraging customers to do the same by offering to spread the cost out over a period of time by converting it into a property tax assessment.

City of Calgary, Alberta

According to Huston (2011a), the City of Calgary had only about 900 LSLs in service in 2011, in a water system with over 300,000 connections. However, to protect against freezing in a cold climate, water service lines are typically buried at least 8 feet deep, with many about 10 to 12 feet deep. Replacing an LSL that deep in the ground typically costs over $10,000, so the city had been evaluating lining and coating technologies as an alternative to replacement. One of the city's concerns was that customers were reluctant to replace private-side LSLs, viewing the cost as prohibitive, yet the city was finding lead levels above the MAC in some homes. This made linings and coatings appealing because they could potentially be used to line the entire service line, resulting in cost savings for both parties and improved health protection for the customers (Huston 2011b).

In 2010 the city hosted a field trial of the Neofit® system involving four homes with LSLs and high levels of lead in their first-draw tap-water samples (Huston 2010 and 2011a). The PET liners were successfully installed and subsequent sample collection and analysis demonstrated the effectiveness of the PET liners in reducing tap-water lead concentrations, as shown in Table 5.1. Three different sampling methods were used: 1) a 1-L first draw sample collected after >6 h stagnation; 2) four consecutive 1-L samples collected after 30 min. stagnation (profile sampling) and 3) a 1-L sample drawn after the line was flushed for 5 minutes.

Table 5.1
Lead levels before and after lining LSLs with PET in Calgary

Sample Parameter	Before Liner Installation	After Liner Installation	Lead Removal Effectiveness (%)
Avg., all first-draw samples (µg/L)	14.5	9.5*	35
Avg., all 1-4 L samples (µg/L)	13.4	2.7	80
Avg., after well flushed (µg/L)	9.5	1.1	88
First-draw sample ≥10 µg/L (no. of sites)	3	1	67
Avg., 1-4L ≥10 µg/L (no. of sites)	3	0	100
Well-flushed ≥10 µg/L (no. of sites)	1	0	100

Source: Adapted from Huston 2010 and 2011a
* At one address, the lead concentration in the first draw sample, most likely from the residence's internal plumbing, was quite high, raising the average.

One of the four liners failed soon after installation, but this was due to a delay in entering information into the city's GIS system, which should have included a note that this LSL had been lined all the way through the service valve (Huston 2010 and 2011b). When a crew arrived in response to a call regarding low-pressure, they were unable to operate the service valve and cut it out, thereby compromising the liner. The LSL had to be replaced, since the contractor who installed the liner was not local (Huston 2011b). At least two city employees were of the opinion that PET lining would be more feasible if a local contractor acquired the necessary installation equipment so it would be available when needed (Huston 2011a), not only to line LSLs but also for other purposes; and there is now a contractor (Pipe Shield) in Calgary licensed to install PET liners. In subsequent discussion after the project (Huston 2017), city personnel concluded that if a liner is placed through a service valve, rendering it inoperable, steps should be taken to ensure that either an internal shut-off valve is maintained by the resident or a service valve should be moved to or placed in the public right-of-way; otherwise, any emergency shut down for those residences would require the water main to be shut down, putting other customers out of water.

DC Water, Washington, D.C.

In 2001–2004, lead levels in Washington, D.C. tap water rose well above the action limit, and DC Water (then known as the DC Water and Sewer Authority, or DCWASA) took action to address the problem. The challenges faced by DC Water and the steps taken to meet them were highly publicized, and the details will not be repeated here. In summary, DC Water re-optimized corrosion control treatment, began feeding orthophosphate, and began replacing LSLs as required under the LCR for water utilities in a mandatory LSL replacement program. Since 2005, DC Water has maintained a 90th percentile lead level below 15 µg/L, and the levels have dropped over time (Hawkins 2017).

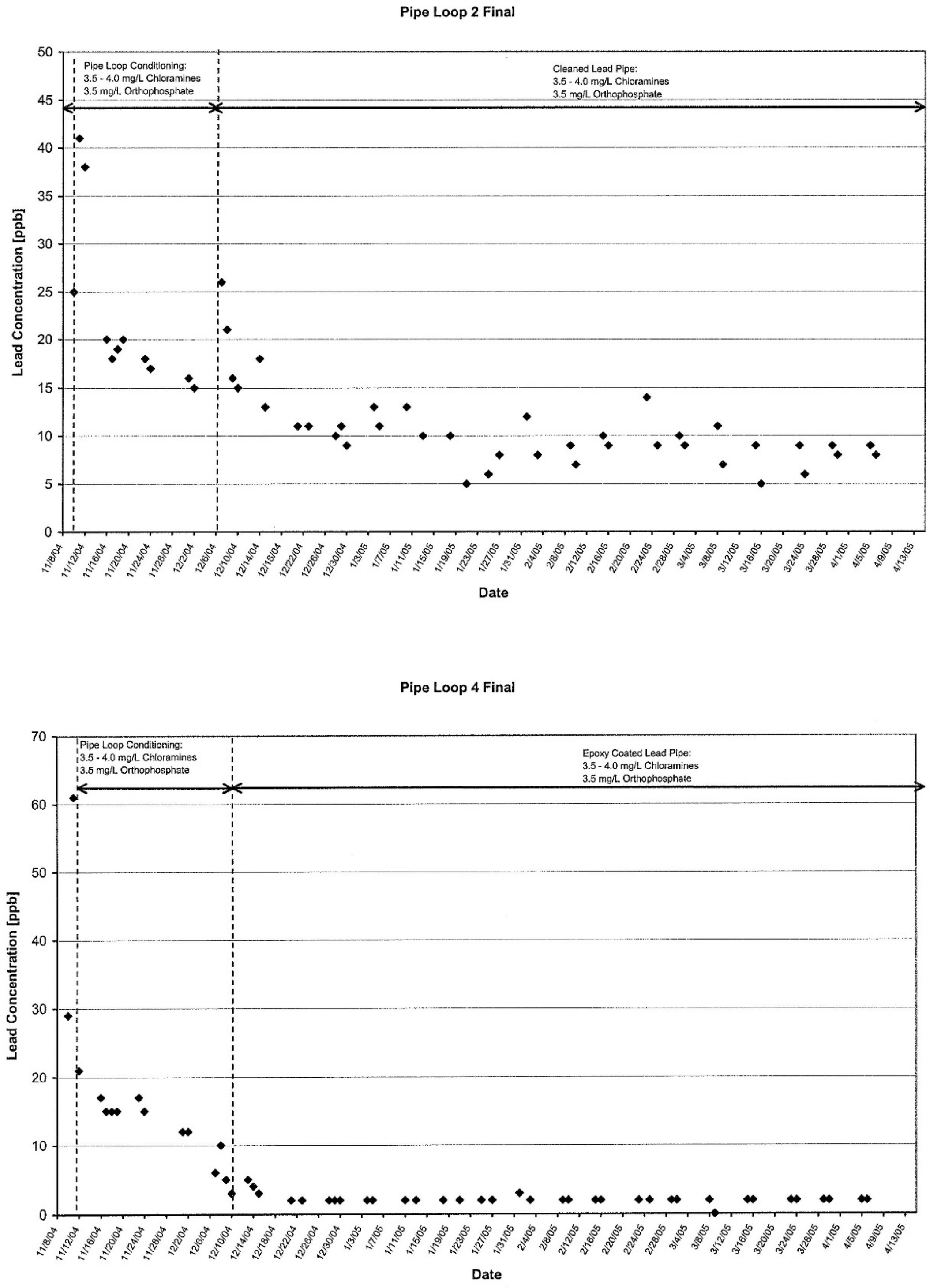
Today, DC Water replaces LSLs in public space during water main replacement projects, and encourages their customers to replace the portion in private property at the same time. Replacing both portions at the same time reduces the cost to the customer, though customers must pay their own share of the cost, since the utility is prohibited from using public funds to replace LSLs on private property (Giani 2011). According to Hawkins (2017), DC water also offers to its customers: assistance in identifying LSLs; advice on filtering their water if their household plumbing is not lead-free; free lead testing; and, for those who want to replace a privately-owned

LSL, cooperation in replacing the utility-owned portion at the same time. Schmelling (2016) described in detail the construction methods DC Water employs in replacing LSLs and how the utility communicates and cooperates with its customers for both full and partial LSLRs.

Recognizing the high cost of LSL replacement to both the utility and its customers, and the reluctance of homeowners to replace their LSLs, DC Water began exploring the possibility of lining or coating LSLs to reduce costs and increase homeowner buy-in (Giani 2011). As described by Wujek (2004), a demonstration test was conducted, in cooperation with American Pipe Lining, Inc., to examine the performance of two epoxy coatings, one having a 12 h curing time and one a 5 h curing time. Two piping configurations were set up in the lawn of DC Water's Fort Reno building. Each consisted of the following components, all coupled together to form a single conduit for coating: 6 or 7 sections of 3/4-in. nominal ID (~5/8 in. actual ID) LSLs harvested from the distribution system, each at least 3 ft. long; 2 or 3 10-ft lengths of 1-in. PVC pipe; and a meter setter. The pipes were cleaned by sandblasting, dried with hot air, then epoxy coated.

After the coating process was completed, three epoxy-coated LSL sections from one configuration were installed in test loops in an apparatus being used at Fort Reno to examine the impacts of corrosion control treatment on lead levels in water recirculating through sections of LSLs removed from the distribution system. One pipe section cleaned in preparation for coating, but not epoxy coated, was used as a control section. Each loop was flushed at 2 gpm several times each day, and a flow rate of 1.2 ft./sec was maintained for 16 h per day using a timer and a 100-L tank filled with test water. Samples were drawn from the tank for analysis of lead and other constituents of interest, and the tank was refilled daily with fresh test water.

Figure 5.1 shows the lead monitoring results for the first four months for the control section and one of the epoxy-coated sections, both of which were fed chloraminated water treated with orthophosphate. The effectiveness of corrosion control treatment in reducing lead levels below the action limit is evident for the control section, and the same treatment also proved effective in controlling lead levels in the full-scale distribution system. The epoxy coating was much more effective, reducing the lead concentration to below the detection limit (2 μg/L) in all but four samples. Figure 5.1 shows only about four months of data following epoxy coating, but the lead levels remained non-detectable for the next 7 years (Giani 2011).



Source: Courtesy of DC Water.

Figure 5.1 Lead monitoring data for a cleaned (control) LSL section in DC Water's pipe-loop test apparatus (top) and for an epoxy-coated pipe section (bottom)

In June 2011, two members of the research team visited Mr. Rich Giani (who at that time was Water Quality Manager for DC Water) at the Fort Reno building. Discussion focused on the demonstration described above, the test-loop experiment (which was still on-going then but is now nearing an end), DC Water's experiences with LSL replacement, and their thoughts about, LSL lining and coating as an alternative to replacement. The thoughts he shared included the following (Giani 2011):

- The epoxy tended to pool in the risers, where the pipes rose vertically in the meter setters (The potential for this problem to occur is recognized by the manufacturers and has been addressed by changes in application procedures).
- The pipes were cleaned by sandblasting, so lead-contaminated grit and dust must be caught to protect both workers and customers (This is standard practice in epoxy coating procedures, and suitable equipment is provided by the manufacturers).
- No volatile organic chemicals were detected leaching from the epoxy into water, based on a full VOC scan by the Washington Aqueduct Laboratory of the U.S. Army Corps of Engineers.
- They were informed by a representative of EPA that they could epoxy coat LSLs, but an epoxy-coated LSL would not be considered permanently "replaced" and would therefore not count toward their 7% replacement quota. An LSL sampled after being epoxy coated could "test out" (if the lead level was below the action limit); but, if the utility again exceeded the action limit, epoxy-coated LSLs would not be exempt from resampling requirements.
- Once they found that orthophosphate could effectively keep lead levels below the action limit, their interest in epoxy coating and other lining and coating methods subsided. They had been considering lining or coating as "plan B" if orthophosphate treatment did not achieve the desired results.
- The epoxy manufacturer offered a 10-year warranty and claimed the epoxy would last 50 years; but the length of the warranty period was of significant concern because copper service lines (their current standard installation) in their service area typically last 50 or more years. Even if significant cost savings could be realized, the coating would have to last about 20–25 years or more to be cost effective. Thus, they see little advantage of epoxy coating over replacement unless they can be assured of a longer service life.
- They do not experience frozen service lines, so they are not concerned about the damage freezing or certain methods of thawing might cause to a lining or coating.
- When LSLs are found during water main construction, the utility side is always replaced, but most customers are unwilling to pay to replace the customer-owned portion. DC Water typically replaces their LSLs using trenchless methods in most cases and excavating trenches when obstructions prevent moling or pulling the pipe through.
- One engineering consultant noted that lining or coating would save about $500 if a wall penetration could be avoided by installing the lining or coating from inside the wall of a basement or crawl space. LSL replacement normally requires a wall penetration, which typically costs $500.
- They estimate the cost of LSL replacement at about $100 per foot, excluding the costs of plumbing disconnect and reconnection, excavation and backfilling, traffic control, pavement repair, and temporary restoration. By their estimate (which exceeds the

estimate provided by the epoxy manufacturer), epoxy coating would cost only about $40 per foot, so significant savings could conceivably be realized.*

- They have not considered slip lining of small-diameter HDPE pipes through LSLs, and have no opinion about it. Booster pumps, which could potentially be used to boost flow/pressure after slip lining with small-diameter pipes, are legal in their service area, and most commercial buildings have them; but they must be maintained.
- They are now putting in 1-in. copper service lines as their standard installation and are hesitant to approve anything smaller as part of a rehabilitation project, since the service would not be brought up to code.

Denver Water, Denver, Colorado

Denver Water is a good example of a water utility facing some challenges that lining and coating technologies may be helpful in meeting. Denver Water currently replaces LSLs primarily as they are encountered in the course of their normal activities (Price 2016). According to Denver Water (2016) and Price and Walsh (2017):

- In 2016, Denver Water performed 1,028 full LSL replacements, which were done in conjunction with leak repairs (429), main replacements (310), or pipe rehabilitation projects (289). This doesn't include two to three hundred more LSLs replaced by private contractors and property owners. Denver Water expects to replace another 1,000 to 1,200 LSLs in 2017.
- Denver Water is exploring a partnership with Denver Urban Renewal Authority to provide a funding mechanism for customers to replace their LSLs. The concept is to develop a revolving loan fund with interest based on income level, thereby reducing partial LSLRs and increasing full LSLRs.
- In Denver, the customer owns the full LSL all the way to the corporation stop at the main. When a customer wants to replace a full LSL, the customer pays. However, when Denver Water uncovers an LSL during a Denver Water construction project, they pay for a full LSL replacement; and when a leak is encountered Denver Water pays to replace the LSL from the main to the meter and the customer pays to replace the portion from the meter to the house.
- In its 2017 Lead Reduction Program, Denver Water plans to continue water quality testing by sending a kit with three sample bottles to single family homes and a single bottle to multi-family customers.
- Denver Water is using a field scanning analyzer to provide quick and economical analytical results to help evaluate the possible presence or absence of lead service lines in the field.
- Denver Water will expand consumer outreach using both traditional and social media methods, with a special focus on vulnerable populations.

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* In a letter dated October 27, 2004 to Ms. Karen Johnson, Chief, Safe Drinking Water Branch, EPA Region 3, Mr. John Dunn, Deputy General Manager and Chief Engineer of DCWASA noted that the utility's budgeted cost for a full LSL replacement was about $12,200 (including $2,500 for replacing the privately-owned portion, which would be paid by the homeowner), but the estimated cost for epoxy lining a full LSL was only $7,500, representing a savings of about 38 percent.

- Denver Water is working with other agencies and entities to encourage local and state lawmakers to consider legislative changes which would require LSL disclosure for housing sales and leases, mandatory testing for child-care facilities, low-income assistance, and plumber disclosure requirements.

Because Denver has an estimated 60,000 LSLs (Price 2016), it will take many years to replace them all if they continue to be replaced at the current rate. This is a reasonable and economical approach under the current LCR, but future changes in federal, state, or local regulations or policies may necessitate or encourage a change in the LSL replacement rate.

Denver Water is interested in, and is currently evaluating, lining and coating technologies as alternatives to LSL replacement, for several reasons (Price 2016): 1) some of their LSLs are located in congested urban areas, and lining or coating them might significantly reduce traffic disruptions or help reduce lead levels on an interim basis until a water main scheduled for replacement many years in the future is actually replaced; 2) they normally replace LSLs using a cable-pulled splitter to split the LSL while pulling a new service line into place, but if this method cannot be used (e.g., when there are brass connectors in the LSL), the usual alternative (directional drilling) is much more expensive and can damage other utility lines, so they are looking for better options; and 3) in urban areas they may encounter larger LSLs (e.g., 2 in. diameter LSLs serving institutions or office buildings), for which rapid and minimally disruptive alternatives would be attractive.

EPCOR, Edmonton, Alberta

EPCOR is a municipally owned private utility, and the City of Edmonton is its sole shareholder. EPCOR began in 1891 as the Edmonton Electric Lighting and Power Company; became EPCOR Utilities Inc. in 1996 in a merger of natural gas, power, and water utilities; and adopted EPCOR as its universal brand name in 2001 (EPCOR 2017). Today EPCOR provides power, water, and wastewater services to about 1.9 million people in three Canadian provinces and three U.S. states (EPCOR 2017).

Only about one percent of Edmonton homes (most built before 1950) now have service lines suspected to be made of lead, down from earlier estimates of about 2 percent due to removal of some LSLs and to growth of the city. As in most other cities with LSLs, the portion of an LSL from the main to the property line is the utility's responsibility and the section from the property line to the home is the property owner's responsibility (EPCOR 2015). EPCOR started a lead response program in 2008 to ensure that residents of homes and businesses receiving water through a lead service line (LSL) receive high quality water. This program, described in detail by EPCOR (2010), includes:

- Annual reminders to residents of homes and businesses with LSLs that include an offer to test their tap water for lead and, for those who chose not to replace their LSLs, an offer to provide a point-of-use filter that removes lead (an offer 4800 customers accepted)
- Prioritized replacement of EPCOR-owned LSLs, with priority given first to LSLs associated with high lead concentrations (>0.010 mg/L), then to those serving high risk individuals (children under six years of age and pregnant women), and then to homes or building where the owner chooses to replace the private-side LSL in response to the program

- Public education on lead in tap water

EPCOR's 2015 Annual EnviroVista Report (EPCOR 2015) summarizes the results of EPCOR's lead monitoring efforts, and their progress in replacing LSLs. When samples were collected using Health Canada's standard sampling protocol, 70 percent of homes with LSLs had lead concentrations below the maximum acceptable concentration (MAC) of 0.010 mg/L, and the 90th percentile was 0.023 mg/L. Using a random daytime sampling protocol, the average lead concentration was 0.0067 mg/L and the 90th percentile was 0.0145 mg/L. As of 2015, 1,244 LSLs had been removed from service, 416 proactively, as part of the lead response program, and 804 reactively, due to leaks or other emergency repair, as part of main replacement projects, or for other reasons. EPCOR discourages partial LSL replacements due to concerns about their effectiveness and their potential to temporarily increase lead concentrations (EPCOR 2010 and 2015).

Due to Edmonton's long, cold winters, water distribution pipes, including LSLs, are buried deep in the ground to avoid freezing (Craik 2013), making trenchless technologies even more economical than they might be in warmer locations. As reported by EPCOR (2010), epoxy coating of LSLs was proposed as an alternative to LSL replacement and was considered attractive because it would avoid damaging finished basements and sewer lines (typically located close to water lines in older areas of Edmonton), and could potentially result in significant cost savings. EPCOR does not replace privately owned service lines – property owners hire their own contractor for that purpose; but EPCOR was interested in lining or coating mainly as a possible alternative for customers with LSLs (Craik 2017).

Bradley Mechanical Services (Mississauga, Ontario) had developed a patented epoxy-coating process (PipeShield^{TM}), used to coat the insides of water line in buildings with an epoxy having a service life rated for 70 years, and was eager to test their process on LSLs. EPCOR was interested enough in exploring the potential use and benefits of the process to underwrite a trial involving six homes with relatively long LSLs, buried about 9 feet deep in the ground, and with tap-water lead concentrations exceeding 0.030 mg/L (Craik 2013). Unfortunately, due primarily to the very cold temperature of the LSLs (<3 °C), for which Bradley Mechanical Services attempted to adjust the epoxy formulation, only one LSL was successfully coated. Two were partially coated, one was plugged when the epoxy hardened prematurely, and the other two were not coated due to time constraints.

The LSL that was successfully coated was placed back into service, and the customer was satisfied with its performance. There was no evidence of any taste or odor problems associated with the epoxy. The lead concentration dropped from 0.024-0.030 mg/L before the epoxy coating was applied to 0.004 mg/L by the end of the year, and even lower concentrations were found in subsequent years (Table 5.2).

Table 5.2
Tap-water lead concentrations in a home with an epoxy-coated LSL

Date	Dissolved Pb mg/L*	Total Pb mg/L	Before or After Epoxy Coating
2008-09-09	ND	0.030	Before
2009-06-04	0.020	0.024	Before
2009-07-06	0.002	0.006	After
2009-07-20	0.004	0.005	After
2009-09-11	0.003	0.004	After
2009-10-22	0.003	0.004	After
2010-10-08	ND	0.003	After
2011-09-07	<0.001	0.001	After
2013-10-23	0.0008	0.0026	After

Source: Data courtesy of Mr. Steve Craik, EPCOR
* Pb was determined by GFAAS, except for the 2013 sample, which was analyzed using ICP-MS; ND = not determined

Bradley Mechanical Services has developed procedures to avoid the problems encountered during the trial in Edmonton, as have other providers of epoxy-coating services. In locations where cold water temperatures are common, e.g., in the UK, installation practices are adjusted for LSL temperature, and numerous LSLs have been successfully epoxy coated. It helps that LSLs are very thick-walled and therefore hold heat well, since once they are heated, e.g., using compressed air or hot water, they stay warm long enough to accommodate installation. Some manufacturers have developed special software to guide installation practices, taking into consideration factors such as ground temperature, pipe length, and time since the epoxy ingredients were mixed. Thus, problems such as those experienced in Edmonton can now be avoided.

EPCOR recognized in 2009 that the technical difficulties Bradley Mechanical Services experienced could be overcome, but did not pursue epoxy-coating further primarily because the economic benefits were unclear (EPCOR 2010). For the process to be economical, a local contactor would need to purchase a license to use the technology, but before purchasing a license, the contractor would want to know how many customers could be counted on to use the technology, which would be difficult to accurately predict (EPCOR 2010). Scheduling installations close together (to reduce costs) would also be difficult, since the LSLs in Edmonton tend to be scattered throughout the older parts of town, and those that are closer together tend to be found in lower income areas where the property owners are less likely to be willing to pay to have their LSLs lined, coated, or replaced (Craik 2013).

Health Canada followed the progress of the EPCOR pilot project, but did not formulate any guidelines on LSL linings or coatings since EPCOR did not move forward with any of these technologies (Lemieux 2016).

Louisville Water Company, Louisville, Kentucky

Louisville Water Company (LWC) has a long history of proactively replacing LSLs, exploring ways to more efficiently replace LSLs, evaluating linings and coatings as alternatives to LSL replacement, and encouraging and helping homeowners to avoid exposure to lead and to replace privately owned LSLs. As noted by Sandvig et al. (2008):

- LWC began replacing LSLs in the 1980s, in conjunction with a main replacement program, typically bundling them in projects including 50-200 LSLs to achieve an economy of scale and save approximately 50-70 percent of the cost of individual replacements
- By September 2005, LWC had already replaced 52,000 of their 72,000 LSLs, giving priority to those found leaking, those associated with high tap-water lead levels, those connected to water mains being replaced, and those in certain neighborhoods selected for removal of all LSLs
- Between 1980 and 2005, LWC cleaned and lined 280 miles of unlined cast iron pipe, which had the beneficial side effect of covering all the lead- or leadite-filled joints with cement mortar

According to Grunow (2017), LWC now has only about 6,500 LSLs left in their distribution system. They are replacing about 2,000 per year and plan to have them all removed by the year 2020. Their LSL replacement program actively encourages removal of private-side LSLs, and they offer to pay 50 percent of the cost, up to $1,000. Low income customers are encouraged to apply for the grant from the Louisville Water Foundation to cover the other half of the cost; and customers who choose not to replace their LSLs are provided with a water filter and encouraged to use it.

In 1996, LWC conducted a field demonstration of epoxy coating of LSLs in cooperation with American Pipe Lining (APL). As reported by Kirmeyer et al. (2000):

- The demonstration involved 14 homes on a cul-de-sac, so APL was able to use a manifold to epoxy coat the LSLs for two groups of 8 and 6 homes.
- The demonstration was coordinated with a main replacement, so water was already being provided to these homes using a bypass.
- A novel approach to epoxy coating was used, in which the excess epoxy was discharged into the water main, with the intent of scraping it out, before it fully hardened, using the same scraper being used to clean the main. Unfortunately, main cleaning was delayed, and by the time it began the epoxy had become so hard it caused several cable breaks.
- All 14 LSLs were subsequently extracted and inspected, and the epoxy coverage was found to exceed LWC's expectations.

Since the LSLs were removed long ago, they were not available to the research team for resampling or evaluation of their long-term performance.

In 1998, as part of the study reported by Kirmeyer et al. (2000), four more LSLs connected to single-family homes were epoxy coated, and epoxy coating was compared to three methods of LSL replacement (open trench and two involving cable pulling). Epoxy coating was found to take longer than the other methods (since the epoxy was allowed to cure overnight), but was less disruptive and less expensive than open-trench replacement and required less site restoration than cable pulling.

As reported by Ball (2016), LWC conducted another demonstration test in 2008, one that evaluated PET lining of the LSLs connected to 8 homes. Lead concentrations in the first-flush samples collected after an unspecified holding time ranged from 1.6 to 3.8 μg/L, well below the action limit. Following the demonstration, the PET-lined LSLs were left in place, but water was supplied to the homes through CSLs that served as bypass lines during the demonstration. Thus, the PET-lined LSLs sat idle for 8 years until 5 of them were switched back on and retested in 2016.

In February 2016, the reconnected lines were flushed for 48 hours, then left standing for at least 8 hours. Lead was detected in the first-flush samples, but LWC personnel noticed some debris in the first flush samples, which may have been deposits dislodged from the brass meter stops that had been sitting idle for 8 years, and there were brass fittings on the ends of the flushing hoses that may have contributed lead to the samples. In April 2016, after installing a secondary valve in each line, so the meter stops could be left open, and using PVC fittings instead of brass fittings on the flushing hoses, two more rounds of samples were collected following stagnation times of 8 and 48 hours. Total and dissolved lead concentrations were non-detectable (≤1 μg/L) in first-flush samples from 3 sites, ≤2 μg/L at one site, and 8-15 μg/L at the fifth site. After removing a brass elbow in the meter stop at the fifth site, the total and dissolved lead concentrations in a sample collected after an 8 h stagnation period were <2 μg/L. Ball concluded that brass fittings in water service lines should be replaced with lead-free fittings when installing a PET liner, and that the PET liners proved to be an effective barrier between LSLs and potable water.

Grunow (2017), asked whether lining or coating techniques might be potentially useful in dealing with some of LWC's remaining LSLs or those of its customers, replied that such situations would likely be rare. He noted that even if 100 LSLs proved troublesome to replace and cost twice as much on average as the others, this would not make much difference in the total cost of removing another 6,500 LSLs. Nevertheless, he could think of situations, such as an LSL running through an embankment wall, where lining or coating might come in handy, and noted that it would be good to have such an option available as another "tool in the toolbox." Making such options available to customers might also help increase their participation rate.

Madison Water Utility, Madison, Wisconsin

In 1992 and again in 1997, the 90th percentile lead concentration measured in Madison's tap water, 16 μg/L, exceeded the action limit of 15 μg/L (Grande 2012). About 6,000 of the city's 66,000 water service lines, and about 5,000 of the private-side lines, were LSLs, and this was thought to be the primary source of the lead found in the tap-water samples (Grande 2012 and 2014). From 1993 to 1998, Madison Water Utility conducted corrosion control studies that confirmed that LSLs were the primary source of the lead and also determined that corrosion control treatment was not a viable solution (Grande 2012). Chemical treatment was not considered economically viable for the following reasons (Sandvig et al. 2008, Process Research Solutions 2010):

- The city's source of supply is groundwater, saturated with calcium carbonate, drawn from more than 20 distinct sources, with no centralized treatment or distribution facilities; thus, pH and alkalinity adjustment is not economically feasible (and would encrust the distribution system unless the water were stabilized by softening or polyphosphate addition)
- Polyphosphate addition, rather than lowering lead levels, was found to increase them by as much as a factor of four
- Orthophosphate addition would lower lead levels, but a recently installed biological phosphorus removal system was not designed to handle the added load, and runoff from water not discharged to the collection system would carry the phosphorus into nearby lakes

In lieu of chemical treatment, the City of Madison proposed to the Wisconsin Department of Natural Resources (WDNR) that it be permitted to remove LSLs instead. A consent order signed by the two parties in 2000 required mandatory full LSL replacement within 10 years, enforceable by means of a city ordinance and providing equivalent health protection to what could have been achieved through chemical treatment (Grande 2014).

After spirited debate over who should pay for the LSL replacements, the city adopted an ordinance (MGO 13.18) that established a strict schedule for mandatory LSL replacement; authorized the city to pay half the cost (up to $1,000) for private-side LSL replacements; authorized low-interest loans for unreimbursed expenses (with zero interest for three years for qualified low-income owner-occupants); and required LSL replacement at the time of sale for any property having an LSL (Grande 2012 and 2014). The rationale for having the city pay half the cost of the private-side LSLs was that all citizens would benefit from the avoided costs of centralized chemical treatment of the drinking water and the avoided costs of wastewater treatment for phosphate removal (Grande 2012).

The city's LSLR program prioritized replacements to accelerate health risk reduction and minimized costs by replacing utility-side and customer-side LSLs at the same time and by scheduling replacements to optimally utilize the city's crews and those of two private contractors (Grande 2014). Most of the LSLs were removed by 2006, and all but a handful by 2012 (Grande 2012 and 2014). Another LSL is found every now and then (Grande 2017), and the city's offer to pay half the cost of replacement is still in effect (City of Madison 2017). The average cost to the utility of full LSL replacement was $2,985, including reimbursements; the average rebate paid to cover half the cost of the private-side replacements was $670, which was also equal to the average out-of-pocket expense paid by the property owner; thus, the average full cost of LSL replacement was $3,655 ($2,985 plus $670) (Grande 2012). This cost is similar to the estimated cost of $3,100 per full LSLR incurred by the Lansing, MI, Board of Water and Light to replace 13,500 LSLs (Roost 2016).

Madison's LSLR program also conducted a public education program and follow-up monitoring to verify that LSL replacement was in fact lowering tap-water lead levels as expected (Grande 2014). The lead levels dropped more slowly than expected, which was attributed to the gradual release of particulate lead adsorbed to manganese-bearing deposits (Process Research Solutions 2010, Sandvig et al. 2008, Schock et al. 2014). Nevertheless, the city's 90th percentile lead levels were <5 μg/L by 2011 (Grande 2012), which had been the goal established for achieving the desired level of risk reduction.

Madison Water Utility did not explore the possible use of linings or coatings as an alternative to LSL replacement because it was not specified as an option in the LCR or in the ordinance adopted by the city (Heikkinen 2011, Grande 2017). Nevertheless, Madison's LSLR program is widely cited (e.g., City of Madison 2016) as an excellent example of involving the public in adopting a well-designed, system-wide LSLR program that reduces costs by taking advantage of economies of scale and maximizing worker productivity. Other city and water utilities would do well to emulate this example, whether or not their LSLR program includes the use of lining or coating technologies, which may in some locations be found advantageous.

Providence Water, Providence, Rhode Island

Providence Water serves a major portion of central Rhode Island, with a single treatment plant using source water from Scituate Reservoir. In 2011, when this research project began, Providence Water was in the midst of an extensive LSL replacement program due to the system's exceedance, in 2006, of the 90th percentile lead Action Level (AL) of 0.015 mg/L (Ripstein 2011, Commons 2011). According to Ripstein (2011), the system at one time had 25,600 utility-owned LSLs, and approximately 2,000 LSLs were replaced in both 2009 and 2010. By 2011, the utility had begun replacing LSLs primarily in conjunction with main replacements, and was offering customers the opportunity to replace their privately-owned LSLs at utility rates (typically about \$2,500, but ranging from about \$1,700 to \$7,500 depending setback distance and other factors), though the response rate was only about 1.5 to 2 percent. As of 2017, Providence Water continues to replace utility-owned LSLs as water mains are replaced, and the system now has an estimated 13,000 utility-owned LSLs and 30,000 privately owned LSLs (Ripstein 2017). The utility maintains an on-line map of its remaining LSLs (Providence Water 2017).

Providence Water's interest in the possibility of lining or coating LSLs in lieu of replacing them was instrumental in generating the proposal that led to this research project. Almost all of their LSL replacements in the 2009-2010 timeframe involved inserting a cable through the existing LSL to pull the lead pipe out and drag in a new 1-in. copper service line behind. Some LSLs could not be replaced in this manner, and this required full excavation of the street (for long-side replacements) to remove the LSL and install the 1-in. copper service line. As part of their in-house research into lining and coating methods, Providence Water hosted two demonstrations, one in 2011 involving PET lining of an LSL, and one in 2016 involving epoxy coating of LSLs. These demonstrations are summarized in the following paragraphs.

PET Liner Demonstration

On November 29, 2011, Providence Water hosted a demonstration of the Neofit® lining system on a residential LSL and, at their invitation, a member of the research team travelled to Providence, RI to watch the demonstration. Representatives of the Rhode Island Department of Health, EPA, EPA Region 1, two water utilities, and several consultants were also invited to watch the demonstration. The demonstration involved lining a cross-linked polyethylene (PEX) pipe at grade level, and then lining an LSL providing water to a single-family home on South Street in Cranston, a suburb south of Providence served by Providence Water.

Demonstration of the lining system was led by Mike Gonder, Vice-President of Operations for Flow-Liner Systems, Ltd. (Zanesville, OH). Flow-Liner's literature indicates that they have been installing Neofit® PET liners in the U.S. for a number of years now in water service lines and for other applications involving small-diameter pipes having inner diameters ranging from 3/8 to

2 inches in diameter. The liners are made by Wavin, a large manufacturer of a wide variety of plastic products. The lining system has been used in Europe for approximately 35 years, with many installations in England and especially in France. The liner is made of polyethylene terephthalate (PET), is considered a semi-structural lining, and is certified to NSF-61. The life expectancy of the liner is advertised as 50 years, but could potentially be longer. The liners in the oldest installations have now been in place for about 35 years.

The demonstration began with the lining, in the roadway at grade level, of a length of 5/8 in. ID PEX service line having 3/16 in. holes drilled into it about 3-3/4 in. apart to simulate leaks in an old or damaged service line. A new PET liner about 3/8 in. (10 mm) in diameter was pushed through the PEX service line, then connected to insulated hoses on either end of a process control unit (Figure 5.2) containing a heater, pump, and compressor. The control unit pressurized the system, heated the water to 85 $^{\circ}$C, and recirculated the heated water through the liner, causing the line to expand and press against the walls of the pipe being lined. Cold water and then air were used to cool the liner. The entire process typically takes about 12-15 minutes once the connections are made. Once cooled, the newly lined pipe is ready to be returned to service. The liner effectively sealed the holes drilled into the PEX pipe, demonstrating the ability of the liner to seal holes in an aging or damaged service line. In fact, this lining process can be used, and is used, to repair leaking service lines, and it is especially attractive for this purpose when the property owner wants to repair an otherwise functional service line while avoiding damage to landscaping, pavements, and foundation walls or other structures.

The second part of the demonstration involved lining a full LSL from a main to inside a house. First, compressed air was used to force a small pig, with a string attached, from inside the house to an access pit (3 ft. wide, 5 ft. long, and 5 ft. deep) near the main. The pig was used to clear water, remove deposits from the LSL (which in many parts of the world develop only a thin layer of deposits), and deliver the string to the other end of the pipe. The string was then attached to the liner at the access pit (Figure 5.3), and a combination of pushing the liner and gently pulling the string was used to attempt to get the liner all of the way through the LSL to the inside of the house. However, the liner hit an obstruction in the LSL, and would not go all the way through. A decision was made in the field to complete the lining in two sections – from the main to the curb stop and then from the curb stop to the inside of the house. This approach worked fine for the section between the main and curb stop, which took about 30-40 minutes to line because a large water heater in the equipment trailer, normally used to preheat the water, was not used.

As described by Phillips (2011), it took a fair amount of time (30-40 minutes) to get the liner through the second section, from the curb stop to inside the house. Two bulbous joints were noted close to where the LSL went through the pit wall, and these appeared to be a possible source of the problem. The liner was connected to the control unit, but shortly after the unit was turned on, the liner burst. After attempting to remedy the problem, the LSL was pulled out using a cable and dragging a new LSL behind; and the contractor who pulled the LSL also had difficulty maneuvering the cable past the same spot that had been problematic for the liner insertion.

Following the demonstration, Flow-Liner cut out a section of the LSL containing one of the bulbous joints and sent it to one of their technicians for analysis. The joint was found to contain a flanged edge that obstructed about 50-75% of the cross-sectional area of the LSL, had a burr sharp enough to score the liner and cause it to fail, and was evidently responsible for making it difficult to slip a cable through the LSL (Fox 2011). The technician noted that this type of deformity is not common in LSL joints.

When the demonstration ended, the utility-owned section of the LSL was removed and replaced with a copper service line so the utility could receive credit for a full LSL replacement (Phillips 2011). Although the demonstration did not go as smoothly as hoped, problems can be encountered with any method of lining, coating, or replacement. In this case, had the contractor been unable to maneuver the cable past the obstruction in the joint, a more expensive replacement method, such as trenching or directional drilling, would have been needed to replace the LSL.

Without knowing how commonly obstructions such the one encountered at this home would be encountered, it is not clear how much time liner installation would save compared to LSL replacement. Flow-Liner (2006) estimates a success rate of more than 90 percent using their Neofit® system. Staff from Providence Water estimated that a typical crew can replace 5-8 LSLs per day using their usual pulling process. Wavin (2010) estimates that 4-5 service lines per day can be lined using a Neofit® system.

Epoxy Coating Demonstration

In June 2016, Providence Water hosted a two-day demonstration of the ePIPE® process, which was used to epoxy coat LSLs at four residences in their service area. Only two LSLs were coated each day, because this was a demonstration; but the equipment used was reported to be capable of lining six nearby LSLs simultaneously using a manifold to distribute the epoxy. An important objective of the demonstration was to see if LSLs running through obstructions could be lined, thereby avoiding extensive excavation labor costs (Ripstein 2017), so the sites were selected to represent challenging conditions. The installation at one site was notable because a large tree had grown up over the curb stop, rendering it inaccessible (Figures 5.4 and 5.5). The successful installation at this site, described in detail by Phillips (2016), involved:

- Using compressed at (40-80 psi) to blow out trapped water and dry the line
- Cleaning the inside of the LSL by sandblasting it with 8-10 blasts of aluminum oxide, following by a blast of air only to remove any remaining residue
- Heating the LSL until the entire line was at 68 °F
- Using compressed air to apply the epoxy in a series of measured shots, pushing it from the basement of the house through the LSL (including the inaccessible curb stop), and expelling the excess epoxy into the access pit near the water main
- Circulating hot water through the LSL to cure the epoxy
- Installing a new curb stop, since the original one was buried under the tree
- Installing a sample tap, to monitor water quality

As described by Gillanders (2017) and confirmed by Ripstein (2017), two of the other three installations were also successful, but the fourth was not. At one residence, a pit, where a pit had been dug for a new curb stop, the LSL was successfully epoxy coated in two installments – from the house to the curb stop and from the curb stop to the main. At another residence, the LSL was successfully epoxy coated in a single pass, from the house to the main, going right through the curb stop, which was manipulated several times so it would not be stuck when the epoxy hardened. At a fourth residence, the LSL was epoxy coated all the way from the house to the main, but a "rippling defect" in the coating, attributed to hydraulic effects downstream from a partial obstruction, restricted the flow. In normal practice, flow tests are conducted before and after an LSL is epoxy coated and, if the flow is found to be restricted, the LSL is replaced. See Chapter 2 for additional discussion of installation success rates for linings and coatings.

Source: Photo by Alan R. Roberson.

Figure 5.2 Demonstration of PET liner installation for Providence Water

Source: Photo by Alan R. Roberson.

Figure 5.3 A PET liner being prepared for installation

Source: Photo by John J. Phillips.

Figure 5.4 Demonstration of an epoxy-coating system for Providence Water

Source: Photo by John J. Phillips.

Figure 5.5 Demonstration of a battery-powered epoxy injection gun

City of Rochester Water Bureau, Rochester, New York

The City of Rochester has a population of 210,000, 600 miles of distribution mains, and approximately 58,000 metered water service accounts (City of Rochester 2015, Kozman et al. 2016). In 2011, the city had an estimated 30,000-35,000 LSLs still in service, so slightly over half its customers were being supplied through an LSL (Schantz 2011). Although the 90th percentile lead concentrations had remained below the action limit since the LCR went into effect, lead levels had been gradually increasing since about 2000, so the city retained a consultant to review its water quality history and lead corrosion issues, perform diagnostic sampling, study the effect of increasing pH on lead release, and conduct a laboratory study on segments of LSLs removed from the distribution system (HDR 2011).

The project report (HDR 2011) concluded that the increases in lead concentration were largely attributable to a varying redox environment, i.e., greater variability in pH and residual free chlorine concentrations than in the past, and recommended changes in treatment and operations to mitigate this variability. The report also recommended orthophosphate addition to control lead release, but the city is reluctant to add orthophosphate to its primary water supply because this would likely promote algal growth in its open distribution storage reservoirs (Schantz 2011). Therefore, the report recommended that other options be explored, such as adding orthophosphate at selected points in the distribution system where it is most needed, or revising its wholesale agreement with the Monroe County Water Authority so that orthophosphate-treated water can be used in the main pressure zone.

Like many other utilities in 2011, the Rochester Water Bureau was replacing LSLs as they were encountered when replacing or rehabilitating water mains (Schantz 2011). This practice has continued, and there are now only about 23,000 city-owned LSLs left in service (Rowley 2017). One thing that appears to be rather unique to Rochester compared to other cities is that very few customers supplied by a utility-owned LSL have a private-side LSL (Shantz 2011, Rowley 2017). Schantz (2011) estimated that about 99 percent of customers with a utility-owned LSL had a private-side service line made of galvanized iron or, less commonly, copper. Private side LSLs are typically found only in the more affluent homes built from about 1900 to 1930, suggesting that the wealthy could afford what was then viewed as the best available material and the less affluent decided to purchase a less expensive material (Schantz 2011, Rowley 2017).

Since galvanized iron pipes tend to become heavily encrusted with rust over long periods of time, and since rust is known to adsorb relatively high concentrations of lead (see Chapter 1: LSL Contributions to Lead in Tap Water), it seems likely that significant amounts of lead may have accumulated in the private-side lines made of galvanized iron. However, it is unclear whether partial LSL replacements in Rochester will have impacts similar to those commonly observed elsewhere, i.e., temporarily elevated tap-water lead levels attributed to disturbance of the private-size service lines (usually LSLs in other cities). Therefore, the City of Rochester plans to initiate a study to examine the impacts of removing city-owned LSLs on tap-water lead levels so they can better advise contractors and customers regarding actions that should be taken following removal of an LSL (Rowley 2017).

The city has not lined or coated any LSLs, but is comfortable with these technologies since they are used in rehabilitating water mains; and they would consider using them in situations where they appear to be economically viable (Schantz 2011, Rowley 2017). For this reason, the city was willing to send the research team numerous 4-ft long sections of LSLs harvested from their distribution system for use in the experimental portions of this research project. If elevated lead levels are found in the deposits in galvanized private-side service lines in Rochester, lining or coating them might prove to be a viable option for controlling lead release and human exposure to lead, provided the lines are in good enough condition to be cleaned and coated. Galvanized iron pipes tend to accumulate much greater amounts of deposits, and to undergo much more corrosion, so it is not unusual for them to deteriorate to the point where they cannot be lined or coated, or where replacement simply makes more sense because they have reached the end of their useful life.

PRACTICES AND EXPERIENCES IN COUNTRIES OUTSIDE NORTH AMERICA

In addition to considering what other water utilities in North America are doing to address their LSLs, some stakeholders may find it informative to consider the practices and experiences of other countries and some of their major water utilities in controlling exposure to lead in drinking water and more specifically with lining, coating, and/or replacement of LSLs. The countries selected for this purpose are:

- Australia
- France
- Germany
- Ireland
- Japan
- The Netherlands
- United Kingdom (and Scotland?)

These countries represent a wide range of circumstances and practices. Ireland and the UK still have a relatively large percentage of their population obtaining water through LSLs; French water utilities have removed or rehabilitated about two-thirds of their LSLs in the past 15 years, and German utilities have replaced nearly all of theirs. Australia never had many LSLs, but leaks caused by corrosion of copper service lines are common.

Many countries, including those listed above, have a standard for lead in drinking water, measured at the tap, consistent with the current World Health Organization (WHO) standard of 0.010 mg/L (WHO 2011). This limit is substantially lower than the 0.050 mg/L limit that existed 40 years ago in most of these countries and others, including the U.S. Some countries lowered their limit directly from 0.050 to 0.010 mg/L, while others set intermediate limits. In the European Union (EU), for example, a 1998 directive (Council of the European Union 1998) lowered the limit to 0.025 mg/L in 2003, with a 0.010 mg/L limit taking effect in December 2013.

During the course of the project, a number of individuals, including representative of all stakeholder groups, asked members of the research team why the U.S. standard (i.e., the action limit of 15 µg/L) is less stringent than the 0.010 mg/L standard in most other countries. Some also asked whether the U.S. was lagging behind, or if other countries were being overly cautious. What many individuals fail to realize is that sampling methods differ from one country to another and can result in very significant differences in measured values.

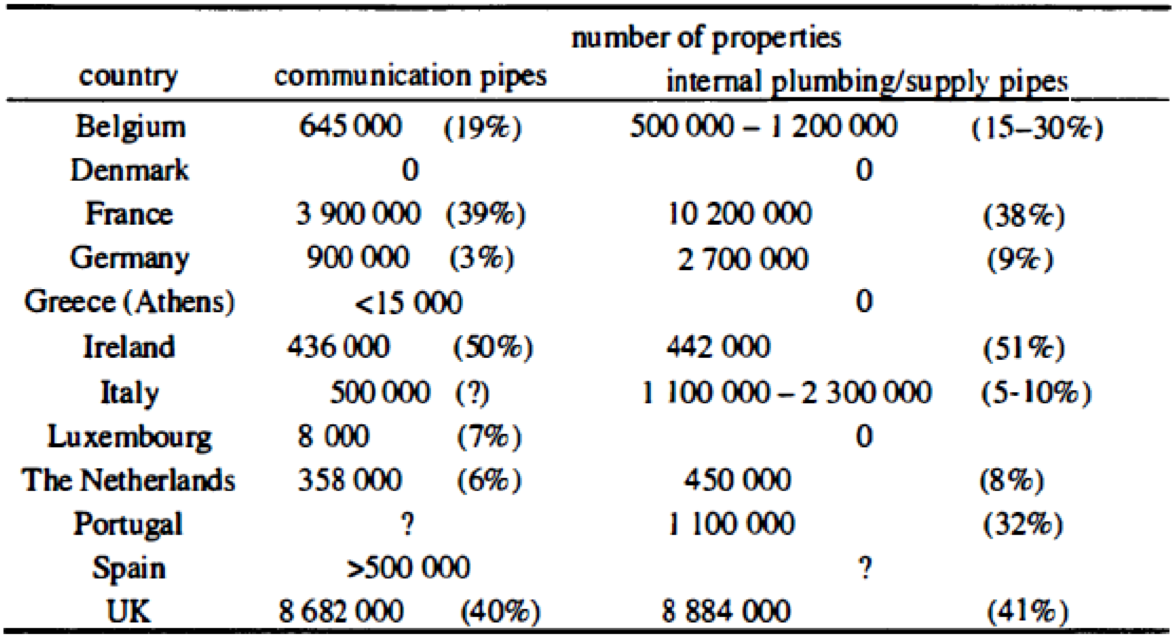
In the U.S., sampling for LCR compliance is based on one-liter first-draw samples following a stagnation period of at least six hours. The results, though influenced by the presence of LSLs, are strongly influenced by the composition of plumbing fixtures and the corrosivity of the water. In fact, LCR compliance samples are more or less intended to provide a surrogate measure of corrosivity. In contrast, WHO, EU, and other standards for lead in drinking water, including Canada's, target lead levels in consumed water, based on sampling methods such as random daytime sampling or collection of four-liter samples following a 30-min. stagnation period. The results of such methods are likely to be more strongly influenced by the presence of LSLs, and less strongly influenced by the composition of plumbing fixtures, than those from LCR compliance samples. Comparing the results from LCR compliance samples with those of other sampling methods is a proverbial "apples to oranges" comparison and, without substantial additional information and reliable data, it is generally not possible to conclude, in a given situation, that one approach, including the standard it is used to enforce, is more stringent than the other.

All countries who lowered their limit on lead in drinking water in the past 40 years did so for similar reasons, i.e., growing concern about the effects of lead on human health, and especially on young children and pregnant women. However, despite the uniformity of current standards and the rationale for them, countries adopted their current standards at different times and under differing circumstances, and adopted differing compliance schedules and compliance strategies. Other practices, such as use of lead solder, standards for lead in plumbing fixtures, and use of galvanized iron pipe for interior plumbing, also vary considerably among countries. Thus, lead levels in tap water, and the occurrence of LSLs in distribution systems (on public and private property), can vary considerably from one country to another.

It seems common for individuals in North America to believe that the incidence of LSLs and lead problems is much higher in Europe because many large cities there are so much older. However, Europe is not as homogeneous as some people imagine and, as shown in Table 5.3, the incidence of LSLs varies greatly from one country to another. Also, as in the U.S. and Canada, within a given country having numerous LSLs, there are no doubt considerable differences from one city to another, and one service area to another, in lead levels and the incidence of LSLs remaining in service. In EU countries, as in the U.S. and Canada, the water utility (or water company) is typically responsible for the "connection pipe" (the portion of the service line conveying water from the main to the curb stop (property line), while the property owner is responsible for the "supply pipe" (the portion on private property running from the curb stop to the house or building) and for the interior plumbing.

Lead control programs in other countries typically include many of the same elements as lead control programs in the U.S. and Canada, including public notification and education, monitoring of lead levels (sometimes at utility expense), corrosion control treatment, and LSL replacement. However, there is one notable exception. In the guidelines or national strategies of some countries, LSL rehabilitation (i.e., lining or coating) is explicitly stated as an alternative to replacement. In the U.S. and Canada, the regulations and guidelines are silent on this topic.

Table 5.3
Occurrence of lead plumbing in European countries as reported in 1999



	number of properties			
country	communication pipes		internal plumbing/supply pipes	
Belgium	645 000	(19%)	500 000 – 1 200 000	(15–30%)
Denmark	0		0	
France	3 900 000	(39%)	10 200 000	(38%)
Germany	900 000	(3%)	2 700 000	(9%)
Greece (Athens)	<15 000		0	
Ireland	436 000	(50%)	442 000	(51%)
Italy	500 000	(?)	1 100 000 – 2 300 000	(5-10%)
Luxembourg	8 000	(7%)	0	
The Netherlands	358 000	(6%)	450 000	(8%)
Portugal	?		1 100 000	(32%)
Spain	>500 000		?	
UK	8 682 000	(40%)	8 884 000	(41%)

Source: van den Hoven et al. 1999

Australia

The Australian Drinking Water Guidelines (ADWG), published by the National Health and Medical Research Council (NHMRC), are similar in form and function to the Guidelines for Canadian Drinking Water Quality (Health Canada 2014) described in Chapter 1, serving as authoritative guidelines for the provinces to use to maintain good quality drinking water. The 2011 Australian guidelines, which were updated in 2016, specify a health-based limit of 0.010 mg/L, but note that "the issue of plumbosolvency is rare in Australia" (NHMRC 2016). The guidelines also note, in language similar to that used by NDWAC (EPA 2015a), that:

> "The primary responsibility for ensuring that water supplied beyond the water meter remains safe and aesthetically acceptable rests with various stakeholders including building and site owners or managers; plumbing and building regulators; plumbers; plumbing material suppliers; [and] private individuals. Under the catchment-to-consumer tap preventive management framework promoted by these Guidelines, however, water quality should be managed up to the point of consumption, usually the customer tap, to account for water quality changes that may arise as a result of the internal plumbing arrangements on customer properties. This management may be achieved by liaison between the water supplier and the stakeholders listed above."

Parkinson (2014) noted that historical use of LSLs in Australia was not as common as in the U.S. and Europe; nevertheless, lead solder and brass fitting used with copper service lines and interior plumbing can still cause lead to leach into the water upon standing, so consuming water from the first-flush in the morning can potentially pose a health hazard. Various entities in Australia, for example, Northwest Territory Government (2012), recommend flushing the tap for a short while (e.g., 30 seconds) in the morning before using the water. To examine the occurrence of lead, copper, and other constituents in tap water in New South Wales, where elevated tap-water lead levels had previously been reported, Harvey et al. (2016) analyzed 212 first-draw samples from taps in consumers' kitchens. Eight percent of the samples had lead concentrations exceeding the ADWG limit of 0.010 mg/L, and 5 percent exceeded the copper limit. Kitchen tap fittings were determined to be the primary source of the lead and copper found in the samples, and the authors recommended that such fittings be manufactured from materials free of lead and copper.

Given the limited use of LSLs in Australia, it is not surprising that the research team found little information during the course of the project regarding the use of linings or coatings on LSLs in Australia. However, several manufacturers noted that copper corrosion is a common problem in Australia, and both PET liners and epoxy coatings have been used there to rehabilitate copper service lines, especially to repair leaks and prevent future leaks. Tanner (2016) noted that the crew that installed the PET liners for the Louisville trial in 2008 had come over from Australia. An undated promotional brochure provided by Tanner stated that Australian Southeast Water has been experiencing problems with corrosion of copper service pipes, that PET lining had been introduced as an alternative to replacement, and that more than 350 PET liner installations had been performed in South East Melbourne in the first year after the technology was introduced there.

In Australia, as in other countries, materials used in drinking water treatment and distribution that come into contact with potable water must meet applicable standards. Australia and New Zealand Standard AS/NZS 4020 requires that products do not affect the taste or appearance of water; do not support the growth of microorganisms; and do not release cytotoxic or mutagenic compounds or metals (Australian Water Quality Centre 2009). The tests required are specific to the type of product submitted, as is also the case for NSF 61.

France

France used lead pipes extensively in drinking water distribution systems and household plumbing through the 1950s, with the use of lead pipes allowed through 1995. In 1999 there were an estimated 3.9 million LSLs remaining in France (39% of homes) (van den Hoven et al. 1999, Hayes and Kubala 2009). Prior to 1998, the allowable level for lead in drinking water in France was 50 µg/L. A 1998 EU directive reducing allowable lead concentrations to 25 µg/L in 2003 and 10 µg/L as of December 2013 (Council of the European Union 1998) has led to an extensive overhaul of France's drinking water distribution systems to meet these requirements.

The primary approach chosen for compliance with the lower lead limit has been replacement of existing lead service lines with other materials. At the end of 2013, it was reported that 2.7 million lead connections in the public water system had been replaced in France in the 15 years since the 1998 directive, with 1.2 million lead service connections still to be replaced (Minstere des Affaires sociales et de la Sante 2015). As in the United States, water utility responsibility ends at the point of delivery, so this replacement does not include private plumbing. Replacement rates on the private side are likely to be much lower.

The use of linings and/or coatings as an alternative to full LSL replacement has been demonstrated in France, but the research team was unable to find any definitive information in the literature on the extent of their use in France. Epoxy coatings meeting certain health-related requirements (based on chemical leaching) were approved for use in drinking water distribution systems as of at least 2003 (Epoxy Europe 2015); and Boyd et al. (2001) described several coating technologies being tested in France in the mid-1990s. Specific examples of these approaches by water utilities in recent years could not be obtained. Two epoxy coating manufacturers contacted by the research team stated that they had not lined any LSLs there. PET liners appear to have been more widely used. Alferink and Elzink (2010) estimated that 45,000 PET liners had been installed in France, but did not indicate the timeframe nor how many of the installations were associated with LSLs as opposed to the many other potential uses of PET liners. However, a company representative (Clayson 2017) stated that nearly all of the installations were in LSLs and there are now well in excess of 100,000 PET installations in France. PET lining was identified as part of the strategy for addressing LSLs in specific municipalities, e.g., in Melun (Toumit 2003) and Dole (Alferink and Elzink 2010). A search of the existing literature failed to find any retrospective studies addressing the long-term performance (durability and effectiveness in controlling lead) of PET liner installations in France. Clayson (2017) confirmed this, and indicated that PET lining of LSLs is now considered a routine and reliable solution.

Germany

Germany adopted the EU standard of 0.010 mg/L for lead in drinking water as of December 1, 2013. According to Umwelt Bundesamt (UBA, or Federal Environment Agency), Germany's equivalent to EPA, the new limit effectively spelled the end of LSLs in Germany. Under German law, if the lead limit in a pipe is exceeded, a water utility or landlord can be forced to eliminate the cause; and lead levels in lead pipes in Germany are generally higher than the 0.010 mg/L limit (UBA 2013). Fortunately, as shown in Table 5.3, Germany had relatively few LSLs remaining in service in 1999, long before the new standard took effect, and many of those were replaced when the standard was lowered to 0.025 mg/L in 2003 (Noll 2013). Many property owners did not remove their LSLs at that time, either because they were not informed that they should do so or because their lead levels did not exceed the limit (Noll 2013); and some presumably wished to avoid the cost of replacement. However, lead plumbing has not been used in buildings in Germany since 1970, and not for over 100 years in southern Germany (Zietz et al. 2010, UBA 2013); so, compared to some EU countries (Table 5.3), Germany already had relatively few privately-owned LSLs and few buildings with interior lead plumbing.

In Germany, connection pipes (utility owned service lines) are generally the responsibility of the water utility, and the water pipes on private property and in homes or other buildings are the responsibility of the owner, who "assumes responsibility for the good quality of drinking water and for the replacement of any lead pipes which may have been installed" (UBA 2013). By December 1, 2013, utility-owned LSLs had been largely if not entirely eliminated; and, per UBA (2013), if any lead pipes remained in private-side connections or inside building, the property owner was required to notify affected consumers in writings, whether or not lead levels exceeded the limit. The website of the utility serving the nation's capital, Berlin Water Services (2016), indicates that:

- Lead pipes are no longer used in the utility's distribution system
- Water will be tested for lead for free, by an accredited lab, for households with pregnant women or with children up to 12 years old (but others must pay)
- Compliance with the 0.010 mg/L limit depends on the supply pipes being free of lead, for which the owner of the house or building is responsible

In response to an inquiry about the use of linings and coating to rehabilitate LSLs in Germany, Klinger (2016) noted that:

- The German philosophy is that unsuitable materials cannot be protected by lining.
- Linings and coatings are not regarded as being sufficiently long-lasting.
- All utility-owned water service lines are now lead free because of replacement programs.
- At the moment, there is no successfully tested lining material suitable for use in small diameter pipes.

Some LSLs may have been replaced with stainless steel pipe, which is reportedly being used, at least in some instances, for domestic water supply purposes in Germany, Switzerland, Italy, and Denmark (Buijs 2011), and also in Japan, as discussed below.

Although UBA believes there are sufficient grounds for concern about BPA, they and the majority of EU member states believe that, with proper use of products containing BPA, there is no cause for concern about health risks; and, unlike France and Denmark, they have not enacted extra precautionary measures (UBA 2010). Germany also has de minimis guidelines for review of organic materials in contact with drinking water (UBA 2011). Their guidelines for coatings in contact with drinking water (UBA 2015, 2016) are in many ways similar to NSF 61 guidelines and include toxicology-based limits on leaching of BPA (12 µg/L), BPF (2.5 µg/L), and BADGE and its hydrolysis products (450 µg/L).

Ireland

Ireland’s national water utility, Irish Water, is regulated by (Ireland's) Environmental Protection Agency (EPA). Ireland's EPA sets drinking water standards based on EU and national regulations, and the legal lead limit on lead in drinking water in Ireland is the same as the EU's, 0.010 mg/L. In 2013, Ireland's EPA and the Health Services Executive (HSE) issued a joint position paper on lead in drinking water (EPA and HSE 2013). One of their many conclusions was that “all lead pipes and plumbing in public and private ownership should be replaced over time.” The position paper also stressed mitigation strategies, such as flushing before use, and recommended that an alternative source of water be used when lead levels remain above 0.010 mg/L, stressing the importance of this for infants, children, and pregnant women.

Using wording similar to that of NDWAC (EPA 2015a), EPA and HSE (2013) also took the position that “the responsibility for actions to reduce the level of lead in drinking water is collective and requires actions on behalf of the Water Services Authorities, property owners (public or private) and water suppliers or personnel installing or carrying out works on drinking water supply pipes.” Ireland’s Department of Environment, Community, and Local Government (DECLG) established a grant program to assist low-income households in replacing their lead pipes as part of a national strategy to reduce lead in drinking water developed by DECLG and the Department of Health (DoH) (DECLG and DOH 2015). The maximum grant is the lesser or €4,000 or 80% of the cost for those with household incomes less than €50,000, and the lesser of €2,500 or 50% of the cost for those earning between €50,000 and €75,000.

In 2016, Irish Water published and requested comment on a Draft Lead in Drinking Water Mitigation Plan (Irish Water 2016). As part of the mitigation plan, Irish Water is evaluating both PET liners and epoxy coatings, and has already conducted trials. Four different contractors were invited to demonstrate their technologies, each on a group of six LSLs buried in a trench and representing different conditions (with and without leaks, holes, and kinks). The results were described as a "work in progress," but the report did note that the demonstrations produced "mixed results" and "low levels of confidence in the methodologies ability to resolve all service issues." However, the report also noted that one supplier indicated that their technology was suitable for use in between 50 to 70 percent of lead connection pipes. The report concluded that:

- "Further trials and testing are required so as to generate a definitive set of results relating to compliance with the lead limit of 10 μg/L"
- "Lining of the lead service connection does not currently address the Irish Water objectives of long term lead removal, thereby leaving some legacy risk for customers"
- "The technology has certain advantages and is an ever evolving technology…. Irish Water will continue to monitor developments in this area and adjust our Plan as required to ensure that the most effective mitigation measures are utilised to achieve compliance target objectives"
- "Should it be deemed to be an effective mitigation option in the future, this non-invasive lead pipe rehabilitation would be an attractive option for customers and would minimise disruption associated with replacing privately owned lead supply pipes"

Japan

The current drinking water standard for lead in Japan is 0.010 mg/L (Ministry of Health 2017), consistent with World Health Organization recommendations. As of 2000, Japan was estimated to have approximately 12 million properties using lead water service pipes (Kirmeyer et al. 2000). According to Kawakita (1998):

- Lead service lines were used prior to 1980, when their use was replaced by stainless steel
- In the City of Tokyo, in particular, this decision was largely driven by effort to reduce leaks, presumably both to save water and to reduce repair work, especially under roads
- In 1980, the city's Bureau of Waterworks mandated that pipes less than 50 mm running under roads be made of stainless steel resistant to soil corrosion, and the bureau developed its own flexible, earthquake-proof joints to connect lengths of stainless steel pipe
- By 1997, about 80% of water service pipes were made of stainless steel, and leakage rate fell nearly in half, from 16.1 to 8.4 percent, between 1975 and 1997

Tokyo has continued targeting LSLs lines for removal as part of their overall leakage reduction activities (Bureau of Waterworks 2014). As in other countries, however, utility replacement activity does not typically address residential plumbing lines.

The use of epoxy coating for pipe rehabilitation is often cited as having begun in Japan. Kirmeyer et al. (2000) state that the initial use of epoxy coatings was to address aging service lines in Japanese buildings in the 1960s. Their report also contains multiple references to epoxy coating techniques developed in Japan for lining either gas service pipes or water supply pipes. At the same time, they say that, as of their report (2000), there was "no indication that any further developmental work of the above lining systems for lining water service pipes is ongoing in

Japan." A study of the existing literature for this report did not find more recent examples of LSL lining or coating applications in Japan, suggesting that this has not changed. Internal coating of water main pipes (usually ductile iron) as part of the production process using various materials, including epoxies or polyethylene, appears to be relatively common. This approach, however, would not be suitable for rehabilitation of existing service lines.

The Netherlands

The Netherlands adopted the EU directive of 0.010 mg/L lead as of January 1, 2006 (van Dongen et al. 2007). As in other European countries, older drinking water supply systems, particularly in more urban areas, used lead service lines extensively before 1945. Efforts to address lead pipes in distribution systems focused primarily on removal and replacement of the pipes themselves. As described in van Dongen et al. (2007) for a lead pipe removal project in the Hague, this process was often made more difficult by low levels of cooperation from customers, who were reluctant to replace their portions of the plumbing system due to disruption and inconvenience.

A significant and early study of PET liner installations in the Netherlands was described by Mesman et al. (1995), who assessed two pilot projects by the East Twente water supply company, conducted laboratory studies, and examined data provided by the manufacturer of the PET liners. In an initial study in Henglo, PET installation was attempted in ~20 LSLs, with a 90% success rate. In Enschede, PET liners were installed in the LSLs supplying 56 houses along a single street. Installation was completed in 1/2 in. LSLs at a rate of 8 to 10 pipes per day. The only issues reported were with pipes >12 m in length, as these pipes contained connections that caused problems for liner installation. The report concluded that the cost of PET lining would be lower than the cost of conventional replacement if the LSLs were at least 5 m long. For LSLs 12 m long, they estimated the cost savings to be about 20 percent, or about 40 percent when LSL replacement required wall penetrations and additional repaving. They noted that this cost comparison was valid only for the installations involved in the project, since the cost functions would vary with regional differences in prices and practices; however, others have reached similar conclusions, i.e., that, in the absence of obstructions (such as structures, trees, or other utility lines), lining or coating relatively short LSLs produces little or no savings over replacement.

Based on laboratory testing, Mesman et al. (1995) concluded that PET liners are resistant to incidental disinfectant application (e.g., high doses of chlorine used to disinfect a portion of the distribution system following repair work), and that the liners meet taste and odor standards. Based on assessment of existing data from burst stress tests provided by the manufacturer, they estimated a durability of at least 50 years. The biofilm formation potential of PET liners was determined to be similar to that of polytetrafluoroethylene (better known as Teflon®), and the authors concluded there should be little issue with biofilm growth.

A small-scale demonstration installation (two service lines) in Enschede in 1997 is also described in Kirmeyer et al. (2000). The use of PET liners in the Netherlands for LSL rehabilitation appears to be ongoing, based on data from the liner manufacturer (Alferink and Elzink 2010). However, further studies or follow-up investigations of the long-term performance of these early installations do not appear to be available in the current literature.

United Kingdom

The United Kingdom (UK), comprising England, Scotland, Wales, and Northern Ireland, limits the concentration of lead in drinking water to 0.010 mg/L. Lead concentrations are measured at the tap using 1-L first-draw samples collected during a random daytime visit. The regulations are enforced in England and Wales by the Drinking Water Inspectorate (DWI), a regulatory agency charged with "ensuring that water companies supply safe drinking water that is acceptable to consumers and meets the standards set down in law" (DWI 2017). Scotland and Northern Ireland have their own regulatory authorities. As is generally the case elsewhere, UK water companies are responsible only for the "connection pipes" (utility owned water service lines). In 2013, DEFRA solicited comments on a proposal to allow future regulations to transfer ownership of privately owned "water supply pipes" to the water companies (DEFRA 2013); but after the comment period ended, no legislative action was taken to proceed along these lines.

The UK's "water companies" are privatized water companies that operate as regulated monopolies in similar fashion to private water companies in North America. There are more than 20 water companies in England and Wales, and one each in Scotland and Northern Ireland. Some provide only water and others provide both water and sewerage services. Those in England and Wales are economically regulated by Ofwat (formerly the Office of Water Services and now the Water Services Regulation Authority), which every five years sets the rates water companies are allowed to charge customers for their services (Ofwat 2017).

DWI can require a water company to replace or rehabilitate service lines when the lead limit is exceeded, and can also require treatment, where practical and effective, to help property owners meet the limit (DWI 2012). The most common treatment is orthophosphate dosing. Fortunately, of the 3,483 samples analyzed for lead in 2015 in England and Wales, only 10.9 percent exceeded the limit, and most of these were due to the presence of lead plumbing in older properties (DWI 2016). However, since roughly two-thirds of the millions of lead pipes estimated to be present in the UK in 1999 (Table 5.3) are still in service, exceedances of the lead limit will continue to occur, and further action is needed to reduce their frequency. For this reason, Ofwat approved water rates and business plans for some water companies that include the cost of replacing or rehabilitating a substantial number of LSLs during the current five-year asset management period (AMP6), the sixth such period since UK water companies were privatized, covering the years 2015-2020.

Since the cost of replacing lead connection and water supply pipes is estimated to be quite high, approximately €1,000 to €4,000 per house according to Hayes (2012), rehabilitation of LSLs by lining or coating them, in lieu of replacement, is receiving considerable interest as a possible cost saving measure. Furthermore, since water companies are evaluated in part on customer satisfaction and the level of service they provide, lining and coating methods are also of interest because of their potential to minimize disruptions and to avoid damage to property, landscaping, and other utilities. Return-to-service times are also important, since water outages can reflect negatively on a water company's performance and are a factor in setting rates for water service.

Beginning in the 1970s, the UK played a leading role in the development of potable water applications of epoxy coatings, initially focusing on in sit*u* rehabilitation of water mains and later exploring lining and coating of smaller-diameter pipes, including water service lines. The organizations involved in this research, and in other research related to water supply and water quality, include not only those mentioned above (DWI, DEFRA, Ofwat, and the water companies), but also WRc (formerly the Water Research Center, before it was privatized) and UKWIR (UK Water Industry Research, an organization similar in some ways to the Water Research Foundation and whose members are 20 water companies).

DWI approval is required for products used by the water companies that come into contact with drinking water; and DWI publishes, at least annually, a list of approved products. DWI approved products are sometimes referred to as DWI Reg. 31(4)(a) approved, making reference to the applicable water supply (water quality) regulation. As part of the approval process, linings or coatings, installed as directed in the manufacturer's instructions for use, are extracted with chlorinated and unchlorinated water. Samples of each are tested by a qualified lab against BS 6920 (British Standards Institution 2014), which evaluates effects of products on water quality, including odor, flavor, appearance, growth of aquatic microorganisms, and substances that may be of concern with respect to public health. Once approved, the products must be installed in strict accord with the instructions for use.

The UK's high incidence of LSLs and its historic acceptance and use of lining and coating technologies for rehabilitating water mains, coupled with the recent lowering of the lead standard for drinking water in the EU, set the stage for the UK to play a leading role in studying, testing, and installing linings and coatings in LSLs. During the past two decades, numerous demonstration tests have been conducted in the UK on LSL lining and coating technologies, involving a number of water companies as well as leading manufacturers, some of which are now reportedly under contract or negotiating contracts to perform hundreds or thousands of lining or coating installations on LSLs. Examples of past, on-going, or pending demonstrations and live installations in the UK include:

- Tuckwell (1996) reported lead concentrations in tap-water samples collected before and after installation of a PET liner in the LSL of a house served by Wessex Water. The initial lead concentrations were 75-110 µg/L, but in 16 of the 17 tap-water samples collected 5 to 25 months after the PET liner was installed, the lead concentration was equal to or less than the detection limit (5 µg/L), and it was 7 µg/L in one sample.
- Kirmeyer et al. (2000) and North West Water conducted a demonstration test to evaluate PET lining of three LSLs in Blackburn, Lancashire.
- Yorkshire Water, seeking an alternative to moling due to the proximity of rocks to the surface in much of its service area, joined 3M and Whirlwind Technologies in a consortium to test and develop a cleaning and lining process suitable for use on lead communication pipes (Haley 2012), a process now known as the Serline^{TM} process.
- Reed (2012) stated that hundreds of lead pipes had been lined over an 18-month period as part of the trial of the Serline^{TM} system in Yorkshire, and that trials were being conducted by Anglian Water to evaluate the ePIPE$^{®}$ epoxy-coating process marketed through Pipe Restoration Services.
- Severn Trent Water conducted a demonstration in which 176 connection pipes and 71 water supply pipes were epoxy coated using the ePIPE$^{®}$ process, some from the main to the first internal tap; and the tap-water lead levels were consistently reduced to well below 10 µg/L (Gillanders 2015). In a follow-up study of 19 dwelling units, all having initial tap-water lead levels above 10 µg/L (13 above 25 µg/L), samples collected 12-18 months after lining had lead levels ranging from <0.5-4.2 µg/L, with an average of 1.3 µg/L (Gillanders 2016b).
- Affinity Water has reportedly contracted with Aquam Corporation to line LSLs for 29,000 homes with a hybrid PUA/PUR liner using the Serline^{TM} process (Farr 2016, Manners 2017b), and has also contracted with Pipe Restoration Services Limited to line LSLs for 30,000 to 40,000 homes in the Watford and Finchley areas of London with epoxy using the ePIPE$^{®}$ process (Gillanders 2017).

- Yorkshire Water recently partnered with Aquam Corporation to line LSLs for 1,000 homes using the Serline^{TM} process in conjunction with vehicles designed to provide bypass water to the homes as the lining is installed (Aquam Corporation 2017).

CHAPTER 6
SUMMARY AND CONCLUSIONS

OVERALL SUMMARY

The purpose of this research project was to evaluate lead service line (LSL) lining and coating technologies as alternatives to full or partial LSL replacement, and as a means of protecting and repairing copper service lines (CSLs), and to provide information and recommendations to water utilities, engineering consultants, consumers, property owners, state and provincial regulators, and other stakeholders to assist them in making informed decisions regarding lining and coating of both lead and copper service lines. To accomplish this, the investigators:

- Gathered, reviewed, and critically evaluated published and unpublished articles and reports regarding lining and coating of water service lines and the technologies and materials used
- Sought and obtained information from water utility personnel (especially utility and distribution system superintendents); consulting engineers; technical experts having specialized knowledge in relevant subdisciplines; state regulatory agencies and regulatory agencies outside the U.S.; NSF International and other organizations involved in product certification; and manufacturers of lining and coating technologies and their representatives
- Identified issues stakeholders should consider before lining or coating LSLs, and developed a list of criteria for evaluating lining and coating technologies
- Identified lining and coating technologies potentially suitable for controlling lead release from LSLs and evaluated them with respect to their availability, effectiveness, cost, ease of installation, suitability for use in contact with potable water, estimated and warranted service life, potential impacts on water quality, and other advantages and disadvantages
- Identified three promising technologies and conducted laboratory studies on two of them – epoxy coating and polyethylene terephthalate (PET) lining – focusing primarily on their effectiveness in controlling lead and copper release and their potential to leach chemical constituents that might be of concern with respect to health or water quality issues (The third technology is relatively new and samples of the material used could not be obtained.)
- Based on the results of the above efforts, developed general recommendations for all stakeholders and more specific recommendations for water utilities and their consultants; consumers and property owners; state and provincial regulators; and manufacturers and contractors

The investigators conclude that three currently available lining or coating technologies can effectively reduce or eliminate release of lead from LSLs, are expected to have a long service life, and can potentially result in significant cost savings and other benefits relative to LSL replacement, depending on site-specific conditions. Other possible benefits include fewer and shorter disruptions of vehicular and pedestrian traffic; reduced damage to landscaping, trees, sidewalks, and driveways; less potential for damage to other utility lines (gas, electric, phone, cable, sewers); and facilitating delay of LSL replacements until they can be more efficiently and more cost-effectively performed in concert with main rehabilitation or replacement projects that may be scheduled many decades in the future. Therefore, the investigators recommend that lining and coating technologies be considered by all stakeholders to be potentially useful tools for reducing public exposure to lead through drinking water; that public water systems and property owners consider using them, to the extent permitted by all applicable regulations, in situations where significant cost savings and/or other benefits can be realized; and that their possible use be incorporated into well organized, system-wide LSLR programs to help minimize costs and maximize benefits.

Three technologies are deemed to be especially promising and are therefore recommended for consideration by both public water systems and property owners: PET lining, epoxy coating, and polyurea/polyurethane coating. Each of these technologies can effectively reduce or eliminate lead release and is, or has been, commercially available and certified for use in contact with potable water in the U.S., Canada, and/or the UK. Each of these technologies involves materials that could potentially affect water quality by leaching certain constituents into the water; but that is true of every material that is used, or could conceivably be used, in water service lines. This issue has been effectively addressed for many years by requiring any material that may come into contact with potable water, in a public water system, to be certified as meeting NSF/ANSI Standard 61.

OTHER RESULTS AND CONCLUSIONS

Laboratory Experiments on Epoxy-Coated LSL and CSL Sections

The effectiveness of epoxy coatings in limiting lead release from LSLs was demonstrated in fill-and-dump experiments on 4-ft. lengths of LSLs obtained from the Rochester (NY) Water Bureau. The lead concentrations in samples from a heavily disturbed uncoated control LSL section ranged from 1,200 to 25,000 µg/L, whereas lead was non-detectable (≤0.5 µg/L) in 16 of 27 samples drawn from the epoxy-coated LSL sections. Only one sample (from the first extraction of an epoxy-coated pipe section after a 6 h holding time) had a lead concentration exceeding the AL, and when the same pipe section was extracted twice more with low pH (6.5) water, first for 6 h and then for 4 d, neither sample contained a detectable amount of lead. Epoxy coatings also effectively limited release of copper from epoxy-coated CSL sections (4-ft. lengths of virgin copper pipe). The mean increase in copper concentration was only 5.3 µg/L, a negligible increase relative to the levels observed in samples from the control section (270–910 µg/L) and relative to the action level for copper (1,300 µg/L); and some or all of the increase may have been due to leaching from the fittings used on the ends of the CSL sections, leaching from the epoxy itself (which contained a small amount of copper), or traces of copper left in the CSLs when they were flushed with tap water.

Freshly applied epoxy coatings exposed to chlorinated extraction water in fill-and-dump experiments exerted a strong demand for free chlorine. Most of the chlorine was consumed in 6 h, and only traces remained after 24 h. Follow-up experiments on epoxy-coated pipe sections yielded similar results for both free and combined chlorine; for pipes stored for 7 months, whether they were stored wet or dry; and for pipes repeatedly exposed to a high concentration of free chlorine (100 mg/L as Cl_2). Triethylenetetramine (TETA), a common epoxy ingredient, was found to react with both free and combined chlorine in a manner similar to what was observed in fill-and-dump experiments on epoxy-coated pipe sections. Since chlorine was found to be unreactive with the major ingredient in the epoxy resin, these results suggest that chlorine is reacting primarily with constituents in the amine-based hardening agent.

A significant chlorine demand associated with a lining or coating could potentially influence biofilm growth, disinfection byproduct formation, or other water quality parameters in a service line or downstream interior plumbing. However, in this project, the chlorine demand of the uncoated control pipe sections in the initial fill-and-dump experiments was similar to that observed in the epoxy-coated pipe sections, suggesting that, at least in some cases, the chlorine demand associated with an epoxy coating may have little or no net impact on water quality.

Freshly applied epoxy coatings were found to leach an average of 0.58 mg/L of TOC into two of the extraction waters, but there was no significant change in the average TOC concentration of samples obtained using dechlorinated pH 8 tap water as the extraction water. TOC leaching from epoxy coatings into water is expected to decrease over time, to negligible amounts, and a study on aged epoxy coatings (Jackson et al. 2007) supports this expectation.

Freshly applied epoxy coatings were found to leach low concentrations of bisphenol A diglycidyl ether (BADGE) and two BADGE hydrolysis products. Finding BADGE was not surprising, since the epoxy was known to contain BADGE; and BADGE is included in NSF 61 certification testing for epoxy coatings in contact with potable water. Leaching of these compounds from epoxy is expected to decrease over time. In this study, two epoxy-coated pipe sections were stored wet for 7 months, with the water replaced with fresh reagent water every 7 days. When these pipe sections were again extracted in a series of fill-and-dump tests, BADGE and one hydrolysis product were not detected in any of the samples, and the second BADGE hydrolysis product was detected in only a single sample, the first sample collected, at a concentration of 1.8 µg/L, slightly above the detection level of 1.0 µg/L. This compound was not detected in any samples with holding times of 7 d, nor in any samples collected after the pipe sections were reflushed.

Although leaching of BADGE from epoxies into potable water is already addressed by NSF 61 certification requirements, the investigators wondered: 1) how fast BADGE was hydrolyzing, which would affect human exposure to both BADGE and its hydrolysis products; 2) whether these compounds were reacting with free or combined chlorine to form other, unrecognized and unregulated byproducts; and 3) whether bisphenol A (BPA), a chemical over which there has been considerable controversy in recent years, might be hydrolyzing or reacting with chlorine and therefore going undetected. Therefore, additional experiments were conducted to examine hydrolysis and chlorination of BADGE, BPA, and bisphenol F diglycidyl ether (BFDGE), another common epoxy ingredient already included in NSF 61 certification testing.

BADGE hydrolysis was studied as a function of pH (2–12) and temperature (15–40 °C). BADGE was found to hydrolyze to BADGE-H_2O and then to BADGE-$2H_2O$, and mass balances show that BADGE-$2H_2O$ is the major end product under these conditions. Experimentally measured BADGE hydrolysis rates agreed well with modeled rates; thus, the model can be used to estimate BADGE concentrations remaining in water over time, facilitating exposure assessments. The half-lives of BADGE at pH 7 and 15, 25, 35, and 40 °C were found to be 11, 4.6, 2.0, and 1.4 days, respectively. At 25 °C and pH 2–12, BFDGE hydrolyzed at a rate very similar to that of BADGE, with a half-life of 5 days at pH 7 and 25 °C. No hydrolysis or decay of BPA was observed for reaction times up to 30 days for pH values of 2–12 at 25–40 °C.

Chlorination of bisphenols and BADGE was investigated using both free chlorine (~2 mg/L as Cl_2) and combined chlorine (~4 mg/L as Cl_2). In contrast to the results for hydrolysis, BADGE was found to be unreactive with free or combined chlorine at pH values of 7.6–9.0 at 25 °C, but the bisphenols reacted relatively rapidly with free chlorine at pH values of 3–12 at 10–25 °C. Estimated BPA half-lives for a free chlorine residual of 1 mg/L as Cl_2 ranged from 3–35 minutes at pH values of 6–11 over the temperature range of 10–25 °C, but half-lives of 1–10 days were estimated for a monochloramine residual of 3.5 mg/L as Cl_2 under similar conditions. These results and a model based on them can be used to characterize the concentrations of bisphenols and BADGE in drinking water distribution systems, after leaching from epoxy coatings, thereby facilitating future risk assessments.

Laboratory Experiments on PET-Lined LSL and CSL Sections

In fill-and-dump experiments on PET-lined LSL and CSL pipe sections, very high lead and copper concentrations were found in samples drawn from the unlined (control) LSL and CSL pipe sections; lead increased by 1,400–21,000 µg/L, and copper by 310–910 µg/L, respectively. Only trace amounts of lead were found in the samples from the PET-lined pipe sections. In one fill-and-dump experiment, the maximum concentration found was only 2.9 µg/L, in a sample from a PET-lined CSL. The average lead concentration found in samples from PET-lined LSLs was 1.2 µg/L, and the average found in samples from PET-lined CSLs was 1.3 µg/L. In a second fill-and-dump experiment involving LSL and CSL pipe sections re-lined with PET, the average lead concentration found in samples from the PET-lined LSLs was 1.9 µg/L, and the average found in samples from the PET-lined CSLs was 1.0 µg/L. The levels found in both experiments were only slightly above the method detection limit (0.5 µg/L) and about an order of magnitude lower than the AL for Pb (15 µg/L). The investigators believe the traces of lead found in these samples came from the fittings used on the ends of the pipe sections (any effects of which would have been accentuated on relatively short LSL sections) and from inadvertent contamination during sample collection and handling, and not from lead permeating through the PET lining, which would not be expected to occur.

Antimony is a common ingredient of PET, so the samples from the first fill-and-dump experiment on PET-lined pipe sections were also analyzed for antimony (Sb) in addition to lead and copper. Sb was detected in all but two samples, but the concentrations were very low. The average increase in Sb using dechlorinated pH 8 tap water as the extraction water was only 0.09 µg/L; the increases using chlorinated pH 8 and low pH (6.5) extraction waters were 0.09 and 0.29 µg/L, respectively; and the median increase for both LSLs and CSLs was 0.13 µg/L. The Sb concentrations increased with holding time, from an average of 0.09 µg/L for samples held 6-24 h to an average of 0.33 in samples held 4 d. The antimony concentrations in all of the samples from PET-lined pipe sections were not only well below the MCL (6 µg/L) but also below the concentrations found in samples from the unlined LSL control section (0.42–3.94 µg/L). Thus, despite the small increases in antimony that were observed, PET liners can actually reduce exposure to Sb if there is Sb present in the pipe being lined, as was the case for the LSL sections used in this study. PET liners (and epoxy coatings) can also serve as effective barriers against numerous other traces constituents found in pipe deposits.

There was no significant increase in TOC associated with the PET liners. None of the 10 phthalate esters determined using GC-MS and none of the 3 phthalic acids determined using LC-MS/MS were detected in any of the extraction water samples; nor were these compounds detected in solvent extracts of an unexpanded section of PET liner. The PET liners exhibited very little chlorine demand in the first set of fill-and-dump tests; only about half of the initial free chlorine residual of 2 mg/L as Cl_2 was consumed after 96 hours. In subsequent tests, the chlorine demand dropped to less than 0.1 mg/L in 24 hours.

Experiences in the United States, Canada, and Elsewhere

When evaluating new technologies, or when developing or revising a program to address a complex and important challenge, it is often helpful to consider the experiences of others – what they have tried, what worked well and what did not, what could be done differently or better in the future, and what aspects or program elements are most applicable to the local situation being addressed. For this reason, brief case studies were prepared to describe the challenges faced by eight utilities in the U.S. and Canada in dealing with their LSLs, and to describe practices and experiences in other countries in lining, coating, and replacing lead and copper water service lines.

Over the past two decades there have been demonstration trials of PET lining and epoxy coating installations in LSLs in a number of locations in the U.S., Canada, and in various locations elsewhere around the globe. More recently, a new polyurea/polyurethane coating designed for use in LSLs has been successfully demonstrated and approved for use in the UK. In the U.S. and Canada, few lining or coating installations in LSLs have been left in place, since most were solely for demonstration purposes. In other locations, outside North America, larger trials have been conducted, and greater numbers of linings or coatings have been installed in LSLs that remain in service. One manufacturer reports having installed more than 100,000 PET liners in LSLs in France, and manufacturers of two different coating technologies (one using an epoxy product and the other a polyurea/polyurethane product) are reported to have recently signed contracts for tens of thousands of installations in the UK.

What is clear from these trials and installations, based on lead levels measured before and after the linings or coatings were installed, is that linings and coatings can and do effectively reduce lead leaching from LSLs. What is less clear is how many linings and coatings installed in LSLs remain in service, how long they have remained in service, and how well they have performed over time with respect to both effectiveness in controlling leads levels and physical durability. Attempts to obtain such information from utilities, manufacturers, and the literature were largely unsuccessful, apparently because retrospective studies on linings and coatings installed in LSLs are rare. However, the limited information available from studies of lined or coated LSLs, and from other studies involving related applications (e.g., epoxy coating of water mains), indicates that PET liners and epoxy coatings are durable and can be expected to remain effective for very long periods of time. These technologies are old enough that some installations have now been in place for more than 30 years, and manufacturers report that they are holding up well, although those contacted by the investigators said they were not aware of any retrospective studies on older installations of their products. The investigators have identified this as a research need that could potentially be addressed by well-designed surveys (which were not permitted in this project under the terms of the funding agreement).

Anticipated LCR Revisions and the Use of Linings and Coatings

A report by the LCR Working Group of the National Drinking Water Advisory Committee in the U.S. (NDWAC; EPA 2015a) recommends full replacement of LSLs, to the building wall, over a 30-year front-loaded timeframe. Developing an LSLR program that ultimately replaces all LSLs all the way to the building wall (which necessarily includes LSLs on private property) will be a challenge for every public water system in the U.S. that has LSLs in their service area. The NDWAC report did not address linings and coatings, nor is clear whether they will be addressed in future revisions to the LCR or, if they are addressed, what the relevant provisions will be.

Challenges public water systems will encounter as they develop or revise system-wide LSLR programs will include: significant financial costs; disruptions of vehicular and pedestrian traffic; damage to structures, historic sites, landscaping, and other utility lines (gas, electric, sewer, and telecommunications); and the reluctance of property owners to replace their LSLs, if not mandated. Lining and coating technologies can potentially help public water systems and property owners meet these challenges, and to promptly and effectively reduce human exposure to lead in drinking water. Therefore, public water systems and property owners should consider using them for these purposes, when and where their use is advantageous, to the extent permitted by all applicable regulations and certification requirements.

RECOMMENDATIONS FOR FUTURE RESEARCH

The epoxy used for experimental purposes in this study exerted a strong demand for both free and combined chlorine. Based on discussions with various epoxy manufacturers and technical experts, this is known to be true of at least some other epoxies, and based on typical epoxy formulations it is reasonable to assume that most if not all epoxies used in contact with chlorinated water will exert a demand for both free and combined chlorine, whichever form is present. If so, this is potentially significant with respect to maintaining residual chlorine concentrations in distribution systems, controlling biofilm growths, disinfection byproduct formation, taste and odor control, and other aspects of drinking water quality. Therefore, the investigators recommend:

- Testing the chlorine demand of other epoxy coatings certified for use in contact with potable water, not only those used in LSLs but also those used to coat the inside of other components of distribution systems, such as water mains, pumps, pipes, water storage tanks, and valves, as well as those used to coat water lines inside homes and buildings to control corrosion and repair leaks
- Long-term testing of representative epoxy coatings (or studies on sections of pipe that were epoxy coated many years ago) to examine their chlorine demand over time and to determine whether this has any effect on their physical properties, such as permeability and adhesion, and on their ability to control corrosion, prevent leaks, and (where applicable) control lead release
- A study to examine the interactions of free and combined chlorine with the surface of epoxy coatings and to determine whether residual chlorine is available on the surface of the epoxy (perhaps in the form of organic chloramines) and, if so, whether it is capable of oxidizing chemicals in solution and has any germicidal properties
- A study of homes and buildings with and without epoxy-coated water lines to see if there are significant differences in the chemical or biological quality of the water that may be attributable to the use of epoxy coatings (which would presumably be much more pronounced in homes and buildings with epoxy-coated interior plumbing than in those having only an epoxy-coated service line), with follow-up studies as needed to determine the cause of any differences noted, and factors influencing those differences

PET liners performed as very effective barriers to Pb and Cu in this project, but the research did not experimentally address the long-term performance PET liners. Additionally, the available literature contains little information on aging of PET liners or their estimated service life. It is unclear how suitable comparisons to studies of HDPE, or similar materials used in stand-alone pipes, are in this regard, since liners could experience issues related to corrosion or breakage of the surrounding pipe that would not affect stand-alone materials. Where possible, the investigators recommend that long-term testing of PET liners, or testing of PET lines that have been in service a long time, be conducted to examine 1) their long-term stability under potable-water conditions (including the long-term effects of exposure to chlorine disinfectants); 2) the leaching of antimony from aged PET; and 3) the long-term likelihood of Cu and Pb diffusion through the liner as it ages. Accelerated aging tests could also be carried out, although the notably different behavior of PET observed at higher temperatures in existing studies would require careful development of a suitable protocol for such tests.

Use of polyurea (PUA) and polyurethane (PUR) coatings is reportedly growing rapidly in many areas of application, though they still represent only a small share of the market for drinking water applications relative to epoxy coatings. None were tested as part of this project, but one PUA/PUR coating suitable for use in water service lines came on the market several years ago in the UK, and may soon be available for use in the U.S. and Canada. Perhaps other PUA or PUR products suitable for coating water service lines will become available in the future. Tests similar to those recommended above for epoxy coatings are also recommended for PUA and PUR coatings, which are also expected to exert a significant chlorine demand and to leach measurable amounts of organic matter for a period of time after they are installed.

Consumers, and perhaps most utility personnel as well, are less familiar with PUA and PUR than they are with PET and epoxies, which most people knowingly encounter on a daily basis and tend to view favorably. The investigators recommend research to pull together information on PUA and PUR coatings and incorporate it into educational materials that can be used to help familiarize public water system personnel, consumers, and others with their properties, their many uses in common consumer products, efforts to minimize the use of toxic chemicals (such as isocyanates) in manufacturing them, and certification to NSF 61 to address concerns about chemicals that may leach out of them into potable water – the same standards used for other materials in contact with potable water. Such materials would help facilitate public discussion of options for controlling lead in drinking water.

Surveys were not permitted under the terms of the grant that supported this project, but surveys conducted using other sources of funding could prove helpful in efforts to reduce human exposure to lead released from LSLs. Surveys of current practices, attitudes of consumers and property owners, perceived costs and benefits of lead control strategies, and other aspects of lead exposure and control options could prove helpful in several ways. In the short term, they would be helpful to various stakeholders in formulating comments in response to proposed revisions to the LCR, and developing suggestions for modifications that might improve the effectiveness or reduce the cost of the revised rule. They would also be helpful to public water systems with LSLs as they worked to adopt or revise LSLR programs to comply with the revised rule. Furthermore, they would also be helpful in the future by serving as a benchmark for reviews of progress or studies of changing attitudes or practices among both consumers and utility personnel. A survey done before a revised LCR takes effect would provide an opportunity to document subsequent changes in practices and attitudes. A well-designed survey of the effectiveness and durability of the numerous PET liners installed in France could potentially be very helpful in assessing the long-term performance of that technology. Surveys of water utilities and customers involved in current large-scale LSL coating programs in the UK would potentially be helpful in evaluating current costs, customer satisfaction, and things that could be improved in future programs of this sort.

CHAPTER 7
RECOMMENDATIONS TO STAKEHOLDERS

Based on the results of the research summarized in earlier chapters of this report, recommendations were developed for key stakeholder groups. General recommendations were developed for all stakeholders, and more narrowly tailored recommendations were developed for utilities (public water systems) and their consultants; consumers and property owners; state and provincial regulators; and manufacturers and contractors. Readers should note that since this project was funded by EPA, the investigators are not permitted to provide recommendations or other advice to EPA, as part of this project, regarding policy or regulatory matters. Comments here in this chapter or elsewhere in this report regarding regulatory matters are either factual or, like the recommendations below, are directed to state, provincial, and other non-federal regulators, and not to EPA.

GENERAL RECOMMENDATIONS TO ALL STAKEHOLDERS

Since 1991, when EPA finalized the Lead and Copper Rule (LCR), knowledge regarding the sources and effects of lead exposure has evolved, as has knowledge of the occurrence and control of lead in drinking water, including the effectiveness and limitations of optimized corrosion control and full or partial lead service line replacement (LSLR). From the exposure perspective, it is now generally accepted a safe level of lead in drinking water cannot be established; thus, the goal from a public health perspective should be zero. The health risks of lead exposure are greatest for those least able to protect themselves, i.e., those still in the womb, infants, toddlers, and young children.

The NDWAC LCRWG (EPA 2015a) recommended the removal of all lead services lines, all the way to the building wall, over a 30-year timeframe. The NDWAC LCRWG also concluded that "[minimizing] exposure to lead in drinking water is a shared responsibility; public water systems, consumers, building owners, public health officials and others each have important roles to play." The authors agree with this assessment, and recommend that manufacturers of LSL lining and coating systems be counted by all stakeholders as being among the "others [having] important roles to play."

Linings and coatings can effectively reduce exposure to lead, on either a short-term or long-term basis, and should be considered tools that can be used for that purpose, where appropriate, taking their pros and cons into consideration on a site-specific basis. Any system-wide lead control or LSLR program is going to be full of challenges, and linings and coatings can potentially play an important role in meeting some of those challenges in a timely and cost-effective manner. Besides reducing exposure to lead, linings and coatings may also provide other water-related benefits, including:

- Corrosion control
- Leak repair
- Improved hydraulics (flow and pressure)
- Elimination of metal leaching from scale deposits
- Less favorable conditions for biological growth
- Improved aesthetic quality of water (taste and odor, clarity, color)

Other potential advantages of linings and coatings include:

- Fewer and shorter disruptions of vehicular and pedestrian traffic
- Reduced damage to landscaping, trees, sidewalks, and driveways
- Less potential for damage to other utility lines (gas, electric, phone, cable, sewers)
- Increased property value (relative to leaving an LSL in service)
- Cost savings relative to LSL replacement, especially where service lines are buried deep in the ground to avoid freezing, where the soil or subsoil is rocky, or where other factors render less expensive replacement methods impractical
- Facilitating delay of LSL replacements until they can be more efficiently and more cost-effectively performed in concert with water main replacement and rehabilitation projects

Potential disadvantages of linings and coatings include:

- Resurfacing of a lead problem in the future, if the lining or coating deteriorates, even if that happens many decades later, since the LSL remains in place
- Uncertainty regarding their service life, which though expected to be very long is likely to be known with less certainty than that of a new copper service line (though perhaps with no less certainty than the service life of alternative water service line materials, such as plastic pipe, being used or considered for use because of the high cost of copper)
- Any monitoring that may be required to verify continued performance
- Disparities between anticipated service life and warranty period
- Failure to meet future regulatory requirements
- Leaching of traces of various constituents into the water

Linings and coatings could potentially leach chemical constituents into the water, or fail to meet future regulatory requirements, but that is true of every material that is used, or potentially could be used, in water mains, service lines and interior household plumbing. The leaching concern is currently and effectively addressed by requiring materials in contact with drinking water, including plumbing materials and linings and coatings, to be certified as meeting NSF 61. The known health risks of lead exposure far exceed those associated with traces of other constituents that may leach from other plumbing materials, including linings and coatings. Thus, concerns about leaching of trace chemicals should not be used as an excuse to avoid lining or coating an LSL to reduce exposure to lead. Nevertheless, reasonable caution is recommended in selecting materials for applications involving materials that are difficult and expensive to replace, such as water service lines and household plumbing, in contrast to materials used above ground, such as exposed process piping and water treatment chemicals, which can be more readily replaced if the need arises.

Since 1991, partial LSLR has been the dominant practice by most public water systems, primarily for two reasons. First, the overwhelming majority of property owners with an LSL have chosen not to replace their portion of LSL, even when invited by a public water system to save money by splitting the cost of a full LSLR. Since lining and coating technologies can potentially reduce costs even further, while also minimizing damage to landscaping and other disruptions, they should be considered by all stakeholders as an alternative means of eliminating lead release from customer-owned LSLs that are not replaced. Second, most public water supply systems replace LSLs only when they are encountered in the distribution system during normal activities (such as repairing leaks or replacing water mains), unless their systems exceed the action level for lead and they are placed on a mandatory LSLR schedule. They take this approach primarily because they are striving to avoid or minimize future rate increases, a goal which they view as being in the best interest of the customers and which receives strong public support. Gradually replacing LSLs over an extended period of time, as opportunities present themselves, is viewed as a good way to minimize costs.

Support for gradual approaches relying primarily on partial LSLRs is currently eroding, in part because partial LSLRs fail to eliminate an important source of lead (the privately-owned portions of the LSLs) and in part because of growing concerns regarding both the short-term and long-term effectiveness of partial LSLRs. For these and other reasons, the NDWAC LCRWG (EPA 2015a) recommended a full LSLR approach and proposed that it be completed by all public water systems within 30 years, with the majority of the LSLRs completed within 15 years. This approach is gaining support, not only because of NDWAC's recommendations but also because of growing public concerns about lead in drinking water, which were raised to a new level by the widespread publicity surrounding the crisis in Flint, MI Subsequent investigations have revealed that elevated lead levels may be present in homes, schools, and other buildings in the older areas of many communities nationwide in the U.S. Therefore, public support for full LSLR on an accelerated schedule is likely to increase, and this approach may soon become the preferred approach for many, if not most, public water systems and for most properties. There is speculation that such an approach may even become mandatory in the U.S., depending on the changes to the LCR that EPA is expected to propose in 2017.

The cost of a full LSLR program, especially if implemented on an accelerated schedule, will clearly be higher than the cost of a partial LSLR program implemented over a longer timeframe. Cost estimates for a full LSLR vary widely, but most fall within the range of $2,000 to $8,000 per service line, with those in lower half of this range being more likely for a well-organized, system-wide LSLR program. Property owners are typically required to pay only for replacing their portion of the LSL, but the cost of replacing the utility-owned portions will ultimately be paid by the system's customers as they pay their water bills.

Public water systems should recognize that the cost of replacing the privately-owned portion of an LSL will be very significant to most homeowners, especially those in less affluent neighborhoods. At the same time, public water systems need to recognize, and help property owners recognize, that the cost of replacing an LSL is typically modest compared to other costs of property ownership such as painting a house or building, putting new shingles on a roof, or replacing a major component of an aging heating, ventilating, and air conditioning system. Public water systems can help mitigate the impacts of LSLR expenses on property owners using creative financing arrangements, such as adding a small monthly charge to their water bill, as noted by the NDWAC LCRWG (EPA 2015a).

To minimize the cost of a full LSLR program, all stakeholders should work cooperatively to plan and implement a proactive system-wide approach, taking advantage of economies of scale and maximizing the productivity of the various work crews involved in scheduling, site preparation, traffic control, installation, and road and sidewalk repair. The approaches used by public water systems in Madison (WI), Lansing (MI), and Saskatoon (SK) are excellent examples of how to plan and implement a system-wide approach.

In planning a system-wide LSLR program, all stakeholders should evaluate using lining and coating technologies, if permitted under all applicable regulations, in locations where they have potential to generate significant cost savings (or to provide other benefits). Examples include:

- Congested urban areas, where construction activities and traffic disruptions need to be minimized
- Locations where installing a new service line poses a safety risk, e.g., puncturing a gas line, cutting into an underground electrical wire, or damaging a communications cable serving a large office building
- LSLs connected to a water main, perhaps one in a congested urban area, that is not scheduled to be replaced for another 30-50 years
- Homes for which LSLR would pose a significant risk of damage to landscaping, other utility lines, or structures

The LCR does not currently address the use of linings and coatings as a compliance strategy in the U.S., and it is not yet known whether linings and coatings will be addressed in the revisions to the LCR expected to be proposed in 2017. All U.S. stakeholders who have considered or evaluated the use of linings and/or coatings to control lead release from LSLs, and who have formed opinions regarding their use for compliance purposes, as either an interim or long-term solution, should carefully review the proposed revisions to the LCR, when they are proposed, and consider submitting comments to EPA.

RECOMMENDATIONS TO WATER UTILITIES AND THEIR CONSULTANTS

Public water systems with LSLs should take the lead in working with all stakeholders to cooperatively plan and implement a proactive system-wide LSLR program. The managers and employees of a public water system usually have a wealth of knowledge about their system and are already in communication with most if not all of the other stakeholders, who will be looking to the public water system to provide leadership. They will also bear primary responsibility for paying for the LSLR program and fairly allocating the costs among the rate payers.

Public outreach will be an extremely important means of informing consumers and property owners about their “shared responsibility,” including financial responsibility for replacing privately owned portions of LSLs. Water systems should provide information for consumers and property owners that emphasizes the importance of shared responsibility for minimizing exposure to lead, engages them in the planning process for the service area, clearly informs them about plans and progress to date, recommends actions they can or should take, and starts a dialog about possible financing options. The water system should recommend full LSLR, where reasonably possible, to consumers and building owners.

Public water systems developing (or revising) an LSLR program should involve regulatory stakeholders from the beginning of the planning process and maintain their involvement into the implementation phase. In the U.S., the applicable regulations associated with the LCR are in flux, so all stakeholders, most especially public water systems with LSLs, would be well advised to keep abreast of proposed or newly promulgated regulations. Until the regulatory picture is clear, public water systems should approach using any lining or coating system as part of their compliance strategy with caution.

Public water systems are responsible not only for meeting the requirements of the LCR, but also for meeting state and local regulations, including building codes, that apply to their LSLR programs. State primacy agencies in the U.S., and provincial regulatory agencies in Canada, may adopt policies or regulations that differ from those established or recommended at the federal level. As always, public water systems are strongly encouraged to ensure that any materials in their system, including linings and coatings, are certified to NSF/ANSI Standard 61 by an accredited certification body, and in most states and provinces this is legally required. Public water systems should also require post-installation testing of LSL linings and coatings for tap-water lead levels, adequate flow, and integrity (e.g., visual inspection using a high resolution mini-camera).

Public water systems should also engage manufacturers (or vendors) of lining and coating systems in the planning process, as well as contractors – if they plan to hire contractors to perform some or all of the work instead of doing all the work "in house" using their own crews. The potential cost savings and other benefits associated with lining and coating technologies can be more effectively realized if they are evaluated ahead of time and incorporated into the program in an organized fashion, rather than considering them on a case-by-case basis, as individual situations are encountered where they might be advantageous. Both manufacturers and contractors are likely to have some excellent suggestions as to how a public water system can maximize the cost savings associated with lining and coating technologies.

For specific situations where full LSLR does not appear to be technically feasible, or economically or socially acceptable, lining or coating the customer-owned portion of the LSL should be considered as an option, if allowed under the applicable regulations. During the planning process, public water systems should identify potential needs and/or opportunities for use of linings and coatings to reduce short-term and/or long-term exposure to lead, such as avoiding:

- Disturbances of historic sites or structures
- Environmental damage (e.g., to mature trees)
- Traffic disruption
- Interference with, or damage to, other utilities (gas, phone, cable, sewer, electric)

If such needs and/or opportunities exist for using linings or coatings, public water systems should take the lead in exploring them with all other stakeholders. As part of the exploration process, public water systems should assess their customers' attitudes on the following issues:

- Importance of (and willingness to pay for) minimizing exposure to lead
- Expected length of service interruptions for LSL replacements, linings, and coatings
- Disruptions to yard, trees, driveways, sidewalks, etc.
- Potential cost savings associated with linings or coatings
- Expected service life of new service lines versus lined or coated service lines
- Concerns about materials used in service lines

Epoxy coatings have been used in building plumbing systems for many years, in many countries, including the U.S. However, the purpose of such coatings usually has little to do with lead. Coatings have primarily been used in building plumbing systems to control corrosion, to repair leaks (especially pin-hole leaks in copper pipe), and to improve the aesthetic quality of the water. Due to the growing recognition that lead can be released from interior plumbing, especially from corroded galvanized pipes, use of epoxy coatings primarily for lead control in buildings is likely to become more common in the future. While interior plumbing in buildings is not the responsibility of public water systems, building owners, public health officials, building inspectors, and others are likely to look to water utilities for information and guidance on lead control, use of epoxy coatings, potential impacts of materials on water quality, and related topics. Public water systems should strive to become more familiar with such matters to better serve their customers, and as a sign of their commitment to provide their community with safe drinking water.

RECOMMENDATIONS TO CONSUMERS AND PROPERTY OWNERS

The overwhelming majority of stakeholders are consumers and/or property owners, which could be collectively referred to as the water system's customers or the public; and they have a lot at stake. Consumers' health may be adversely affected by elevated lead levels, and property owners are usually financially responsible for replacing, lining, or coating the privately-owned portions of their LSLs. Consumers include not only bill-paying customers, but also children, tenants whose water bill is included in their rent, school teachers and students, occupants of office buildings (who may live outside the service area), visitors, and other members of the general public. The first thing consumers (especially bill-paying customers) and property owners should do is develop a general knowledge of drinking water in their community, including lead levels in residences, schools, and office buildings. In most cases, this can be accomplished by reviewing the water system's annual Consumer Confidence Report (CCR) and other information posted on the system's website. Many water systems in communities with LSLs have posted at least some information about lead control on their website; if not, consumers and property owners should request that they do so.

Home and building owners should determine whether or not they have an LSL. Materials developed to assist public water systems in developing LSLR programs also provide guidance for property owners to assist them in determining whether a home or other building has an LSL (AWWA 2014a). In many cases, this information will be available on the public water system's website if there are LSLs in their service area; if not, property owners should request that this information be made readily available. Property owners who have an LSL should consider full LSLR. Even though full LSLR is not currently mandated, it is a wise thing to do – to protect themselves and their families, or their tenants or other occupants, as well as guests and future residents or occupants, from unnecessary exposure to lead. Property owners should recognize that although replacing their portion of an LSL is expensive, the cost is typically modest compared to other costs of home or building ownership. Full LSLR might also improve the value of the property in the long run. It would not be surprising to see, in the near future, information about LSLs included on disclosure forms for real estate transactions or included as part of property inspections. If full LSLR is not technically feasible, or economically or socially acceptable, property owners should investigate the possibility of lining or coating their portion of the LSL.

Many public water systems have already reached out to consumers and property owners, by means of billing inserts or website postings, to inform them about lead in their community, lead monitoring results, the presence or absence of LSLs in their service area, corrosion control practices, the status of any system-wide plans for lead control, any financial incentives or financing arrangements that are available to property owners wanting to replace their portion of an LSL, and recommendations for limiting exposure to lead, especially inside homes and buildings. Consumers and property owners whose water system has yet not provided this information should request it, if LSLs are known to be present within the service area. Property owners with LSLs should consider taking advantage of any financial incentives their water system offers to help property owners pay to replace their portion of an LSL.

Disturbing an LSL and/or the plumbing connected downstream from it is likely to cause temporarily increased lead levels that may persist for a month or two and perhaps as long as a year. Possible causes of disturbances include full or partial LSLR, lining or coating an LSL or a portion of it, and various other construction activities in the vicinity of an LSL, such as landscaping, foundation repair, or sprinkler installation. In the event of such a disturbance, consumers or property owners with an LSL should monitor their tap water for lead and/or filter their water (specifically the water used for drinking, cooking, and preparing beverages) using a filter designed (and certified to NSF 53) for removal of both particulate and dissolved lead, until the lead level is consistently within the recommended limits. Consult the public water system's website (or contact them directly if necessary) for information about lead monitoring (which they may be able to assist with, especially if they were involved in the disturbance, e.g., an LSLR) and for recommendations regarding filtration. All interior water lines should be thoroughly flushed any time a service line (whether or not it is an LSL) or other component of a plumbing system in a home or building is worked on by a plumber or contractor.

In homes and buildings having interior water lines heavily encrusted with lead-bearing deposits, especially interior plumbing made of galvanized iron pipe, the deposits may be releasing more lead into the water than an LSL, even if the LSL is the source of the lead that slowly built up inside the pipes over many years. Consumers and property owners who encounter such situations should either replace their interior plumbing with lead-free materials, coat their interior water lines to prevent lead leaching, or purchase a water filter (one certified to NSF 53 for removal of both dissolved and particulate lead) and carefully follow the operating and maintenance instructions.

RECOMMENDATIONS TO STATE AND PROVINCIAL REGULATORS

State and provincial regulators should assist public water systems in their efforts to educate the public about lead in drinking water and to develop LSLR programs and other lead control strategies that minimize public exposure to lead in drinking, meet all applicable regulations, and effectively utilize any and all available tools that can contribute to this effort at a reasonable cost. Consistent with the NDWAC recommendations (EPA 2015a and 2015b), full LSLR should be the preferred option for controlling lead associated with LSLs.

When replacing an LSL does not appear to be technically feasible, or economically or socially acceptable, lining or coating it should be considered as an option, if allowed under applicable regulations. State and provincial regulators should help make both current and proposed regulations, including the aspects listed below, clear to other stakeholders with respect to both utility-owned and privately owned segments of LSLs:

- Are linings and coatings allowed and, if so, under what conditions and how are lined or coated LSLs treated with respect to compliance requirements?
- If full LSLR is mandated, will exceptions or exemptions be granted permitting the use of linings and coatings in situations where exposure to lead can be more rapidly controlled, where significant savings can be realized, or where damage to historic sites, landscaping, structures, or other utility lines can be avoided?
- If public water systems and/or property owners can apply for exceptions or exemptions, will they be permanent or temporary, and what criteria will be used to decide whether to approve exceptions or exemptions?
- What monitoring requirements apply to lined or coated LSLs?

RECOMMENDATIONS TO MANUFACTURERS AND CONTRACTORS

Manufacturers of lining and coating technologies, and their representatives, including local contractors licensed to install their products, should familiarize other stakeholders with their technologies, the potential benefits they can provide, and the situations in which they are most likely to provide significant cost savings or other benefits. As manufacturers know, and should be prepared to help public water systems and other stakeholders recognize, LSL lining and coating costs depend heavily on the number of LSLs to be lined or coated, where they are located, and how they are scheduled. In other words, there are significant economies of scale involved, and much greater cost savings can be realized if the LSLs can be lined or coated as part of a well-organized, system-wide lead-control program that most likely will also include full and/or partial LSLRs.

To promote their products while also helping communities minimize exposure to lead in drinking water, manufacturers of linings and coatings and their representatives are encouraged to:

- Recognize that a disparity between the expected service life of a product and the warranty period can be a stumbling block for other stakeholders
- Document and publicize supporting information regarding product service life
- Consider increasing warranty periods, when appropriate, and finding creative ways to share real or perceived financial risks in partnership with other stakeholders
- Continue to develop new or improved products and faster, better, and less disruptive installation methods
- Encourage public water systems to adopt a proactive system-wide approach for controlling lead release from LSLs, and to take advantage of the potential cost savings and other benefits of lining and coating technologies
- Consider installing sampling taps at selected locations to facilitate performance monitoring of lined or coated LSLs, since tap-water samples may be contaminated with lead from sources other than the LSLs, making it difficult to document the true effectiveness of linings or coatings
- Place a permanent tag on a lined or coated water service line to alert water utility crews, residents, and plumbers to the need to properly handle it when making repairs to the service line or other pipes, fittings, or devices connected to it

APPENDIX A
SOP FOR PREPARING EXTRACTION WATERS, VER. 1.0

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lead and copper pipe sections. This SOP describes the steps needed to prepare the water used for these tests. Preparation of these waters is adapted from NSF/ANSI Standard 61, Annex B.

DEFINITIONS

RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.

Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

PREPARATION

Dechlorinated pH 8 Tap Water for Fill-and-Dump Experiments

Water will be collected from a sink in 1116 Learned Hall 24–48 hours prior to each fill-and-dump experiment. The cold water tap will be turned on and flushed for at least five minutes prior to water collection. Water will be collected in a 30 L Nalgene carboy, which will first be rinsed with the tap water before it is filled. Prior to initial use, this carboy will be washed with Liquinox soap and water, then rinsed three times each with tap water and RO water and allowed to air-dry. After each use, the remnants will be dumped and the container will be rinsed three times with RO water, allowed to air dry (upside down), and then stored with the lid in place to keep out dust.

Immediately upon filling, samples will be drawn for the following QC purposes: pH, alkalinity, residual chlorine, and TOC. The samples will be promptly analyzed to determine whether the QC objectives described below (see Quality Control) are met. If not, start over or obtain approval from the PI or a co-PI to proceed. After checking the residual chlorine concentration, dechlorinate the water, but do not adjust the pH of the water until immediately prior to use.

Immediately prior to use, samples of this water will be drawn for the following analyses: pH, conductivity, metal ions (lead, copper, antimony when appropriate, sodium and potassium, and other metals by ICP when desired), alkalinity, water hardness, anions, organic compounds, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

Dechlorination

Dechlorinate the tap water by drop-wise addition of a 17 g/L solution of sodium sulfite (1.7 g Na_2SO_3 per 100 mL) or a 14.6 g/L solution of sodium bisulfite (1.46 g $NaHSO_3$ per 100 mL). One drop of each solution should remove ~ 0.5 mg of residual chlorine. Begin by adding the amount needed to stoichiometrically remove the residual chlorine, test for residual chlorine, then add more as needed until a test for total residual chlorine demonstrates the absence of a chlorine residual. Do not add excess dechlorinating agent beyond that needed to dechlorinate the water, as this will affect the dissolved oxygen level. Test for residual chlorine using any convenient method: a Hach TCR ampule, DPD solution with buffer and iodide added, or amperometric titration. Mix the dechlorinating agent into the water by stirring it with a short (2 ft.) length of clean 3/4-in. (nom.) HDPE tubing.

pH adjustment

The water will be adjusted to pH 8.0 immediately before use using 0.10 N HCl and NaOH solutions, as needed. The sodium hydroxide solution will be a 0.10 N solution prepared by adding 4.0 g of reagent grade sodium hydroxide to reagent water. The hydrochloric acid solution will be a 0.10 N solution prepared by adding trace-metal grade concentrated hydrochloric acid to reagent water. The pH of the water will be adjusted in the Nalgene carboy with gentle stirring. The pH of the solution will be monitored during adjustment using a Fisher AB15 benchtop pH meter or Accumet XL25 pH meter. Consider the pH adjustment complete when the water remains at pH 8.0 ± 0.1 units for 2 minutes following the last acid or base addition. Use a short length of clean 3/4-in. (nom.) HDPE tubing to stir the water in the reservoir.

Low-pH (pH 6.5) Extraction Water

A pH 6.5 extraction water (“low pH water”) will be prepared for metal leaching experiments (and also to examine the effect of pH on leaching of organic contaminants). This water will be prepared and stored in glass containers. Brand-new previously unused containers, containers previously used only to hold LC/MS water, or containers cleaned in a trace-metal acid bath, as described in the SOP for lead analysis, will be used to prepare and store this water. The water will consist of reagent water spiked with 25 mL/L of 0.04 M $NaHCO_3$ and 25 mL/L of 0.04 M $CaCl_2$ per liter of water (per NSF 61) and adjusted to pH 6.5 ± 0.2 units using 0.1 N HCl (and no more than 5 drops of 0.1 N NaOH in the event that a slight excess of HCl is inadvertently added). All solutions will be prepared using reagent-grade chemicals. The pH of this water will be adjusted immediately prior to use in fill-and-dump experiments to minimize exchange of CO_2 with the atmosphere and the resulting change in pH. The container will be kept capped to minimize loss of CO_2.

Immediately prior to use, samples of this water will be drawn for the following analyses: metal ions (lead, copper, antimony when appropriate, and other metals by ICP when desired), organic compounds, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

Chlorinated pH 8 Extraction Water

Chlorinated pH 8 extraction water will be prepared to examine the effects of a free chlorine residual on leaching of organic compound and formation of chlorinated byproducts. This water will be prepared and stored in glass containers. Brand-new, previously unused containers, containers previously used only to hold LC/MS water, or containers cleaned in a trace-metal acid bath, as described in the SOP for lead analysis, will be used to prepare and store this water. The water will consist of reagent water spiked with 25 mL/L of 0.04 M $NaHCO_3$ and 25 mL/L of 0.04 M $CaCl_2$ per liter of water (per NSF 61).

This water may be prepared in advance, but the chlorine should be added and the pH adjusted immediately prior to use – to avoid decay of the chlorine residual and to minimize loss of CO2 (and the need for additional pH adjustment).

Chlorinate the water immediately prior to use by adding the amount of laboratory-grade sodium hypochlorite solution (Fisher Chemical Cat#:SS290-1; 5.65–6%), diluted first if necessary, to produce a free chlorine residual of 2.0 ± 0.2 mg/L. Confirm that the chlorine residual is free (not combined) and immediately before using this water determine the free chlorine residual using the Hach ampule method. The chlorine solution is to be stored in the dark in a refrigerator.

After adding chlorine and immediately prior to use, adjust the pH of this water to pH 8.0 ± 0.1 units using 0.1 N HCl and 0.1 N NaOH. Keep the container capped to minimize loss of CO_2.

Immediately prior to use, samples of this water will be drawn for the following analyses: metal ions (lead, copper, antimony when appropriate, and other metals by ICP when desired), organic compounds, TOX, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

REPORTING

Each batch of water will be uniquely labeled and all measured properties of that batch will be recorded in student notebooks at the time of preparation. This information will be identified with the set of experiments the water is used in for all subsequent data analysis and interpretation. Each batch will be designated in the format XX-YY-Date, where XX will be DT for dechlorinated tap water; LP for low pH water; and CL for chlorinated water, YY will refer to the incremental number of the batch, and Date is the date the water was prepared.

QUALITY CONTROL

Extraction water properties will be analyzed the same day the water is prepared to ensure that the water is within the correct range for the fill-and-dump experiments. All quality control measures for the individual analyses will be conducted in accordance with the specific SOPs for that analysis. The tap water must initially have a pH (before adjustment) of 7–10, an alkalinity of 40–100 mg/L as $CaCO_3$, a combined chlorine residual of 2–4 mg/L, and a TOC concentration ≤ 10 mg/L (measured using either the high-temperature combustion method or UV-persulfate method). If the water does not meet these specifications, it may only be used after direct authorization by the PI or a co-PI. Otherwise, the water should be discarded, and a new batch prepared.

Samples of each batch of extraction water will be collected immediately prior to the fill-and-dump experiments and analyzed for concentrations of water hardness, dissolved metals and organic compounds. These will be considered to be background concentrations of each analyte for the fill-and-dump experiments. Additional aliquots of this water will be collected for use as laboratory fortified matrix blanks in the metal and organic analysis procedures, as outlined in the SOPs for the individual analytes.

APPENDIX B
SOP FOR PREPARING EXTRACTION WATERS, VER. 2.0

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lead and copper pipe sections. This SOP describes the steps needed to prepare the water used for these tests. Preparation of these waters is adapted from Annex B of NSF/ANSI Standard 61.

DEFINITIONS

RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.

Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

PREPARATION

Dechlorinated Tap Water (DT)

Water will be collected from a sink in 1116 Learned Hall 24–48 hours prior to each fill-and-dump experiment. The cold water tap will be turned on and flushed for at least five minutes prior to water collection. Water will be collected in a 30 L Nalgene carboy, which will first be rinsed with the tap water before it is filled. Prior to initial use, this carboy will be washed with Liquinox soap and water, then rinsed three times each with tap water and RO water and allowed to air-dry. After each use, the remnants will be dumped and the container will be rinsed three times with RO water, allowed to air dry (upside down), and then stored with the lid in place to keep out dust.

Immediately upon filling, samples will be drawn for the following QC purposes: pH, alkalinity, residual chlorine, and TOC. The samples will be promptly analyzed to determine whether the QC objectives described below (see Quality Control) are met. If not, start over or obtain approval from the PI or a co-PI to proceed. After checking the residual chlorine concentration, dechlorinate the water, adjust the pH of the water; then check and adjust the pH of the water again immediately prior to use.

Immediately prior to use, samples of this water will be drawn for the following analyses: pH, conductivity, metal ions (lead, copper, antimony when appropriate, sodium and potassium, and other metals by ICP when desired), alkalinity, water hardness, anions, organic compounds, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

Dechlorination

Dechlorinate the tap water by drop-wise addition of a 17 g/L solution of sodium sulfite (1.7 g Na_2SO_3 per 100 mL) or a 14.6 g/L solution of sodium bisulfite (1.46 g $NaHSO_3$ per 100 mL). One drop of each solution should remove ~ 0.5 mg of residual chlorine. Begin by adding the amount needed to stoichiometrically remove the residual chlorine, test for residual chlorine, then add more as needed until a test for total residual chlorine demonstrates the absence of a chlorine residual. Do not add excess dechlorinating agent beyond that needed to dechlorinate the water, as this will affect the dissolved oxygen level. Test for residual chlorine using any convenient method: a Hach TCR ampule, DPD solution with buffer and iodide added, or amperometric titration. Mix the dechlorinating agent into the water by stirring it with a short length of clean 5/8-in. (nom.) PEX tubing.

pH Adjustment

The water will be adjusted to pH 8.0 using 0.10 N HCl and NaOH solutions, as needed. The sodium hydroxide solution will be a 0.10 N solution prepared by adding 4.0 g of reagent grade sodium hydroxide to reagent water. The hydrochloric acid solution will be a 0.10 N solution prepared by adding trace-metal grade concentrated hydrochloric acid to reagent water. The pH of the water will be adjusted in the Nalgene carboy with gentle stirring. The pH of the solution will be monitored during adjustment using a Fisher AB15 benchtop pH meter or Accumet XL25 pH meter. Consider the pH adjustment complete when the water remains at pH 8.0 $\pm$ 0.1 units for 2 minutes following the last acid or base addition; however, the pH of the water will rise upon standing (due to loss of CO_2), so it will need to be adjusted again immediately prior to use. Use a short length of clean 5/8-in. (nom.) PEX tubing to stir the water in the reservoir.

Chlorinated pH 8 Extraction Water (CL)

Chlorinated pH 8 extraction water will be prepared to examine the effects of a free chlorine residual on leaching of organic compound and formation of chlorinated byproducts. This water will be prepared and stored in glass containers. Brand-new, previously unused containers, containers previously used only to hold LC/MS water, or containers cleaned in a trace-metal acid bath, as described in the SOP for lead analysis, will be used to prepare and store this water. The water will consist of reagent water spiked with : 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl (14.0 mL of 0.04 M $NaHCO_3$, 25 mL of 0.04 M $CaCl_2$,and 11.0 mL of 0.04 M NaCl per liter of extraction water). This water is similar in composition to the pH 8 extraction water specified in NSF 61, but is close to equilibrium with the atmosphere with respect to CO_2, so the pH will not change much as it is poured into and out of the pipe sections. Immediately prior to use, check the pH and, if necessary, adjust it 8.0 using 0.1 N HCl or NaOH.

This water may be prepared in advance, but the chlorine should be added immediately prior to use – to avoid decay of the chlorine residual. Chlorinate the water immediately prior to use by adding the amount of laboratory-grade sodium hypochlorite solution (Fisher Chemical Cat#:SS290-1; 5.65–6%), diluted first if necessary, to produce a free chlorine residual of 2.0 ± 0.2 mg/L. Confirm that the chlorine residual is free (not combined) and immediately before using this water determine the free chlorine residual using the Hach ampule method. The chlorine solution is to be stored in the dark in a refrigerator.

Keep the container capped to minimize contamination. Immediately prior to use, samples of this water will be drawn for the following analyses: metal ions (lead, copper, antimony when appropriate, and other metals by ICP when desired), organic compounds, TOX, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

Low-pH Extraction Water (LP)

A pH 6.5 extraction water ("low pH water") will be prepared for metal leaching experiments (and also to examine the effect of pH on leaching of organic contaminants). This water will be prepared and stored in glass containers. Brand-new, previously unused containers, containers previously used only to hold LC/MS water, or containers cleaned in a trace-metal acid bath, as described in the SOP for lead analysis, will be used to prepare and store this water. The water will consist of reagent water spiked with 0.018 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.982 mM NaCl (0.45 mL of 0.04 M $NaHCO_3$, 25 mL of 0.04 M $CaCl_2$,and 24.55 mL of 0.04 M NaCl per liter of extraction water). This water is similar in composition to the pH 6.5 extraction water specified by NSF 61, but is close to equilibrium with the atmosphere with respect to CO_2, so the pH will not change much as it is poured into and out of the pipe sections. Immediately prior to use, check the pH and, if necessary, adjust it to pH 6.5 $\pm$ 0.2 units using 0.1 N HCl (and no more than 5 drops of 0.1 N NaOH in the event that a slight excess of HCl is inadvertently added). All solutions will be prepared using reagent-grade chemicals. The container will be kept capped to minimize the potential for contamination.

Immediately prior to use, samples of this water will be drawn for the following analyses: metal ions (lead, copper, antimony when appropriate, and other metals by ICP when desired), organic compounds, and TOC. Collect at least triplicate samples for TOC analysis. All measurements will be carried out following the appropriate SOPs.

REPORTING

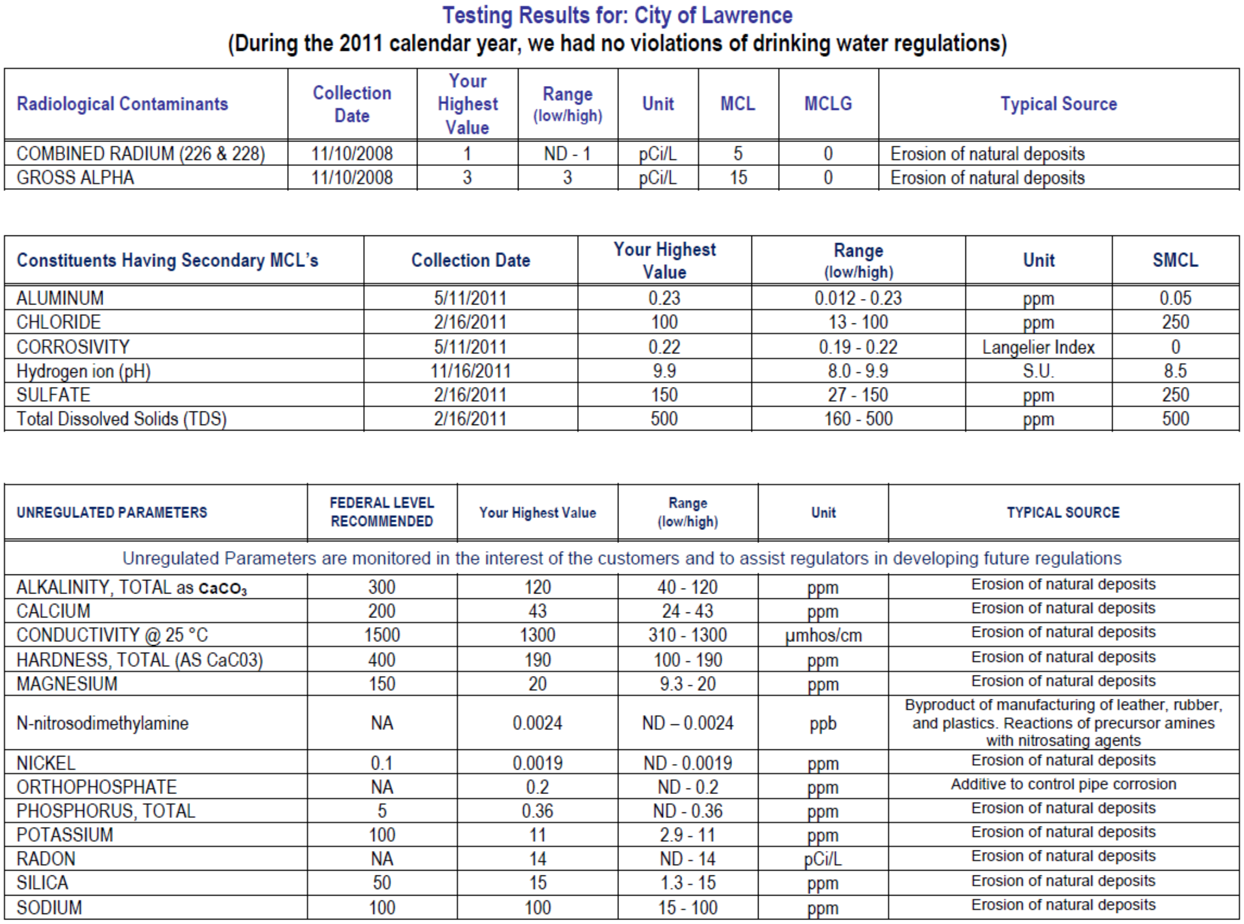
Each batch of water will be uniquely labeled and all measured properties of that batch will be recorded in student notebooks at the time of preparation. This information will be identified with the set of experiments the water is used in for all subsequent data analysis and interpretation. Each batch will be designated in the format XX-YY-Date, where XX will be DT for dechlorinated tap water; LP for low pH water; and CL for chlorinated water, YY will refer to the incremental number of the batch, and Date is the date the water was prepared.

QUALITY CONTROL

Extraction water properties will be analyzed the same day the water is prepared to ensure that the water is within the correct range for the fill-and-dump experiments. All quality control measures for the individual analyses will be conducted in accordance with the specific SOPs for that analysis. The tap water must initially have a pH (before adjustment) of 7–10, an alkalinity of 40–100 mg/L as $CaCO_3$, a combined chlorine residual of 2–4 mg/L, and a TOC concentration $\leq$ 10 mg/L (measured using either the high-temperature combustion method or UV-persulfate method). If the water does not meet these specifications, it may only be used after direct authorization by the PI or a co-PI. Otherwise, the water should be discarded, and a new batch prepared.

Samples of each batch of extraction water will be collected immediately prior to the fill-and-dump experiments and analyzed for concentrations of water hardness, dissolved metals and organic compounds. These will be considered to be background concentrations of each analyte for the fill-and-dump experiments. Additional aliquots of this water will be collected for use as laboratory fortified matrix blanks in the metal and organic analysis procedures, as outlined in the SOPs for the individual analytes.

APPENDIX C
WATER QUALITY DATA FOR LAWRENCE, KS., 2011



Testing Results for: City of Lawrence

(During the 2011 calendar year, we had no violations of drinking water regulations)

Radiological Contaminants	Collection Date	Your Highest Value	Range (low/high)	Unit	MCL	MCLG	Typical Source
COMBINED RADIUM (226 & 228)	11/10/2008	1	ND - 1	pCi/L	5	0	Erosion of natural deposits
GROSS ALPHA	11/10/2008	3	3	pCi/L	15	0	Erosion of natural deposits

Constituents Having Secondary MCL's	Collection Date	Your Highest Value	Range (low/high)	Unit	SMCL
ALUMINUM	5/11/2011	0.23	0.012 - 0.23	ppm	0.05
CHLORIDE	2/16/2011	100	13 - 100	ppm	250
CORROSIVITY	5/11/2011	0.22	0.19 - 0.22	Langelier Index	0
Hydrogen ion (pH)	11/16/2011	9.9	8.0 - 9.9	S.U.	8.5
SULFATE	2/16/2011	150	27 - 150	ppm	250
Total Dissolved Solids (TDS)	2/16/2011	500	160 - 500	ppm	500

UNREGULATED PARAMETERS	FEDERAL LEVEL RECOMMENDED	Your Highest Value	Range (low/high)	Unit	TYPICAL SOURCE
Unregulated Parameters are monitored in the interest of the customers and to assist regulators in developing future regulations					
ALKALINITY, TOTAL as $CaCO_3$	300	120	40 - 120	ppm	Erosion of natural deposits
CALCIUM	200	43	24 - 43	ppm	Erosion of natural deposits
CONDUCTIVITY @ 25 °C	1500	1300	310 - 1300	µmhos/cm	Erosion of natural deposits
HARDNESS, TOTAL (AS CaC03)	400	190	100 - 190	ppm	Erosion of natural deposits
MAGNESIUM	150	20	9.3 - 20	ppm	Erosion of natural deposits
N-nitrosodimethylamine	NA	0.0024	ND – 0.0024	ppb	Byproduct of manufacturing of leather, rubber, and plastics. Reactions of precursor amines with nitrosating agents
NICKEL	0.1	0.0019	ND - 0.0019	ppm	Erosion of natural deposits
ORTHOPHOSPHATE	NA	0.2	ND - 0.2	ppm	Additive to control pipe corrosion
PHOSPHORUS, TOTAL	5	0.36	ND - 0.36	ppm	Erosion of natural deposits
POTASSIUM	100	11	2.9 - 11	ppm	Erosion of natural deposits
RADON	NA	14	ND - 14	pCi/L	Erosion of natural deposits
SILICA	50	15	1.3 - 15	ppm	Erosion of natural deposits
SODIUM	100	100	15 - 100	ppm	Erosion of natural deposits

Source: City of Lawrence 2012

APPENDIX D
SOP FOR TOTAL ORGANIC CARBON (TOC)

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, Standard Method 5310C (Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method; APHA et al. 2005) is used to determine TOC concentrations in selected water samples, following the specific steps outlined below. Where deviations from the standard method exist, this SOP should be followed instead. QA/QC procedures are adapted from Standard Method 1020, while sample collection and preservation guidelines follow Standard Method 1060.

DEFINITIONS

- RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.
- Extraction water – Water prepared for use in these experiments by pH adjustment and/or dechlorination, as described in the SOP for extraction water preparation.
- Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

APPARATUS

To determine TOC concentrations by low-temperature oxidation, a Sievers 900 Portable Total Organic Carbon Analyzer is used. A septum piercing needle is used to extract samples from storage vials. Inside the instrument, phosphoric acid is mixed into the sample to convert bicarbonate to CO_2, the majority of the CO_2 (inorganic carbon, or IC) is removed, and an oxidizer (ammonium persulfate) is added. The flow is then divided into two streams, one of which is exposed to UV radiation to convert the organic carbon to CO_2 and the other is not exposed. The CO_2 is each stream is then measured using a membrane-based conductometric method, and the difference between the two streams is TOC, i.e., Total Carbon – IC = TOC.

SAMPLE PREPARATION

Steps to avoid contamination must be strictly followed. Brand-new, glass vials with PTFE-lined septa and hole caps (to allow the septa to be pierced by the autosampler needle) should be used to store the samples. Glassware cleaned in an acid bath is used to prepare standards. Plastics are avoided to prevent leaching or adsorption of organic contaminants.

For used sample containers, the proper cleaning process is as follows. Containers are scrubbed with Liquinox soap and water. They are then rinsed at least three times each with tap water, then RO water. Containers should be drip-dried upside down in a drying over or drying rack to avoid contamination by laboratory dust. After drying, they should be sealed with either a PTFE-lined cap until use.

For the calibration check standards, use primary-standard-grade potassium hydrogen phthalate (KHP) dried for 2 hours at 120 °C to prepare a 1,000 mg C/L TOC stock standard. Prepare calibration check standards of 1, 5, and 10 mg/L TOC by diluting the stock standard. Typical Lawrence tap water has a TOC concentration of approximately 3 to 5 mg/L. Ensure caps are tight to reduce contact with the atmosphere. Add 1 drop reagent grade 85% phosphoric acid per 10 mL of sample for preservation of samples and standards. Create reagent blanks with reagent water and a proportionate amount of phosphoric acid. Samples should be stored at 4 ^{o}C and protected from sunlight. Samples should be analyzed within seven days of collection if possible, and may not be stored for more than 28 days before analysis.

PROCEDURE

Set up the instrument as instructed by City of Lawrence personnel at the Clinton Water Treatment Plant and as described in the City's SOP for TOC analysis and in the instruction manual for the software and autosampler. The instrument is calibrated annually, so calibration standards are not needed with each run, but calibration check standard must be included with each run to verify that the instrument is still accurately calibrated and that the response is linear over the range of interest (normally 0 – 10 mg/L for tap water). Make 4 or 5 injections of each sample, always discarding the result of the first injection, which is influenced by the TOC concentration of the previous sample.

When setting up a sample run, begin with a rinse sample in the first position, and place the samples in order of increasing (or decreasing) TOC concentration. If a significant change in TOC concentration is expected from one sample to the next, insert a duplicate sample, as the precision (%RSD) is likely to be unacceptable for the first sample due to the inability of the instrument to adjust to a significant change in TOC concentration. With each set of samples include: 1) one set of calibration check standards (e.g., 1, 5, and 10 mg/L TOC) to check instrument response and linearity over the TOC range of interest; 2) reagent blanks (one for every 10 samples) to check the purity of the reagents (reagent water and phosphoric acid) and sample containers, and also to serve as a calibration blank, verifying the lack of instrumental response in the absence of TOC; 3) a continuing calibration check sample (5 mg/L TOC; one for every 10 samples and at the end of the run) to verify that the instrument remains calibrated as the samples are analyzed; 4) a duplicate sample to verify the precision with which sample TOC is determined; 5) a matrix spike (to check recovery of a 2 – 5 mg/L TOC standard from the water being analyzed); and 6) an IC check sample (prepared by spiking 10 mg/L of IC into a duplicate sample) to verify (by comparing the results with an unspiked duplicate) that the instrument is accurately accounting for IC.

A typical sample lineup is shown on the next page. When possible, analyze samples to be directly compared with one another in the same batch of samples, and place them as close to one another as possible in the autosampler tray.

Each sample takes approximately 20 minutes to run (5 injections taking 4 minutes each). The results can be reviewed in real time and should be checked periodically if possible and at the end of the run to insure that the results appear reasonable and satisfactorily precise and to verify that QC requirements have been met. After the run is completed, export the results file in .csv format to a USB device.

Typical Sample Lineup for TOC Analysis

Sample #	Sample ID	Notes
1	Reagent Blank	Rinse
2	Reagent Blank	Reagent Water + H3PO4
3	1.0 ppm KHP*C	
4	1.0 ppm KHP*C	
5	CL-02-R	
6	5.0 ppm KHP*C	
7	5.0 ppm KHP*C	
8	10.0 ppm KHP*C	
9	10.0 ppm KHP*C	
10	DT-01-R-LFM	Matrix Spike (+5 ppm KHP*C)
11	Tap	Rinse
12	DT-01-R	
13	DT-Cu-6-A	
14	DT-Cu-6-B	
15	DT-Cu-24	
16	DT-Cu-4d	
17	DT-Cu-10d	
18	DT-Cu-6-Control	
19	5.0 ppm KHP*C	Continuing Calibration Check
20	Tap	Rinse
21	DT-Pb-6-A	
22	DT-Pb-6-B	
23	DT-Pb-24	
24	DT-Pb-4d	
25	DT-Pb-10d	
26	DT-Pb-6-Control	
27	5.0 ppm KHP*C	Continuing Calibration Check
28	Tap	
29	Tap Duplicate	
30	Tap-IC CHECK	Experiment Water + 10 ppm IC
31	Reagent Blank	Rinse
32	Reagent Blank	Continuing Calibration Blank
33	Reagent Water	Rinse

CALCULATIONS AND REPORTING

Examine the results for each injection of each sample, standard, etc. Discard the result for the first injection, then examine the consistency of the results for the other 3 or 4 injections. If rejecting the result of the second injection improves the %RSD, reject that result as well. Look for trends that may indicate a problem with the instrument or samples. Look for outliers and discard outliers using the criteria in the SOP for outlier rejection, but note all outliers in all data reports and data summaries.

If the instrument is found to be accurately calibrated and linear (all calibration check standards within 10% of the known value), no calculations are required except for samples that have been diluted, matrix spikes, the IC check sample, and the precision of the duplicates. Concentrations recorded by the system software are to be considered as the measured concentrations and should be reported to the nearest 0.01 mg/L. Also report the relative standard deviation (as a percentage) of the results of the replicate injections for each sample. If the calibration standards indicate that the instrument calibration is off or that the response is non-linear, immediately report this to your supervisor and request instructions on how to proceed.

The method detection level (MDL) for this method, using the specified instrument (Sievers 900), has not yet been determined by the research team. Determine the single-day, single-operator MDL by analyzing 7 replicate standards at a concentration of 0.5 mg/L in a single run. Until the MDL is determined, report all measured values, even those for the blanks, as if they are "detectable."

QUALITY CONTROL

General Procedures

The samples are expected to be very close to initial tap water levels, approximately 3 to 5 mg/L TOC. Due to the low levels of TOC being tested, extra care is taken to ensure quality results. Contamination can be avoided by avoiding bringing anything into contact with any surface that comes into contact with the samples. Samples should be run without opening them to avoid contact with atmospheric dust. Proper and consistent sample container cleaning is required. Ensure there is no excessive upward or downward trend in measurements over time that may occur due to instrument instability, depletion of one of the reagents added internally, or other cause.

Reagent Blank

Reagent water acidified with 1 drop reagent grade 85% phosphoric acid per 10 mL of reagent water. The measured TOC must be <0.35 mg/L. If not, check the purity of the reagent water, the phosphoric acid, sample vials, and/or glassware and correct the problem.

Calibration Check Standards

Prepare a 1,000 mg/L TOC standard, as described in Standard Method 5310, using primary-standard-grade KHP dried for 2 hours at 120 °C. Prepare calibration check standards by diluting the 1,000 mg/L TOC standard to 1, 5, and 10 mg/L TOC. Results must agree to within 10% of the stated value at each concentration. If sample concentrations exceed 10 mg/L, either dilute them to below 10 mg/L of prepare additional check standards at a higher concentrations such that the highest check standard exceeds the highest measured sample TOC concentration and the linearity of the instrumental response is verified over the TOC range of the samples.

Continuing Calibration Check Standard

Analyze a 5.0 mg/L TOC standard after every 10 samples, to verify that the instrument remained properly calibrated as the samples were analyzed. Results much agree to with 10% of the stated value, and the precision (%RSD) of multiple injections of the 5.0 mg/L standard must be ≤2% (for the last 4 or last 3 injections when making 5 injections).

Duplicate Samples

Analyze one duplicate sample for every 10 samples, to verify the precision of the analysis for the type of samples being analyzed. Result for second replicate must agree to within 20% of the value for the first.

Matrix Spike

Spike a sample with 2 – 5 mg/L of TOC (using an accurately measured aliquot of the primary standard) and determine recovery versus an unspiked replicate of the same sample. (A 5 mg/L matrix spike can be prepared by adding 0.25 mL of a 1,000 mg/L TOC standard to 25 mL of sample.) Recovery must be within 20% of the add concentration, and the TOC concentration of the spiked sample must be within the range of the calibration check standards.

IC Check Sample

Prepare an IC stock solution by dissolving 0.3497 g reagent-grade anhydrous $NaHCO_3$ and 0.4412 g reagent-grade anhydrous Na_2CO_3 in 100 mL of reagent water. Keep tightly stoppered. Do not acidify. This solution does not require refrigeration for storage and is stable for one year. Spike a 25-mL sample with 0.25 mL of IC stock solution, then determine the TOC of the spiked sample and an unspiked duplicate. Results must agree to within 10%.

Sample Results

Error (precision) can be monitored in real time in the form of %RSD. If the error is increasing with each sample, this may indicate that the instrument is becoming increasing unstable. The relative error is generally higher at lower TOC concentrations (<1 mg/L TOC). Accept the results for a sample if the %RSD for the last 4 or last 3 injections is:

≤2% and TOC is >2000 ppb
≤3% and TOC is ≤2000 ppb
≤5% and TOC is ≤1000 ppb
≤10% and TOC is ≤500 ppb

Dilute and re-run samples having a TOC concentration greater than the highest calibration check standard found to give an accurate and linear response.

APPENDIX E
SOP FOR MEASURING LEAD BY GFAAS

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, Standard Method 3113 (APHA et al. 2005) is used to determine lead concentrations in water samples, following the specific steps outlined below. Where deviations from the standard method exist, this SOP should be followed instead. QA/QC procedures are adapted from Standard Method 1020, while sample collection and preservation guidelines follow Standard Method 1060.

DEFINITIONS

- RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.
- Experiment water – Tap water prepared for use in these experiments by pH adjustment and/or dechlorination, as described in the SOP for experiment water preparation.
- Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

APPARATUS

To test the lead concentrations, a Varian Graphite Tube Atomizer (GTA) 120 is used. The furnace attachment is needed due to the expected concentration range of 1-20 ppb. Advantages of the furnace technique include a much lower detection limit and lower sample volumes needed for analysis due to increased sensitivity (APHA et al. 2005). The sensitivity also creates a disadvantage of increased background interference.

The GTA operates by dispensing a small sample volume into a graphite tube. Various heating stages occur by means of electrical current. The first stage dries the sample. The second stage (ashing) volatizes other matrix components and destroys organic matter. The graphite tube is then heated to incandescence, inert argon gas is injected, and the element of concern atomizes. The ground-state atomic vapor left behind absorbs monochromatic radiation emitted from an element-specific bulb. The intensity of the transmitted radiation is measured by a photoelectric detector and analyzed by computer software. The software used for this method is SpectrAA Version 5.1 PRO by Varian.

The GTA uses a programmable sample dispenser (PSD) to automatically inject samples and modifier, and to create standards. During the testing process, the dispensing arm rinses itself with reagent water between samples to avoid contamination. Due to the extreme temperatures attained for atomization, an Ytron modular cooling system is used.

SAMPLE PREPARATION

Aqueous samples for lead analysis are to be stored in 15- or 50-mL PE centrifuge tubes and acidified to pH < 2 upon collection using concentrated trace-metal-grade nitric acid at a ratio of 2 mL acid per 100 mL sample. Samples intended for dissolved metal analysis should be filtered immediately upon collection through a 0.45-micron filter using a syringe filter (nylon or cellulose-acetate). Samples may be stored at 4 °C for no more than six months before analysis. A dilution multiplier of 1.02 will be included in the sample worksheet for these samples to account for the nitric acid addition to the sample.

If digestion is required for total lead analysis, digestion will be carried out using concentrated trace-metal grade nitric acid at a 1:10 ratio to the sample. The sample will be heated in a block heater to 95 °C for 60 minutes, and allowed to cool before analysis. A dilution multiplier of 1.1 will be included in the sample worksheet for any digested samples, to account for the nitric acid addition compared to the sample.

This SOP assumes that all samples are aqueous samples containing dissolved and/or particulate lead. Digestion procedures for any solid samples will be developed separately. Prepare standards, modifier solutions, blanks, and matrix spikes as follows:

Calibration Standards

Calibration standards are prepared from certified stock standards containing 1000 mg/L Pb in 2% nitric acid. These standards can be purchased from Fisher Scientific (catalog #: PL Pb2-2Y, or equivalent). For AA calibration, prepare a 20 µg/L lead solution by diluting the stock standard into reagent water with 2 mL concentrated trace-metal-grade nitric acid to a total volume of 100 mL. This standard will be automatically diluted by the AA autosampler to produce a calibration curve. Prepare as needed, but do not use if more than six months old. For each new certified stock standard, determine the concentration of lead in an independently prepared (external) check standard to verify the accuracy of the listed concentration; investigate and resolve the problem if the concentration in the check standard differs by more than 10% from the stated value.

Modifier Solution

For the modifier, prepare 100 mL of 5 mg/mL ammonium dihydrogen phosphate solution by adding reagent grade ammonium dihydrogen phosphate to reagent water.

Reagent Blanks

Reagent blanks are prepared by adding 0.2 mL of concentrated trace-metal-grade nitric acid to 9.8 mL of reagent water. Reagent blanks should be prepared at the same time as the analytical samples.

Laboratory-Fortified Blank (LFB)

Prepare a 10 µg/L Pb solution in reagent water with 1 mL of concentrated trace-metal-grade nitric acid to a total volume of 50 mL. Prepare as needed, but do not use if more than six months old.

Laboratory-Fortified Matrix (LFM)

Prepare 50 mL of a 10 µg/L Pb solution in experiment water with 1 mL of concentrated trace-metal-grade nitric acid to a total volume of 50 mL. This sample should be prepared from the same batch of experiment water used to generate the analytical samples.

Due to the increased sensitivity of the furnace technique, steps to avoid contamination must be strictly followed. Gloves should be worn whenever handling samples. Use brand-new, unused, and previously unopened sample containers, or containers cleaned in a trace-metal acid bath, to store the samples.

For used sample containers, the proper cleaning process is as follows. Containers are scrubbed with Liquinox soap and water. They are then rinsed at least three times each with tap water and RO water. Then, the containers are fully immersed in a 0.5% hydrochloric acid bath for at least 3 hours. After the acid bath, the containers are rinsed three times each with RO water, then reagent water. Containers should be drip-dried upside down in a clean drying rack to avoid contamination by laboratory dust. After drying, they should be sealed with either a cap or Parafilm until use.

PROCEDURE

Perform a fluids check to make sure every instrument has what it needs. The modular cooling system needs water to be present above the minimum level to operate. The GTA needs a mild acid solution made up of 0.01 N trace-metal-grade nitric acid (for rinsing, reagent water for standard and sample dilutions) and argon gas for operation. The argon gas should be UHP grade.

Turn on the cooling unit, gas, and GTA. Also, turn on the computer and load the SpectrAA program. Mount the furnace attachment and programmable sample dispenser. Ensure the waste hose is secure and dispensing into a proper disposal container. Mount the bulb required for the element of concern.

In the software program start configuring the method to be used. This is accessed through the tab labeled ‘Develop’ and selecting the ‘edit method’ option. Under the ‘Type/Mode’ tab, the furnace option is selected and lead is used in the element selector. Under the ‘Measurement’ tab, the peak height measurement mode is selected. Under the ‘Optical’ tab, the lamp position number found on the base of the lamp is entered. Lamp current and wavelength are selected based on data found in the manual that accompanies the GTA, *Analytical Methods for Graphite Tube Atomizers* (Rothery 1988). For this experiment a lamp current of 5 mA and a wavelength of 283.3 nm are used. Ensure background correction is turned on. Under the ‘Furnace’ tab, select the ‘Modifier 1’ checkbox. Set the modifier settings to co-inject and the injection volume equal to 10 µL. Check the PSD location for the modifier in this tab and make sure that is the location used on the actual PSD. Under the ‘Sampler’ tab, check the PSD locations for ‘Bulk’ (calibration standard) and ‘Make-up’ (reagent water). The bulk concentration should be set equal to the prepared standard concentration of 20 µg/L. The procedure for lead uses 20 µL of sample with 10 µL of modifier and 5 mL of reagent water. Default temperatures are maintained, including an ashing temperature of 500 C. Test three replicates for each sample.

The furnace bench, dispensing arm, and bulb will need to be optimized before testing can begin. In the software program, access the video feed of the graphite tube. This feed displays the point of injection from the dispensing arm to the graphite tube. The furnace bench must be aligned before calibrating the dispensing arm. Under the ‘Analysis’ tab, select the optimize button. The optimization screen displays an overhead view graphic of the PSD as well as two green bars used to optimize the UV signal. The left green bar is for the lead bulb and is monitored while adjusting the furnace bench and bulb itself. There are two knobs that adjust laterally and front to back on the front face of the furnace bench, just below the PSD. Adjust these until the left UV signal is normalized to about 1.0. Hit the rescale button and re-adjust. Check the video feed while using the knobs to guide you.

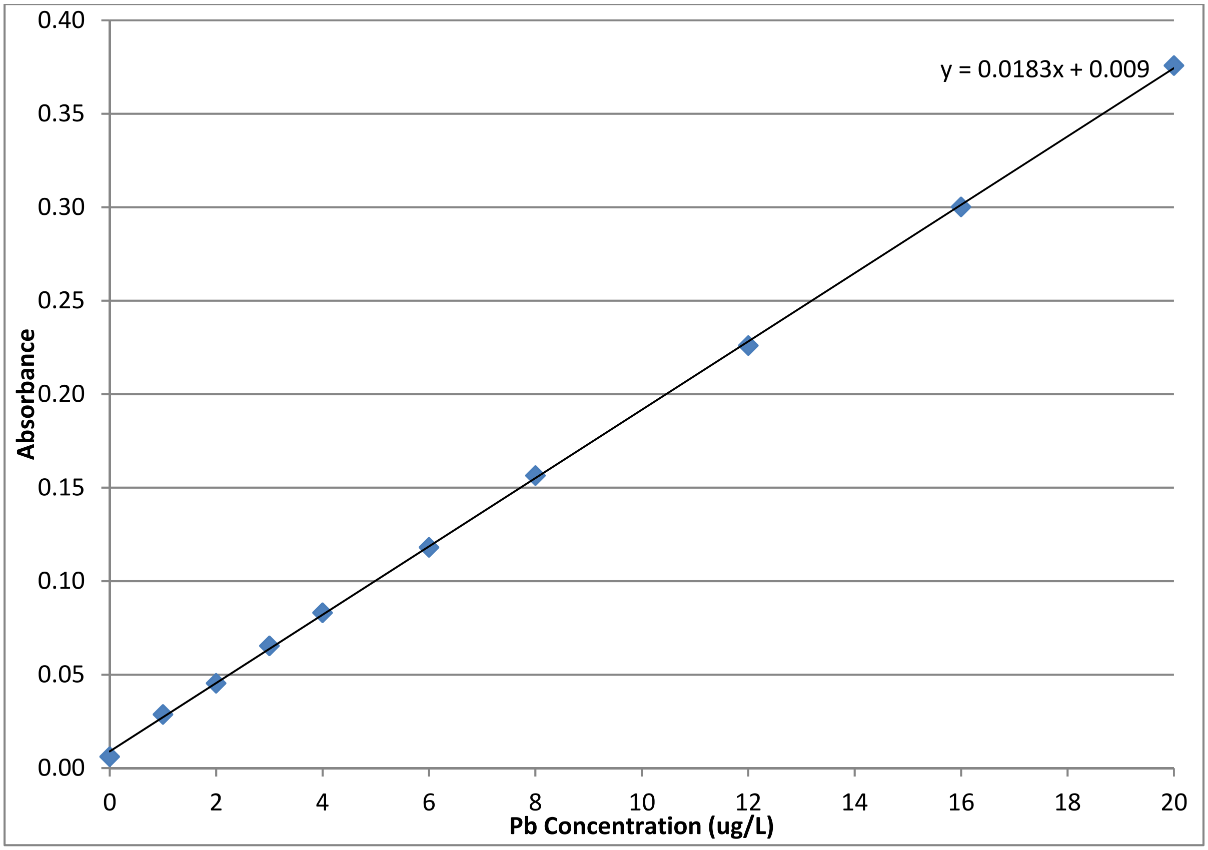
In order to adjust the bulb, UV glasses will be needed when opening the bulb access door. There are two calibration knobs on the bottom of the bulb socket. Adjust these one at a time. Get the green bar as high as possible, rescale, and get the green bar as high as possible again. Repeat the rescaling process until the green bar will go no higher.

Under the PSD graphic, click the carousel alignment button. This will perform a test run of the dispensing arm. Using the video feed as a guide, make sure the dispensing arm dispenses into the center of the tube opening by adjusting the two knobs on the bottom of the PSD. When aligned, lock the tray using the center knob on the bottom of the PSD. The depth of the capillary that enters the graphite tube can be adjusted by using the nut located towards the end of the dispensing arm. Ensure the capillary does not rest on the bottom of the inner graphite tube while dispensing.

Place samples, reagent water, and standard in tray. Run the test. Monitor the results to ensure quality. Save the results as a text document for analysis. Saving can be accomplished by selecting the print option. After accessing the ‘report’ tab, select the ‘write to text file’ option.

CALCULATIONS

A minimum of four and maximum of nine calibration concentrations (plus the blank) should be used for calculating a standard curve, ranging in concentration from 1 to 20 µg/L. A sample calibration curve is shown below. A linear relationship was acquired through regression analysis: $Abs = 0.0183*C + 0.00895$, or $C = 54.72*Abs - 0.4900$.



REPORTING

Using the method above, the minimum reportable limit is 0.5 µg/L or an absorbance value of 0.01 AU, whichever is greater. All samples below this value should be reported as below detection limit. Report the mean result and %RSD for all samples. In cases where two replicates are in agreement (less than 5% RSD) but the third replicate is more than 20% different from the average of these two, remove this replicate. Recalculate the mean value and % RSD for this sample based on the remaining two replicates, and note that the reported value is an average of two replicates.

QUALITY CONTROL

Calibration

The standard curve for lead has been found to be linear. A graphical representation of the results can be monitored in real time that plots the concentration against the absorbance measured. Make sure it follows the established relationship. Do not proceed with sample analysis until a linear calibration curve can be established within the tolerances of the SpectraAA software. A minimum of five calibration points (including the blank) must be used in this calibration and no more than 20% of the initially recorded calibration points may be removed (masked) to achieve a good calibration fit. If the absorbance of the 1 µg/L standard is below 0.01 AU, realign the furnace and/ or the lead lamp and rerun the calibration.

Sample Results

Error can also be monitored in real time in the form of %RSD. The error is generally higher for very low concentrations (~1 ppb for lead). If the error is increasing with each sample, however, this may be an indicator the GTA is getting out of alignment. Reject or re-run samples of Pb > 2 ppb that have an RSD > 5%. Reject or re-run samples of Pb < 2 ppb that have an RSD > 10%. Also, dilute and re-run samples having a concentration greater than 110% of the highest calibration standard (22 ppb).

General Procedures

Due to the low levels of metals being tested, extra care is taken to ensure quality results. Contamination can be avoided by wearing gloves whenever handling samples, by keeping samples covered to avoid dust, by avoiding contact with the interior of the sample tubes, and by minimizing contact between pipet tips and any surfaces. Proper and consistent sample container cleaning is required.

Accuracy and Reproducibility

QC samples should be run with each set of samples to ensure the accuracy of your measurements. *Standard Methods* recommends running check samples (reagent blank, LFB and LFM) periodically to achieve this result. At least one duplicate sample should also be run to determine the precision of the results. The sample for duplicate analysis shall be selected randomly (e.g., using a random number generator) prior to the run. For this method, two sequences have been developed for running samples and check standards, based on the number of samples to be run. These sequences are shown on the following page. This order assumes that the software is programmed to run a reagent blank after the final calibration standard. This sequence means that, for a full 50 position run, a maximum of 40 distinct experimental samples may be run.

1. Runs with fewer than 20 samples for analysis (this example assumes 15 samples)

Sample Order	Description	Sample Order	Description
1	Reagent blank	17	Duplicate sample
2	First analytical sample	18	LFB
3	Next analytical sample	19	LFM
4-15	Additional samples	20	Reagent blank *
16	Last analytical sample	21	Reagent blank

2. Runs with more than 20 samples for analysis (this example assumes 30 samples)

Sample Order	Description		
1	Reagent blank	21	Reagent blank
2	First analytical sample	22	Resume analytical samples
3	Additional samples	23-35	Additional samples
4-15	….	36	Last analytical sample
16	Midpoint of analytical samples	37	Duplicate sample (from samples 16-30)
17	Duplicate sample (from samples 1-15)	38	LFB
18	LFB	39	LFM
19	LFM	40	Reagent blank*
20	Reagent blank	41	Reagent blank

*Note: The purpose of the first of the dual reagent blanks is to assess any possible carryover effect from the LFM samples. If carryover is observed, the first replicate for each sample will be removed from the analysis.

QA/QC samples should be monitored during the sample run. If the first reagent blank results indicate Pb above the minimum reportable limit for that run (0.5 µg/L or 0.01 AU), another reagent blank should be run immediately. If the blank is fine, the run may continue. If not, make up and test a new reagent; if not, address the issue before running samples. If the LFB result is less than 80% or greater than 120% of the actual sample value, another LFB sample may be run. If this sample also does not meet the requirements, further action, including re-running the samples, may be required. If the LFM is less than 80% or greater than 120% of the actual value, the samples may not need to be rerun. A standard addition process should then be carried out to determine matrix effects on the reported results.

During the testing process, there are several things to look for to ensure quality results. Monitor the video feed of the graphite tube injection point. The dispensing arm can become misaligned and need recalibration. This will be evident when it is no longer visible in the video feed during the injection step. Absorbance measured for each sample may also suddenly go to near zero as the samples fail to be injected into the tube.

INSTRUMENT MAINTENANCE PROCEDURES AND TRAINING

All users will be trained to operate the AA before collecting sample data. A logbook will be placed next to the AA unit to record instrument use and maintenance operations. Every time the AA is run, the user will enter basic information into this logbook related to number and type of samples run, number of firings on the current graphite tube, Ar gas pressure, etc. Basic user-performed maintenance, including switching the unit from flame to furnace operation, replacing a graphite tube or cleaning the furnace windows, should also be recorded, along with the date of the operation. If additional maintenance is required, the user should contact Dr. Peltier to inform him of the problem and any solution reached. Signal from the Pb lamp should be monitored as described in the AA User Manual and a replacement lamp purchased when necessary.

A dedicated folder on the AA computer will be set up for each user. All user generated methods, sample lists and results should be placed into their folder and labeled with (at a minimum) the element and date of analysis. Each set of results should also be saved as a text file in the same folder for export to MS Excel or similar program for later analysis, as the AA software has a single-machine license. These folders will be periodically backed up to the School of Engineering servers.

APPENDIX F
SOP FOR MEASURING COPPER BY GFAAS

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, Standard Method 3113 (APHA et al. 2005) is used to determine copper concentrations in water samples, following the specific steps outlined below. Where deviations from the standard method exist, this SOP should be followed instead. QA/QC procedures are adapted from Standard Method 1020, while sample collection and preservation guidelines follow Standard Method 1060.

DEFINITIONS

- RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.
- Experiment water – Tap water prepared for use in these experiments by pH adjustment and/or dechlorination, as described in the SOP for experiment water preparation.
- Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

APPARATUS

To analyze copper concentrations, a Varian Graphite Tube Atomizer (GTA) 120 is used. The furnace attachment is needed due to the expected concentration range of 1-10 ppb. Advantages of the furnace technique include a much lower detection limit and lower sample volumes needed for analysis due to increased sensitivity (APHA et al. 2005). The sensitivity also creates a disadvantage of increased background interference.

The GTA operates by dispensing a small sample volume into a graphite tube. Various heating stages occur by means of electrical current. The first stage dries the sample. The second stage (ashing) volatizes other matrix components and destroys organic matter. The graphite tube is then heated to incandescence, inert argon gas is injected, and the element of concern atomizes. The ground-state atomic vapor left behind absorbs monochromatic radiation emitted from an element-specific bulb. The intensity of the transmitted radiation is measured by a photoelectric detector and analyzed by computer software. The software used for this method is SpectrAA Version 5.1 PRO by Varian.

The GTA uses a programmable sample dispenser (PSD) to automatically inject samples and modifier, and to create standards. During the testing process, the dispensing arm rinses itself with reagent water between samples to avoid contamination. Due to the extreme temperatures attained for atomization, an Ytron modular cooling system is used.

SAMPLE PREPARATION

Aqueous samples for copper analysis are to be stored in 15- or 50-mL PE centrifuge tubes and acidified to pH < 2 upon collection using concentrated trace-metal-grade nitric acid at a ratio of 2 mL acid per 100 mL sample. Samples intended for dissolved metal analysis should be filtered immediately upon collection through a 0.45-micron filter using a syringe filter (nylon or cellulose-acetate). Samples may be stored at 4 °C for no more than six months before analysis. A dilution multiplier of 1.02 will be included in the sample worksheet for these samples to account for the nitric acid addition to the sample.

If digestion is required for total copper analysis, digestion will be carried out using trace-metal grade concentrated trace-metal-grade nitric acid at a 1:10 ratio to the sample. The sample will be heated in a block heater to 95 °C for 60 minutes, and allowed to cool before analysis. A dilution multiplier of 1.1 will be included in the sample worksheet for any total digestion samples to account for the nitric acid addition compared to the sample.

This SOP assumes that all samples are aqueous samples contain dissolved or particulate copper. Digestion procedures for any solid samples will be developed separately. Prepare standards, modifier solutions, blanks, and matrix spikes as follows:

Calibration Standards

Calibration standards are prepared from certified stock standards containing 1000 mg/L Cu in 2% nitric acid. These standards can be purchased from Fisher Scientific (catalog #: PL Cu2-2Y, or equivalent). For AA calibration, prepare a 20 μg/L copper solution by diluting the stock standard into reagent water with 2 mL concentrated trace-metal-grade nitric acid to a total volume of 100 mL. This standard will be automatically diluted by the AA autosampler to produce a calibration curve. Prepare as needed, but do not use if more than six months old. For each new certified stock standard, determine the concentration of copper in an independently prepared (external) check standard to verify the accuracy of the listed concentration; investigate and resolve the problem if concentration in the check standard differs by more than 10% from the stated value.

Modifier Solution

For the modifier, prepare 100 mL of 500 mg/L palladium solution using palladium matrix modifier from Fluka Analytical (catalog #: 1439647), or equivalent.

Reagent Blank

Reagent blanks are prepared by adding 0.2 mL of concentrated trace-metal-grade nitric acid to 9.8 mL of reagent water. Reagent blanks should be prepared at the same time as the analytical samples.

Laboratory-Fortified Blank (LFB)

Prepare a 10 μg/L Cu solution in reagent water with 1 mL of concentrated trace-metal-grade nitric acid to a total volume of 50 mL. Prepare as needed, but do not use if more than six months old.

Laboratory-Fortified Matrix (LFM)

Prepare 50 mL of a 10 μg/L Cu solution in experiment water with 1 mL of concentrated trace-metal-grade nitric acid to a total volume of 50 mL. This sample should be prepared from the same batch of experiment water used to generate the analytical samples.

Due to the increased sensitivity of the furnace technique, steps to avoid contamination must be strictly followed. Gloves should be worn whenever handling samples. Use brand-new, unused, and previously unopened sample containers, or containers cleaned in a trace-metal acid bath, to store the samples.

For used sample containers, the proper cleaning process is as follows. Containers are scrubbed with Liquinox soap and water. They are then rinsed at least three times each with tap water and RO water. Then, the containers are fully immersed in a 0.5% hydrochloric acid bath for at least 3 hours. After the acid bath, the containers are rinsed three times each with RO water, then reagent water. Containers should be drip-dried upside down in a clean drying rack to avoid contamination by laboratory dust. After drying, they will be sealed with either a cap or Parafilm until use.

PROCEDURE

Perform a fluids check to make sure every instrument has what it needs. The modular cooling system needs water to be present above the minimum level to operate. The GTA needs a mild acid solution made up of 0.01 N trace-metal-grade nitric acid (for rinsing, reagent water for standard and sample dilutions) and argon gas for operation. The argon gas should be UHP grade.

Turn on the cooling unit, gas, and GTA. Also, turn on the computer and load the SpectrAA program. Mount the furnace attachment and programmable sample dispenser. Ensure the waste hose is secure and dispensing into a proper disposal container. Mount the bulb required for the element of concern.

In the software program start configuring the method to be used. This is accessed through the tab labeled ‘Develop’ and selecting the ‘edit method’ option. Under the ‘Type/Mode’ tab, the furnace option is selected and copper is used in the element selector. Under the ‘Measurement’ tab, the peak height measurement mode is selected. Under the ‘Optical’ tab, the lamp position number found on the base of the lamp is entered. Lamp current and wavelength are selected based on data found in the manual that accompanies the GTA, *Analytical Methods for Graphite Tube Atomizers* (Rothery 1988). For this experiment a lamp current of 4 mA and a wavelength of 327.4 nm are used. Ensure background correction is turned on. Under the ‘Furnace’ tab, select the ‘Modifier 1’ checkbox. Set the modifier settings to co-inject and the injection volume equal to 10 μL. Check the PSD location for the modifier in this tab and make sure that is the location used on the actual PSD. Under the ‘Sampler’ tab, check the PSD locations for ‘Bulk’ (calibration standard) and ‘Make-up’ (reagent water). The bulk concentration should be set equal to the prepared standard concentration of 20 μg/L. The procedure for copper uses 20 μL of sample with 10 μL of modifier. Default temperatures are maintained, including an ashing temperature of 1000 °C. Test three replicates for each sample.

The furnace bench, dispensing arm, and bulb will need to be optimized before testing can begin. In the software program, access the video feed of the graphite tube. This feed displays the point of injection from the dispensing arm to the graphite tube. The furnace bench must be aligned before calibrating the dispensing arm. Under the ‘Analysis’ tab, select the optimize button. The optimization screen displays an overhead view graphic of the PSD as well as two green bars used to optimize the UV signal. The left green bar is for the copper bulb and is monitored while adjusting the furnace bench and bulb itself. There are two knobs that adjust laterally and front to back on the front face of the furnace bench, just below the PSD. Adjust these until the left UV signal is normalized to about 1.0. Hit the rescale button and re-adjust. Check the video feed while using the knobs to guide you.

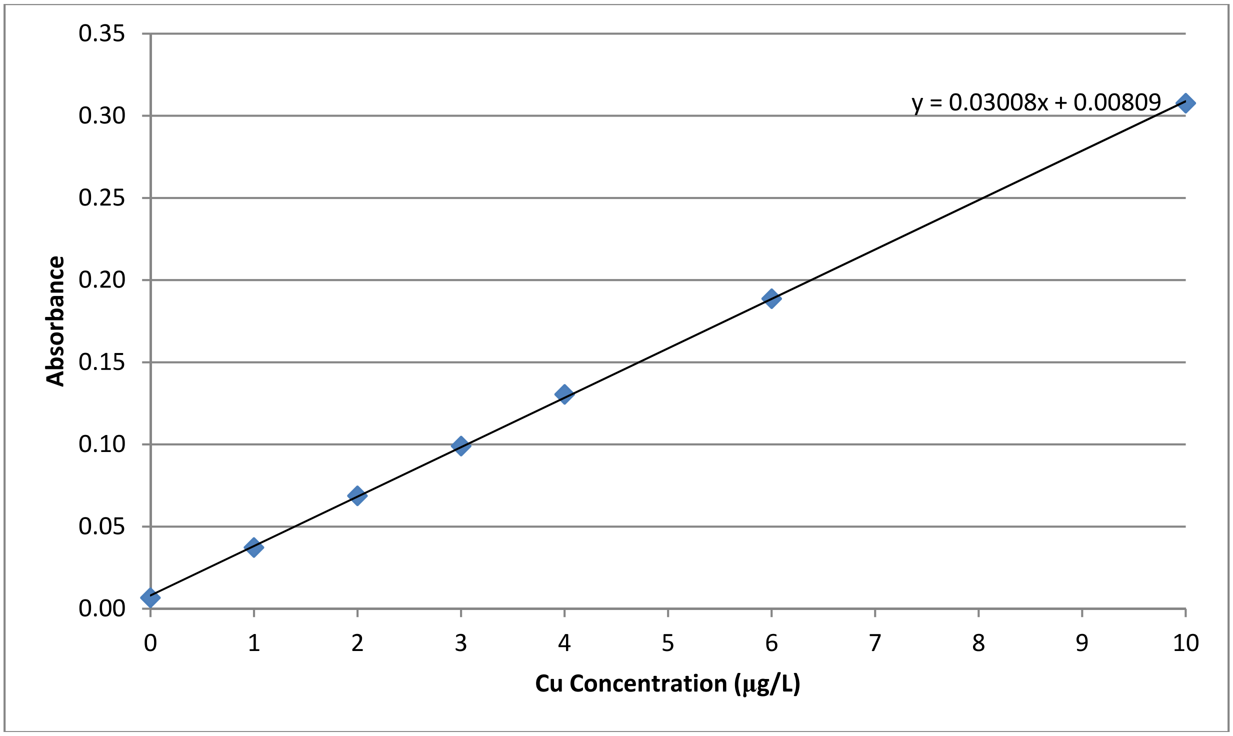
In order to adjust the bulb, UV glasses will be needed when opening the bulb access door. There are two calibration knobs on the bottom of the bulb socket. Adjust these one at a time. Get the green bar as high as possible, rescale, and get the green bar as high as possible again. Repeat the rescaling process until the green bar will go no higher.

Under the PSD graphic, click the carousel alignment button. This will perform a test run of the dispensing arm. Using the video feed as a guide, make sure the dispensing arm dispenses into the center of the tube opening by adjusting the two knobs on the bottom of the PSD. When aligned, lock the tray using the center knob on the bottom of the PSD. The depth of the capillary that enters the graphite tube can be adjusted by using the nut located towards the end of the dispensing arm. Ensure the capillary does not rest on the bottom of the inner graphite tube while dispensing.

Place samples, reagent water, and standard in tray. Run the test. Monitor the results to ensure quality. Save the results as a text document for analysis. Saving can be accomplished by selecting the print option. After accessing the ‘report’ tab, select the ‘write to text file’ option.

CALCULATIONS

A minimum of four and maximum of nine calibration concentrations (plus the blank) should be used for calculating a standard curve, ranging in concentration from 1 to 10 μg/L. A sample calibration curve is shown below. A linear relationship was acquired through regression analysis: $\text{Abs} = 0.0301*C + 0.00809$, or $C = 33.2*\text{Abs} - 0.269$.



REPORTING

Using the method above, the minimum reportable limit is 0.25 µg/L or an absorbance value of 0.01 AU, whichever is greater. All samples below this value should be reported as below detection limit. Report the mean result and %RSD for all samples. In cases where two replicates are in agreement (less than 5% RSD) but the third replicate is more than 20% different from the average of these two, remove this replicate. Recalculate the mean value and % RSD for this sample based on the remaining two replicates, and note that the reported value is an average of two replicates.

QUALITY CONTROL

Calibration

The standard curve for copper has been found to be linear. A graphical representation of the results can be monitored in real time that plots the concentration against the absorbance measured. Make sure it follows the established relationship. Do not proceed with sample analysis until a linear calibration curve can be established within the tolerances of the SpectraAA software. A minimum of five calibration points (including the blank) must be used in this calibration and no more than 20% of the initially recorded calibration points may be removed (masked) to achieve a good calibration fit. If the absorbance of the 1 µg/L standard is below 0.01 AU, realign the furnace and/ or the copper lamp and rerun the calibration.

Sample Results

Error can also be monitored in real time in the form of %RSD. The error is generally higher for very low concentrations. If the error is increasing with each sample; however, it may be an indicator the GTA is getting out of alignment. Reject or re-run samples of Cu > 1 ppb that have an RSD > 5%. Reject or re-run samples of Cu < 1 ppb that have an RSD > 10%. Also, dilute and re-run samples having a concentration greater than 110% of the highest calibration standard (11 ppb).

General Procedures

Due to the low levels of metals being tested, extra care is taken to ensure quality results. Contamination can be avoided by wearing gloves whenever handling samples, by keeping samples covered to avoid dust, by avoiding contact with the interior of the sample tubes, and by minimizing contact between pipet tips with any surfaces. Proper and consistent sample container cleaning is required.

Accuracy and Reproducibility

QC samples should be run with each set of samples to ensure the accuracy of your measurements. *Standard Methods* recommends running check samples (reagent blank, LFB and LFM) periodically to achieve this result. At least one duplicate sample should also be run to determine the precision of the results. The sample for duplicate analysis shall be selected randomly (e.g., using a random number generator) prior to the run. For this method, two sequences have been developed for running samples and check standards, based on the number of samples to be run. These sequences are shown on the following page. This order assumes that the software is programmed to run a reagent blank after the final calibration standard. This sequence means that, for a full 50 position run, a maximum of 40 distinct experimental samples may be run.

1. Runs with fewer than 20 samples for analysis (this example assumes 15 samples)

Sample Order	Description	Sample Order	Description
1	Reagent blank	17	Duplicate sample
2	First analytical sample	18	LFB
3	Next Analytical sample	19	LFM
4-15	Additional samples	20	Reagent blank*
16	Last analytical sample	21	Reagent blank

2. Runs with more than 20 samples for analysis (this example assumes 30 samples)

Sample Order	Description		
1	Reagent blank	21	Reagent blank
2	First analytical sample	22	Resume analytical samples
3	Additional samples	23-35	Additional sample
4-15	….	36	Last analytical sample
16	Midpoint of analytical samples	37	Duplicate sample (from samples 16-30)
17	Duplicate sample (from samples 1-15)	38	LFB
18	LFB	39	LFM
19	LFM	40	Reagent blank*
20	Reagent blank	41	Reagent blank

*Note: The purpose of the first of the dual reagent blanks is to assess any possible carryover effect from the LFM samples. If carryover is observed, the first replicate for each sample will be removed from the analysis.

QA/QC samples should be monitored during the sample run. If the first reagent blank results indicate Cu above the minimum reportable limit for that run (0.25 µg/L or 0.01 AU), another reagent blank should be run immediately. If the blank is fine, the run may continue. If not, make up and test a new reagent; if not, address the issue before running samples. If the LFB result is less than 80% or greater than 120% of the actual sample value, another LFB sample may be run. If this sample also does not meet the requirements, further action, including re-running the samples, may be required. If the LFM is less than 80% or greater than 120% of the actual value, the samples may not need to be rerun. A standard addition process should then be carried out to determine matrix effects on the reported results.

During the testing process, there are several things to look for to ensure quality results. Monitor the video feed of the graphite tube injection point. The dispensing arm can become misaligned and need recalibration. This will be evident when it is no longer visible in the video feed during the injection step. Absorbance measured for each sample may also suddenly go to near zero as the samples fail to be injected into the tube.

INSTRUMENT MAINTENANCE PROCEDURES AND TRAINING

All users will be trained to operate the AA before collecting sample data. A logbook will be placed next to the AA unit to record instrument use and maintenance operations. Every time the AA is run, the user will enter basic information into this logbook related to number and type of samples run, number of firings on the current graphite tube, Ar gas pressure, etc. Basic user-performed maintenance, including switching the unit from flame to furnace operation, replacing a graphite tube or cleaning the furnace windows, should also be recorded, along with the date of the operation. If additional maintenance is required, the user should contact Dr. Peltier to inform him of the problem and any solution reached. Signal from the Cu lamp should be monitored as described in the AA User Manual and a replacement lamp purchased when necessary.

A dedicated folder on the AA computer will be set up for each user. All user generated methods, sample lists and results should be placed into their folder and labeled with (at a minimum) the element and date of analysis. Each set of results should also be saved as a text file in the same folder for export to MS Excel or similar program for later analysis, as the AA software has a single-machine license. These folders will be periodically backed up to the School of Engineering servers.

APPENDIX G
SOP FOR MEASURING ANTIMONY BY ICP-MS

With ICP-MS Protocol by Dr. Gwendolyn Macpherson, Plasma Analytical Laboratory, University of Kansas

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, antimony concentrations in water samples are determined using a modified version of EPA Method 200.8 (EPA 1994), following the specific steps outlined below. Where deviations from that method exist, this SOP should be followed instead. QA/QC procedures are adapted from Standard Method 1020 (APHA et al. 2005), while sample collection and preservation guidelines follow Standard Method 1060. This method has been developed based on the standard operating procedure for liquid analysis by ICP-MS provided by Dr. Gwendolyn Macpherson, Director of the University of Kansas Plasma Analytical Laboratory (Macpherson 2012), which is attached at the end of this SOP.

DEFINITIONS

- RO water- Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.
- Experiment water- Tap water prepared for use in these experiments by pH adjustment and/or dechlorination, as described in the SOP for experiment water preparation.
- Reagent water- Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.

APPARATUS

To analyze samples for antimony concentrations, a VG-Elemental (now Thermo-Scientific) PQII+XS quadrupole inductively coupled plasma mass spectrometer (ICP-MS) instrument is used. This instrument is owned and maintained by the University of Kansas Plasma Analytical Laboratory. This approach allows for better sensitivity for Sb detection in the appropriate range (parts per billion) than the atomic absorption instrument used for Pb and Cu detection for this project. A full configuration of the ICP-MS system is provided in the document "Instrument and Run Conditions for Liquid Analysis by ICP-MS (Macpherson 2012).

SAMPLE PREPARATION

Aqueous samples for antimony analysis are to be stored in HDPE bottles and acidified to pH < 2 using concentrated nitric acid upon collection at a ratio of 2 mL acid per 100 mL sample. Samples intended for dissolved metal analysis should be filtered immediately upon collection through a 0.45-micron filter using a syringe filter (nylon or acetate). Samples should be stored at 4 °C for no more than six months before analysis. A dilution multiplier of 1.02 will be included in the sample worksheet for these samples to account for the nitric acid addition to the sample.

If digestion is required for total antimony analysis of aqueous samples, digestion will be carried out using trace-metal grade concentrated nitric acid at a 1:10 ratio to the sample. The sample will be heated in a block heater to 95 degrees Celsius for 60 minutes, and allowed to cool before analysis. A dilution multiplier of 1.1 will be included in the sample worksheet for any total digestion samples to account for the nitric acid addition compared to the sample.

This SOP assumes that all samples are aqueous samples contain dissolved or particulate lead. Digestion procedures for any solid samples will be developed separately. Prepare standards, blanks, and matrix spikes as follows:

Calibration Standards

Calibration standards are prepared from certified stock standards containing 1000 mg/L Sb in 0.6% tartaric acid and trace amounts of nitric acid. These standards can be purchased from Fisher Scientific (catalog #: CL Sb7-2Y, or equivalent). Standards are prepared by diluting the stock standard into a solution containing reagent water and 0.4 mL nitric acid to a total volume of 50 mL. 200 mL of one standard is prepared for use in instrument calibration and optimization checks. Prepare as needed, but do not use if more than six months old.

Reagent Blank

Reagent blanks are prepared by adding 0.2 mL of concentrated nitric acid to 9.8 mL of reagent water. Reagent blanks should be prepared at the same time as the analytical samples.

Laboratory-Fortified Blank (LFB)

Prepare an LFB sample by diluting the stock antimony standard in reagent water plus 0.4 mL of concentrated nitric acid to a total volume of 50 mL. The LFB concentration should be approximately in the middle of the range of Sb standards used for calibration, typically 5 ppb. Prepare as needed, but do not use if more than six months old.

Laboratory-Fortified Matrix (LFM)

Prepare a LFM sample by diluting the stock antimony standard in experiment water with 0.4 mL of concentrated nitric acid to a total volume of 50 mL. This sample should be prepared from the same batch of experiment water used to generate the analytical samples. The Sb concentration should be approximately in the middle of the range of Sb standards used for calibration, typically 5 ppb

Due to the high sensitivity of the ICP-MS, steps to avoid contamination must be strictly followed. Gloves should be worn whenever handling samples. Use brand-new, unused containers, or containers cleaned in a trace-metal acid bath, to store the samples.

For used sample containers, the proper cleaning process is as follows. Containers are scrubbed with liquinox soap and water. They are then rinsed at least three times each with tap water and RO water. Then, the containers are fully immersed in a 0.5% hydrochloric acid bath for at least 3 hours. After the acid bath, the containers are rinsed three times each with RO water, then reagent water. Containers should be drip-dried upside down on a Kimwipe to avoid contamination by laboratory dust. After drying, they should be sealed with either a cap or parafilm until use.

PROCEDURE

Prior to sample analysis, the instrument is checked to ensure good working order, including proper tuning of the quadrupole FR generator. Mass-calibration and cross-detector calibration for the instrument is repeated weekly. Cones are examined and wiped with a clean laboratory wipe daily, and cleaned weekly, or more frequently if indications of fouling are present. The ICP-MS is warmed up for at least one hour prior to the start of optimization, which is conducted prior to sample analysis. A full description of ICP-MS operating conditions and the instrument optimization procedure is provided in Macpherson (2012).

The optimization and analysis procedure will be carried out by Dr. Macpherson or by students who she has trained in ICP-MS operation using her lab's standard operating procedures. Analysis of antimony samples and standards is carried out using peak jumping, where three points per peak are integrated. This method maximizes the time spent on the signal, resulting in good peak to background signals. The Sb^{211} mass is selected for antimony quantification. Samples are loaded onto the ICP-MS autosampler, which automatically takes up the sample for injection into the instrument for analysis. Sample results are monitored during an experiment run to ensure quality. Data processing is carried out offline after the analysis is complete.

CALCULATIONS

A minimum of three and maximum of nine calibration concentrations (plus the blank) should be used for calculating a standard curve. The range of standard concentration used will vary depending on expected sample concentrations, but will be between 0.1 and 20 µg/L. A linear least-squares fit will be used to establish a relationship between Sb concentration and MS signal intensity for each experimental run. The % relative standard deviation (%RSD) for individual standards should be $\leq$ 10%.

REPORTING

EPA Method 200.8 lists the typical ICP-MS detection limits for antimony at 0.008 ppb (EPA 1994). For this method, actual detection limits during an experimental run are calculated as two times the absolute value of the relative standard deviation of the blanks times the absolute value of the y-intercept of the standard calibration curve. The quantitation limit is then assumed to be 10 times the calculated detection limit. Using this approach, detection limits are approximately 0.005 ppb, giving a minimum reportable limit of 0.05 µg/L. All samples below this value should be reported as below the quantitation limit. Report the mean result and %RSD for all samples. In cases where the % RSD is greater than 20%, the sample should be re-analyzed if possible. If not, a notation should be placed next to the sample results indicating that the measured value has a high uncertainty.

QUALITY CONTROL

Calibration

The standard curve for antimony has been found to be linear in the range of 0.1-20 µg/L. Do not proceed with sample analysis until a linear calibration curve can be established from the standards provided.

Sample Results

Measurement error can be monitored in the form of %RSD. The error is generally higher for very low concentrations (<0.2 ppb). If the error is greater than 20% or is increasing with each sample, however, this may be an indicator of problems with the instrument. Re-run samples with greater than 20% RSD whenever possible, or note that these samples have high uncertainty. Also, dilute and re-run samples having a concentration greater than 110% of the highest calibration standard (22 ppb).

General Procedures

Due to the low levels of metals being tested, extra care is taken to ensure quality results. Contamination can be avoided by wearing gloves whenever handling samples, by keeping samples covered to avoid dust, by avoiding contact with the interior of the sample tubes, and by minimizing contact between pipet tips and any surfaces. Proper and consistent sample container cleaning is required.

Accuracy and Reproducibility

QC samples should be run with each set of samples to ensure the accuracy of your measurements. Standard Methods recommends running check samples (reagent blank, LFB and LFM) periodically to achieve this result. At least one duplicate sample should also be run to determine the precision of the results. The sample for duplicate analysis shall be selected randomly (e.g., using a random number generator) prior to the run.

QA/QC samples should be monitored during the sample run. If the first reagent blank results indicate Sb above the minimum reportable limit for that run (0.5 µg/L or 0.01 AU), another reagent blank should be run immediately. If the blank is fine, the run may continue. If not, make up and test a new reagent; if not, address the issue before running samples. If the LFB result is less than 80% or greater than 120% of the actual sample value, another LFB sample may be run. If this sample also does not meet the requirements, further action, including re-running the samples, may be required. If the LFM is less than 80% or greater than 120% of the actual value, the samples may not need to be rerun. A standard addition process should then be carried out to determine matrix effects on the reported results.

INSTRUMENT MAINTENANCE PROCEDURES AND TRAINING

The ICP-MS used for these experiments is maintained by the University of Kansas Plasma Analytical Laboratory. This laboratory also performs regular maintenance checks on the instrument following their established standard operating procedures. Samples for this project will be analyzed by project personnel only after training by Dr. Macpherson on the operation and use of the ICP-MS. Otherwise, they will be analyzed by Dr. Macpherson or one of her associates. When providing the results of an experiment run to the project personnel, Dr. Macpherson also provides an assessment of data quality and reliability from that run, along with recommendations on whether samples should be re-analyzed. When re-analysis is recommended, project personnel will discuss this recommendation with Dr. Macpherson and then prepare samples for re-analysis as appropriate. Both the raw results provided by Dr. Macpherson and the final processed results (including QA/QC analysis), will be saved as Excel files and will be periodically backed up to the School of Engineering servers.

Instrument and Run Conditions for Liquid Analysis By ICP-MS (V. 1)

Dr. Gwendolyn L. Macpherson, Director
University of Kansas Plasma Analytical Laboratory
18 January 2012

The instrument used is a VG-Elemental (now Thermo-Scientific) PQII+XS quadrupole inductively-coupled plasma mass spectrometer (ICP-MS). Other brands of ICP-MS will have slightly different configurations. The goal of the analyst is to create a stable signal, optimizing the singly-charged ion signal while minimizing interfering species such as doubly-charged ions, refractory oxides (e.g., MO^+, MO_2^+), and polyatomic ions (e.g., ArO^+, ArN^+, ArC^+). As a general rule, the instrument should be in good working condition, with quadrupole RF generator properly tuned and, for Channeltron-type detectors, the electron multiplier detector (pulse-counting mode of detection) voltage should be set at the plateau and the analog detector voltage adjusted to match the manufacturer-suggested multiplier factor. The mass calibration and cross-detector calibration should be repeated weekly. Cones should be examined and wiped with a clean laboratory wipe daily, and cleaned weekly or more frequently if fouling reduces signal strength or causes instability. Equipment configuration for the ICP-MS used to develop the protocol is listed below.

- X-Y-Z autosampler with PEEK sipper probe (Gilson model 222)
- 17 x 1000 mm polypropylene autosampler vials
- PTFE microbore tubing, (0.012” ID, 0.030” OD) between autosampler and peristaltic pump, and between peristaltic pump and nebulizer
- PTFE microbore tubing (0.032” ID, 0.056” OD) for draining spray chamber and supplying rinse to home position of autosampler
- Peristaltic pump with at least 3 stages (Gilson MiniPuls3), one for sample transfer, one for draining the spray chamber, and one for continuous supply of fresh rinse solution to autosampler “home” position. Tygon peristaltic pump tubing, 0.020” diameter, for sample, 0.040” diameter for drain and rinse.
- Glass Expansion concentric nebulizer
- Quartz-glass Scott-type double pass spray chamber, jacketed for cooling purposes
- Quartz-glass single-piece torch
- Nickel sampler cone, ~1 mm diameter opening
- Nickel skimmer cone, ~1 mm diameter opening

The ICP-MS is warmed up for at least one hour prior to the start of the optimization routine. Operating conditions are:

Plasma (cool) gas	~13.8 L/min
Auxiliary gas	~0.8 L/min
Nebulizer gas	~0.8 L/min
Forward power	~1350 watts
Reflected power	<2 watts
Peristaltic pump rate	set to produce sample flow rate of ~1 mL/min
Interface vacuum	~1.4 mbar
Analyzer vacuum	~2 $*10^{-7}$ mbar

The optimization routine is as follows:

1. Tune the instrument, finding the highest signal on ^{115}In with the lowest percent oxides (^{156}[CeO]/^{140}Ce*100) and percent doubly-charged ions (^{69}Ba^{++}/^{138}Ba^{+}*100). Tuning involves torch position (x, y, z) and ion lenses.
2. Run the Startup Scan. This procedure runs 5 60-seconds replicates of a suite of elements and molecular species in scan mode, covering mass 6 to 238 while skipping usual regions where background signals are too high (mass 80 which is ^{40}Ar$_2$, mass ^{40}Ar, ^{23}Na, etc.). Specific masses monitored in this routine and used to check optimization are: ^{9}Be, ^{24}Mg, mass 54 which is ^{40}Ar^{14}N, mass 56 which is ^{40}Ar^{16}O, ^{59}Co, ^{60}Ni, ^{69}Ba^{2+}, ^{84}Kr, ^{115}In, ^{138}Ba, ^{140}Ce, ^{156}CeO ^{208}Pb, ^{209}Bi, and ^{238}U.
3. A mass response curve (log scale) of the abundance-normalized ion signals is plotted, using Be, Mg, Co, Ni, In, Ba, Ce, Pb, Bi and U. The curve should be slightly concave down.
4. Other checks of the startup-scan are made: % RSD (relative standard deviation, which is 1 standard deviation/mean) for all metals in the solution should be <2%. Oxides should be <2%. Doubly charged ions should be <5%. Molecular ions should be of similar intensity as previous days; a log book should be kept recording these levels. The Kr level should be low; high Kr is an indication of impure Ar gas from the gas supplier. The scanning results are examined for peak resolution both at the low mass region (^{24}Mg, ^{25}Mg) and the high mass region (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{209}Bi). Mass 202 is checked for abnormal Hg levels.

For analysis of samples and standards, the analytical routine was peak jumping, where three points per peak were integrated. The peak-jumping technique maximizes the time spent on the signal, resulting in good peak to background signals.

The element menu contains the analyte and internal standard masses.

Usually, for each analysis, 120 seconds of uptake time are allowed, followed by three replicates, each of 20-second duration, followed by 180 seconds of rinse time.

Data are processed offline.

ADDENDA, 16 May 2013

Metals analysis method, including analysis of Cu, Sb and Pb, is always modified from EPA method 200.8.

For analysis of only three elements, 120 seconds of uptake time are allowed, followed by three replicates, each of 10 to 20-second duration (longer time for low concentrations), followed by 180 seconds of rinse time. Selected masses for quantification are ^{121}Sb, ^{63}Cu, ^{65}Cu, and ^{208}Pb.

APPENDIX H
SOP FOR FILL-AND-DUMP EXPERIMENT 1 (FD1)

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lined or coated lead and copper pipe sections (and unlined or uncoated control sections). This SOP describes the steps taken to conduct the first of these tests. This method references other SOPs on the preparation of extraction water and on the measurement of individual water constituents.

DEFINITIONS

- RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.
- Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.
- Extraction waters (described in the SOP for Preparing Extraction Waters, ver. 1.0, Appendix A): 1) dechlorinated tap water adjusted to pH 8.0; 2) chlorinated pH 8 extraction water containing 1 mM $NaHCO_3$ and 1 mM $CaCl_2$ and having a free chlorine concentration of about 2 mg/L; and 3) low pH extraction water having a pH of 6.5 – a more aggressive water used especially to test pipe samples for metal leaching and also for leaching of organic compounds at a lower pH value.

MATERIALS

Pipe Samples

Pipe samples obtained from participating utilities and subsequently lined or coated, except for the unlined / uncoated control samples. The linings and coatings will be installed / applied by representatives of the manufacturers when possible, following their own procedures, so that the lining or coating will confirm to the manufacturer's specifications. For epoxy coating, this includes sandblasting the pipes to remove surface materials, followed by the addition of the coating and overnight curing. The pipes will then be shipped back to the University of Kansas by overnight delivery. Upon receipt of the pipe samples at KU, they will be examined for damage to the pipe or the end fittings. Pipes with significant damage may be removed from the experiment at this time. To minimize any additional curing time, fill-and-dump experiments will begin immediately after the coated or lined pipe samples are received. If enough samples are available, however, some of the coated pipe samples may be set aside for later experiments. For all tests, a control sample consisting of an unlined and uncoated pipe will also be used. This control sample will remain at KU throughout the coating or lining process, to reduce shipping costs and to better maintain the control section in its native state, i.e., so that the results of the lined and coated pipe sections can be compared to those from a relatively undisturbed pipe section and not to one that has been sand-blasted, scraped, or otherwise prepared for lining or coating.

Extraction Waters

Batches of extraction water (dechlorinated tap water, chlorinated pH 8 extraction water, and low-pH extraction water) will be prepared in advance of the fill-and-dump tests following the procedures outlined in the SOP for Preparing Extraction Waters, ver. 1.0 (Appendix A). These waters will be allowed to reach room temperature prior to use in the fill-and-dump experiments. Samples of the dechlorinated tap water will be collected and analyzed for pH, dissolved oxygen, conductivity, alkalinity, and total chlorine prior to use. Additional samples of dechlorinated tap water will be collected and stored for analysis of total hardness, major anions, TOC, lead, copper, and any other relevant metals, as these analyses may be conducted after the fill-and-dump experiments have been carried out. Samples of the chlorinated pH 8 extraction water and the low-pH extraction water will be collected for analysis of all analytes to be determined on extracts. All sample collection, storage, and analysis procedures will be conducted following the relevant SOPs.

EXPERIMENTAL PROCEDURE

Preparation

After the pipe samples are inspected (as described above), the pipe nipples on each end should be thoroughly rinsed with tap water and wiped with a clean laboratory towel (WypAll X60) to remove any loose residues potentially containing lead.

Pipe samples will be flushed with cold tap water for 15 minutes to remove any particles or other debris from the interior of the pipe surfaces. The exact flushing time actually used will be recorded, and should be consistent among individual pipe samples within each fill-and-dump experiment. The pipe samples may be flushed individually or connected in series, but the control pipe samples (having potentially high lead or copper levels) should occupy the last position when placed in series. When connecting pipe samples to the flushing manifold, handle them carefully to avoid damaging the lining or coating. Be especially careful not to twist the pipe nipples, which could create a gap in the lining or coating and expose Pb or Cu metal to the extraction water. Hand tighten all connections if possible. If a wrench is needed to stop a leak, use two wrenches – one to hold the pipe nipples stationary and the other to tighten the fitting.

The flushing water will be discharged directly into the sink, and will not be retained for analysis. Following flushing, each pipe sample will be rinsed with 50-100 mL of the desired extraction water and then filled with that same water. The pipe sample will then be sealed with silicone stoppers, and the date and time recorded as the start time for the fill-and-dump experiment for that pipe section.

Design of the Test Matrix

Fill-and-dump tests will be conducted for different lengths of time on different pipe sections to determine the impact of contact time on leaching of metal and organic compounds. The specific schedule for each set of tests will be determined prior to beginning the fill-and-dump experiment and will depend on the total number of pipe samples available. In each case, similar experiments will be carried out using dechlorinated tap water and chlorinated extraction water. At least one test condition will be carried out in duplicate to examine the reproducibility of our results. For the first set of experiments, we anticipate having at least seven coated pipe sections available for both the lead and copper pipes, along with one control pipe of each material. The full test matrix for this experiment is shown below. This matrix will be applied to both the lead and copper pipe sections, with the fill-and-dump experiments for each type of pipe being conducted simultaneously.

	Dechlorinated Tap Water		Chlorinated Water
Holding Time	# of Coated Sections	# of Control Sections	# of Coated Sections
6 hours	2	1	1
24 hours	1	--	1
4 days	1	--	1

Collection of Water for Analysis

At the end of the designated reaction time for each pipe section, one end of the pipe section will be unsealed. The water within that pipe section will then be poured into a glass beaker that has been pre-cleaned and drip-dried. The pre-cleaning method will consist of 1) rinsing with methanol to remove any organic compounds; 2) rinsing with RO water; 3) immersion in an HCl acid bath for 2–24 hours; 4) rinsing with RO water; and 5) rinsing with reagent water. Beakers that are reused from one test to another will be cleaned in the same manner. Due to the anticipated high levels of lead or copper (and possible lead or copper particles) in the control pipe sections, special beakers will be designated for use with the control pipe sections only. These beakers will be cleaned between uses using Liquinox detergent and water to remove particles, then rinsed in the same manner as the other beakers.

Sections with Dechlorinated Tap Water. Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
Total Organic Carbon	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~ 2

*If limited volume available, collect only 30 mL

The remaining sample will be transferred to a glass bottle for analysis of organic compounds. An additional 10 mL sample will be collected from the control pipe and stored for lead and copper analysis in case a filtered sample is needed for dissolved metals. Excess sample beyond that needed for organic analysis will be used to obtain backup samples for other tests as needed.

Sections with Chlorinated pH 8 Extraction Water. Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
Total Organic Carbon	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~2
Free chlorine	50 mL	150-mL beaker	Analyze immediately
TOX	50 mL	50-mL serum bottle	Dechlorinate, then preserve with HNO_3 to pH ≤ 2†

*If limited volume available, collect only 20-30 mL

† Dechlorinate by adding 1-2 drops of one of the dechlorinating solutions described in the SOP for preparing extraction waters, and preserve by adding 3 drops of concentrated HNO_3 per 50–60 mL sample.

The remaining sample will be transferred to a glass bottle, for analysis of organic compounds, and will be immediately dechlorinated by adding, to each 100 mL of sample, 2 drops of a 1/10th dilution of one of the dechlorinating solutions described in the SOP for Preparing Extraction Waters. Check immediately to verify that the residual chlorine has been quenched; if not, add additional 1/10th-strength dechlorinating solution dropwise until the sample is dechlorinated. Excess sample beyond that needed for organics analysis will be used as backup samples for other tests as needed. If less than 230 mL is initially present in the beaker, the volumes collected for total organic carbon and metals by ICP analysis will be reduced to provide sufficient volume (at least 50 mL) for organics analysis.

Metal Leaching Tests

Leaching tests with the low-pH (6.5) extraction water will be conducted on two pipe sections of each type following the initial fill-and-dump tests. For both lead and copper pipes, one of the pipe samples filled with dechlorinated tap water for 6 hours and one filled with chlorinated pH 8 extraction water will be used for these tests, as well as the control (uncoated) pipe section. This test will begin the day after the six-hour fill-and-dump tests are completed. The pipe sections will be flushed with 100 mL of pH 6.5 water to remove any water from the initial fill-and-dump tests. Then each pipe section will be filled with pH 6.5 water and sealed. After six hours, the water will be poured from the pipe into a glass beaker. Sub-samples of the water will be collected for analysis as described above for sections containing dechlorinated tap water.

Following the 6-hour fill-and-dump test with pH 6.5 water, the same pipe sections will be restoppered and stored up to 48 hours before starting a long-term metals leaching test. They will then be rinsed with 100 mL RO water, rinsed with 100 mL of pH 6.5 water, filled with pH 6.5 water, resealed, and held for one week. At the end of that time, the sections will be emptied and subsamples collected for analysis in the same manner described above for sections containing dechlorinated tap water.

Long-Term Organic Leaching Tests

Upon completion of the 24-hour fill-and-dump tests, the same pipe sections will be rinsed with 100 mL of either dechlorinated tap water or chlorinated extraction water (whichever they previously contained), refilled with the same water and sealed. These sections will be left for 10 days. At the end of that time, the sections will be emptied and subsamples collected for analysis in the appropriate manner for the specific water as described above.

Storage of Pipe Sections after Use

Pipe sections not being reused within 48 hours will be drained and allowed to dry before being resealed with vinyl end caps. Pipe sections being reused within 48 hours for additional testing (including the metal leaching tests and long-term organic leaching tests described above) will be drained and stored while still damp by sealing the ends with clean stoppers or vinyl end caps.

Room Temperature

Record the room temperature in your lab notebook at least twice each day (a.m. and p.m.) when tests are in progress. If the room temperature drop below 20 °C or rises above 25 °C, attempt to remedy the problem (e.g., by adjusting the thermostat or opening a door or window) and notify the PI or a co-PI.

REPORTING AND LABELING

Each coated or lined pipe section, as well as all control sections used in the fill-and-dump experiments, will be assigned a unique identifier. This identifier will consist of the letter L or C (for lead and copper pipes, respectively) and a number. This number will increment from L0 (the lead pipe control section) and C0 (the copper pipe control section) and will not be reused. For each section the date of initial coating will be recorded, as well as the dates and nature (type of water, length of time) for any fill-and-dump experiments that pipe participated in. These data will be recorded in a spreadsheet to allow for tracking of the full experimental history of each pipe section. Any additional observations on the pipe section (damage, corrosion, etc.) will be noted in the same spreadsheet.

Each fill-and-dump experiment will be assigned an experiment number that will be recorded in the laboratory notebook. Experiment numbers for fill-and-dump experiments will be of the format FD-YY-Date, where FD refers to a fill-and-dump experiment, YY is the incremental number of the experiment and Date is the start date of the experiment. All aqueous samples collected during the fill-and-dump experiments will be labeled with the experiment number followed by the sample identification (ID) number. Sample ID numbers will be recorded in the laboratory notebook along with a full description of the sample. These sample ID numbers will also be used in any electronic files produced during analysis of the sample.

APPENDIX I
SOP FOR FILL-AND-DUMP EXPERIMENT 2 (FD2)

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lined or coated lead and copper pipe sections (and unlined or uncoated control sections). This SOP describes the steps taken to conduct one subset of these tests, i.e., FD2, a follow up to the first test (FD1) conducted using epoxy-lined pipe sections. This method references other SOPs on the preparation of extraction water and on the measurement of individual water constituents.

DEFINITIONS

- RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.
- Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.
- Extraction water (described in the SOP for Preparing Extraction Waters, Ver. 2.0, Appendix B): chlorinated pH 8 extraction water (CL) containing 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl and having a free chlorine concentration of about 2 mg/L.

MATERIALS

Pipe Samples

Selected pipe sections used in fill-and-dump experiment FD1, plus two previously unused pipe sections, will be used in this experiment (FD2).

Extraction Water

Batches of extraction water (chlorinated pH 8 extraction water) will be prepared in advance of the fill-and-dump tests following the procedures outlined in the SOP for Preparing Extraction Water for Fill-and-Dump Tests, Ver. 2.0. The water will be allowed to reach room temperature prior to use in the fill-and-dump experiments. Samples of the chlorinated pH 8 extraction water (CL) will be collected for analysis of all analytes to be determined on extracts. All sample collection, storage, and analysis procedures will be conducted following the relevant SOPs.

EXPERIMENTAL PROCEDURE

Preparation

The two previously unused pipe sections will be flushed with cold tap water for 15 minutes to remove any particles or other debris from the interior of the pipe surfaces. When connecting pipe samples to the flushing manifold, handle them carefully to avoid damaging the lining or coating. Be especially careful not to twist the pipe nipples, which could create a gap in the lining or coating and expose Pb or Cu metal to the extraction water. Hand tighten all connections if possible. If a wrench is needed to stop a leak, use two wrenches – one to hold the pipe nipples stationary and the other to tighten the fitting. The flushing water will be discharged directly into the sink, and will not be retained for analysis.

Each pipe sample will be rinsed with 100 mL of extraction water and then filled with extraction water. The pipe sample will then be sealed with silicone stoppers, and the date and time recorded as the start time for the fill-and-dump experiment for that pipe section.

Design of the Test Matrix

Fill-and-dump tests will be conducted for different lengths of time on different pipe sections to determine the impact of contact time on leaching of metals and organic compounds and on chlorine demand. The specific schedule for the tests is shown below. This matrix will be applied to both the lead and copper pipe sections, with the fill-and-dump experiments for each type of pipe being conducted simultaneously.

Pipe	**Relevant FD1 Info**	**Analytes**	**Detention Time**
Pb5802	Stored wet with Milli-Q	All – see below	24 h, then 7 d
Cu1202	Stored wet with Milli-Q, High TOC (4.78)	All – see below	24 h, then 7 d
Pb5805	High Pb (3.8, then 0.8)	All – see below	24 h, then 7 d
Cu1205	Detectable level of Pb (0.7)	All – see below	24 h, then 7 d
Pb5804	Control, never exposed to CL	All – see below	24 h, then 7 d
Cu1210	Control, never exposed to CL	All – see below	24 h, then 7 d
Pb5809	Unused (needs flushed)	All – see below	24 h, then 7 d
Cu5809	Unused (needs flushed)	All – see below	24 h, then 7 d
Pb5808	Exposed only to CL extraction water, High TOC (13.1)	All – see below	6 h
Cu1208	Exposed only to CL extraction water	All – see below	6 h
Pb5806	Exposed only to CL extraction water	Cl_2 Demand & pH Only	1 h, 1 h, …
Cu1206	Exposed only to CL extraction water	Cl_2 Demand & pH Only	1 h, 1 h, …

A separate test will be performed to determine the short-term chlorine demand of two pipe sections and changes over time. Two pipes (Pb5806 and Cu1206) will be filled with chlorinated pH 8 extraction water. After one hour, samples will be collected and immediately tested to determine the amount of free chlorine remaining. These tests will be repeated until either: 1) remaining free chlorine concentration is constant for at least three consecutive tests or 2) free chlorine demand is no longer observed.

Collection of Water for Analysis

At the end of the designated reaction time for each pipe section, one end of the pipe section will be unsealed. The water within that pipe section will then be poured into a glass beaker that has been pre-cleaned and drip-dried. The pre-cleaning method will consist of 1) rinsing with methanol to remove any organic compounds; 2) rinsing with RO water; 3) immersion in an HCl acid bath for 2–24 hours; 4) rinsing with RO water; and 5) rinsing with reagent water. Beakers that are reused from one test to another will be cleaned in the same manner. Due to the anticipated high levels of lead or copper (and possible lead or copper particles) in the control pipe sections (Pb5804 and Cu1210), special beakers will be designated for use with the control pipe sections only. These beakers will be cleaned between uses using Liquinox detergent and water to remove particles, then rinsed in the same manner as the other beakers.

Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
Total Organic Carbon	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~2
Free chlorine	50 mL	150-mL beaker	Analyze immediately

*If limited volume available, collect only 20-30 mL

The remaining sample will be transferred to a 4-oz. glass bottle, for analysis of organic compounds, and will be immediately dechlorinated by adding, to each 100 mL of sample, 2 drops of a 1/10th dilution of one of the dechlorinating solutions described in the SOP for preparing extraction waters. Check immediately to verify that the residual chlorine has been quenched; if not, add additional 1/10th-strength dechlorinating solution dropwise until the sample is dechlorinated. Excess sample beyond that needed for organics analysis will be used as backup samples for other tests as needed.

Samples for analysis of organic compounds will not be collected from the uncoated control pipe sections (Pb5804 and Cu1210) or from those used in the short-term Cl_2 demand tests (Pb5806 and Cl1206). Samples from the latter sections will be analyzed only for Cl_2 and pH.

Storage of Pipe Sections after Use

Once tests are completed on a pipe section, it will be stored in the same manner (wet or dry) as it was previously stored. Those stored dry will be drained and allowed to dry before being resealed with vinyl end caps. Those stored wet will be filled with reagent water and capped with silicone stoppers, then refilled again with reagent water every 7 days.

Room Temperature

Record the room temperature in your lab notebook at least twice each day (a.m. and p.m.) when tests are in progress. If the room temperature drop below 20 °C or rises above 25 °C, attempt to remedy the problem (e.g., by adjusting the thermostat or opening a door or window) and notify the PI or a co-PI.

REPORTING AND LABELING

Each sample will be assigned a unique identifier. This identifier will consist of the letters Pb or Cu (for lead and copper pipes, respectively) followed by the last two letters of the pipe section number and the extraction water retention time. For example, the sample collected from pipe section Pb5802 after 24 hours will be labeled Pb02-24.

For each section the date of initial coating and its use in previous experiments has been recorded. The relevant information from this experiment will be added to the existing data base to allow for tracking of the full experimental history of each pipe section. Any additional observations on pipe sections (damage, corrosion, etc.) will be noted in the same spreadsheet.

Each fill-and-dump experiment will be assigned an experiment number that will be recorded in the laboratory notebook. Experiment numbers for fill-and-dump experiments will be of the format FD-YY-Date, where FD refers to a fill-and-dump experiment, YY is the incremental number of the experiment and Date is the start date of the experiment. All aqueous samples collected during the fill-and-dump experiments will be labeled with the experiment number followed by the sample identification (ID) number. Sample ID numbers will be recorded in the laboratory notebook along with a full description of the sample. These sample ID numbers will also be used in any electronic files produced during analysis of the sample.

APPENDIX J
SOP FOR FILL-AND-DUMP EXPERIMENT 3 (FD3)

INTRODUCTION

For Project 4351: Evaluation of Lead Service Line Lining and Coating Technologies, a series of fill-and-dump tests will be conducted using lined or coated lead and copper pipe sections (and unlined or uncoated control sections). This SOP describes the steps taken to conduct the tests done using PET-lined pipe sections. This method references other SOPs on the preparation of extraction water and on the measurement of individual water constituents.

DEFINITIONS

- RO water – Water processed by the Millipore ELIX reverse osmosis system in Learned Hall 1116, or an equivalent system.
- Reagent water – Water produced by the Millipore Polishing system in Learned Hall 1116 (which consists of a Millipore Elix RO system followed by a Millipore A10 unit) or an equivalent process, such as the single step polishing unit located in Room 4115.
- Extraction waters (described in the SOP for extraction water preparation): 1) dechlorinated tap water adjusted to pH 8.0; 2) chlorinated pH 8 extraction water containing 0.56 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.44 mM NaCl and having a free chlorine concentration of about 2 mg/L; and 3) low pH extraction water containing 0.018 mM $NaHCO_3$, 1 mM $CaCl_2$, and 0.912 mM NaCl and having a pH of 6.5 – a more aggressive water used especially to test pipe samples for metal leaching and also for leaching of organic compounds at a lower pH value.

MATERIALS

Pipe Samples

Pipe samples obtained from participating utilities and subsequently lined, except for the unlined control samples. The linings will be installed/applied by representatives of the manufacturers when possible, following their own procedures, so that the lining will conform to the manufacturer's specifications. For PET liners, this includes scraping, or pigging, the inner pipe walls to remove surface materials, if necessary, followed by the installation of the lining. The pipes will then be promptly shipped back to the University of Kansas. (Overnight delivery is not necessary for PET-lined pipe sections, since there is no "curing" involved as for coatings.) Upon receipt of the pipe samples at KU, they will be examined for damage to the pipe or the end fittings. Pipes with significant damage may be removed from the experiment at this time. The fill-and-dump experiments will begin promptly once the coated or lined pipe samples are received. If enough samples are available, however, some of the pipe samples may be set aside for later experiments. For all tests, control samples consisting of an unlined lead pipe and an unlined copper pipe will also be used. The control samples will remain at KU throughout the coating or lining process, to reduce shipping costs and to better maintain the control section in its native state, i.e., so that the results for the lined pipe sections can be compared to those from a relatively undisturbed pipe section and not to one that has been sand-blasted, scraped, or otherwise prepared for lining or coating.

Extraction Waters

Batches of extraction water (dechlorinated tap water, chlorinated pH 8 extraction water, and low-pH extraction water) will be prepared in advance of the fill-and-dump tests following the procedures outlined in the SOP for Preparing Extraction Waters, Ver. 2.0. These waters will be allowed to reach room temperature prior to use in the fill-and-dump experiments. Samples of the dechlorinated tap water will be collected and analyzed for pH, dissolved oxygen, conductivity, alkalinity, and total chlorine prior to use. Additional samples of dechlorinated tap water will be collected and stored for analysis of total hardness, major anions, TOC, lead, copper, antimony, and any other relevant metals, as these analyses may be conducted after the fill-and-dump experiments have been carried out. Samples of the chlorinated pH 8 extraction water and the low-pH extraction water will be collected for analysis of all analytes to be determined on extracts. All sample collection, storage, and analysis procedures will be conducted following the relevant SOPs.

EXPERIMENTAL PROCEDURE

Preparation

After the pipe samples are inspected (as described above), the pipe nipples on each end should be thoroughly rinsed with tap water and wiped with a clean laboratory towel (WypAll X60) to remove any loose residues potentially containing lead, copper, antimony, or other substances, including organic contaminants.

Pipe samples will be flushed with cold tap water for 15 minutes to remove any particles or other debris from the interior of the pipe surfaces. The exact flushing time actually used will be recorded, and should be consistent among individual pipe samples within each fill-and-dump experiment. The pipe samples may be flushed individually or connected in series, but the control pipe samples (having potentially high lead or copper levels) should occupy the last position when placed in series. When connecting pipe samples to the flushing manifold, handle them carefully to avoid damaging the lining or coating. Be especially careful not to twist the pipe nipples, which could create a gap in the lining or coating and expose Pb or Cu metal to the extraction water. Hand tighten all connections if possible. If a wrench is needed to stop a leak, use two wrenches – one to hold the pipe nipples stationary and the other to tighten the fitting.

The flushing water will be discharged directly into the sink, and will not be retained for analysis. Following flushing, each pipe sample will be rinsed with at least 100 mL of the desired extraction water and then filled with that same water. The pipe samples will then be sealed with HDPE stoppers, using PTFE tape when necessary to prevent leaks, and the date and time will be recorded as the start time for the fill-and-dump experiment for that pipe section.

Design of the Test Matrix

Fill-and-dump tests will be conducted for different lengths of time on different pipe sections to determine the impact of contact time on leaching of metal and organic compounds. The specific schedule for each set of tests will be determined prior to beginning the fill-and-dump experiment and will depend on the total number of pipe samples available. In each case, similar experiments will be carried out using dechlorinated tap water and chlorinated extraction water. At least one test condition will be carried out in duplicate to examine the reproducibility of our results. For the second set of experiments, we anticipate having at least seven lined pipe sections available for both the lead and copper pipes, along with one control pipe of each material. The full test matrix for this experiment is shown below. This matrix will be applied to both the lead and copper pipe sections, with the fill-and-dump experiments for each type of pipe being conducted simultaneously.

	Dechlorinated Tap Water		Chlorinated Water
Holding Time	# of Lined Sections	# of Control Sections	# of Lined Sections
6 hours	2	1	1
24 hours	1	--	1
4 days	1	--	1

Collection of Water for Analysis

At the end of the designated reaction time for each pipe section, one end of the pipe section will be unsealed. The water within that pipe section will then be poured into a glass beaker that has been pre-cleaned and drip-dried. The pre-cleaning method will consist of 1) rinsing with ethanol to remove any organic compounds; 2) rinsing with RO water; 3) immersion in an HCl acid bath for 2–24 hours; 4) rinsing with RO water; and 5) rinsing with reagent water. Beakers that are reused from one test to another will be cleaned in the same manner. Due to the anticipated high levels of lead or copper (and possible lead or copper particles) in the control pipe sections, special beakers will be designated for use with the control pipe sections only. These beakers will be cleaned between uses using Liquinox detergent and water to remove particles, then rinsed in the same manner as the other beakers.

Sections with Dechlorinated Tap Water

Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
Total Organic Carbon	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~ 2

*If limited volume available, collect only 30 mL

The remaining sample will be transferred to a 4-oz. (120 mL) glass bottle with a PTFE-lined cap for analysis of organic compounds. An additional 10 mL sample will be collected from the control pipe and stored for lead and copper analysis in case a filtered sample is needed for dissolved metals. Excess sample beyond that needed for organic analysis will be used to obtain backup samples for other tests as needed.

Sections with Chlorinated pH 8 Extraction Water

Once in the beaker, sub-samples of this water will then be poured out and collected for analysis as follows:

Method	Volume	Storage	Notes
pH	20 mL	50 mL beaker	Analyze immediately
Lead and Copper	10 mL	PE test tube	Preserve with nitric acid
Metals by ICP	20 mL	PE test tube	Preserve with nitric acid
TOC	40 mL*	EPA vial	Preserve with H_3PO_4 to pH ~2
Free chlorine	50 mL	150-mL beaker	Analyze immediately
Organic Compounds	≥102 mL	4-oz. glass vial w/ PTFE lined cap	Dechlorinate immediately; analyze ASAP

*If limited volume available, collect only 20-30 mL

† Dechlorinate by adding 1-2 drops of one of the dechlorinating solutions described in the SOP for preparing extraction waters, and preserve by adding 3 drops of concentrated HNO_3 per 50–60 mL sample.

Any remaining sample will be transferred to a glass bottle, for analysis of organic compounds, and will be immediately dechlorinated by adding, to each 100 mL of sample, 2 drops of a 1/10th dilution of one of the dechlorinating solutions described in the SOP for Preparing Extraction Waters. Check immediately to verify that the residual chlorine has been quenched; if not, add additional 1/10th-strength dechlorinating solution dropwise until the sample is dechlorinated. Excess sample beyond that needed for organics analysis will be used as backup samples for other tests as needed.

Metal Leaching Tests

Leaching tests with the low-pH (6.5) extraction water will be conducted on two pipe sections of each type following the initial fill-and-dump tests. For both lead and copper pipes, one of the pipe samples filled with dechlorinated tap water for 6 hours and one filled with chlorinated pH 8 extraction water will be used for these tests, as well as the control (uncoated) pipe section. This test will begin the day after the six-hour fill-and-dump tests are completed. The pipe sections will be flushed with 100 mL of pH 6.5 water to remove any water from the initial fill-and-dump tests. Then each pipe section will be filled with pH 6.5 water and sealed. After six hours, the water will be poured from the pipe into a glass beaker. Sub-samples of the water will be collected for analysis as described above for sections containing dechlorinated tap water.

Following the 6-hour fill-and-dump test with pH 6.5 water, the same pipe sections will be flushed again with 100 mL of pH 6.5 water. They will then be filled with pH 6.5 water, resealed, and left for one week. At the end of that time, the sections will be emptied and subsamples collected for analysis in the same manner described above for sections containing dechlorinated tap water.

Long-Term Organic Leaching Tests

Upon completion of the 24-hour fill-and-dump tests, the same pipe sections will be rinsed with 100 mL of either dechlorinated tap water or chlorinated extraction water (whichever they previously contained), refilled with the same water and sealed. These sections will be left for 4 days. At the end of that time, the sections will be emptied and subsamples collected for analysis in the appropriate manner for the specific water as described above.

Storage of Pipe Sections after Use

Pipe sections not being reused within 24 hours will be drained and allowed to dry before being resealed with vinyl end caps. Pipe sections being reused within 24 hours for additional testing (including the metal leaching tests and long-term organic leaching tests described below) will be drained and stored while still damp by sealing the ends with vinyl end caps.

Room Temperature

Record the room temperature in your lab notebook at least twice each day (a.m. and p.m.) when tests are in progress. If the room temperature drop below 20 °C or rises above 25 °C, attempt to remedy the problem (e.g., by adjusting the thermostat or opening a door or window) and notify the PI or a co-PI.

REPORTING AND LABELING

Each lined pipe section, as well as all control sections used in the fill-and-dump experiments, will be assigned a unique identifier. This identifier will consist of the letter Pb or Cu (for lead and copper pipes, respectively) and a number. For FD3, this number will increment from Pb11 and Cu11 and no number will be reused. For each section the date of initial coating will be recorded, as well as the dates and nature (type of water, length of time) for any fill-and-dump experiment that pipe participated in. These data will be recorded in a spreadsheet to allow for tracking of the full experimental history of each pipe section. Any additional observations on the pipe section (damage, corrosion, etc.) will be noted in the same spreadsheet.

Each fill-and-dump experiment will be assigned an experiment number that will be recorded in the laboratory notebook. Experiment numbers for fill-and-dump experiments will be of the format FD-YY-Date, where FD refers to a fill-and-dump experiment, YY is the incremental number of the experiment and Date is the start date of the experiment. All aqueous samples collected during the fill-and-dump experiments will be labeled with the experiment number followed by the sample identification (ID) number. Sample ID numbers will be recorded in the laboratory notebook along with a full description of the sample. These sample ID numbers will also be used in any electronic files produced during analysis of the sample.

RETESTING OF SAMPLES DUE TO COMPROMISED END FITTINGS

Based on leaks observed during flushing of the PET-lined pipe sections, a review of the preliminary results, and discussions with the vendor, it was determined that some of the test results, especially those for lead and copper, had been compromised. The end fittings used, which were provided by the research team and were not consistent with the vendor's standard practices, allowed flushing and/or extraction water to pass behind the liner and to directly contact the pipe wall and to become contaminated with Pb, Cu, and perhaps other metals. During the time the ends of the pipe sections were stoppered, the stoppers inserted into the end fittings most likely prevented contaminated water from coming into direct contact with the extraction water. However, contaminated water could have seeped up around the rims of the end fittings, not only before the pipe sections were stoppered but also after the stoppers were removed and as the extraction water was being dumped out, thereby contaminating the samples. To address this problem, the end fittings were removed from 10 pipe sections (5 LSLs and 5 CSLs), two of which were the same controls used earlier and two of which were lined sections that had not been used in previous tests. All these sections were re-extracted with low-pH (pH 6.5) reagent water.

The previously used pipe sections were stored wet (and were not dried as specified in the above protocol), and the previously unused sections were still dry, as they had not been used since being received from the vendor. The end fittings were removed from the previously used sections, exposing several inches of the PET liner on both ends of each pipe. Since it was possible that the pipe liner itself had become contaminated with Pb, Cu, or other materials from the pipe surfaces, the ends of each liner were cleaned by applying a Wypall L30 wipe dampened with 0.5% HCl to the outside. A separate wipe, dampened with reagent water, was applied to provide a second wipe and to remove any HCl. The wiping motion was designed to focus on the rim first, moving to the outer liner surface. Separate wipes were used to clean the inner wall of the liner with 0.5% HCl followed by reagent water, focusing on the inner wall before wiping the outer rim. The previously used pipe sections were not flushed again, as there was no obvious way to accomplish this in the absence of the end fittings without risking additional sources of contamination. Instead, each pipe section was rinsed with 150 mL of pH 6.5 reagent water, first from one end of the pipe and then the other (300 mL total). Then, as each pipe was filled, it was first flushed with 200 mL of pH 6.5 reagent water using a fill-and-dump technique.

The previously unused pipe sections were flushed for 15 min. with tap water (standard protocol) and the end fittings were then immediately removed and the exposed ends of the PET liner were then cleaned as for the other sections.

For this retesting, only pH 6.5 reagent water was used, with an initial exposure time of 6 h followed by refilling and an exposure time of 4 d. New stoppers, freshly cleaned, were used to avoid any contamination potentially associated with the previously used stoppers, which were in direct contact with the rims of the end fittings and may have been heavily contaminated.

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ABBREVIATIONS

AAS	atomic absorption spectroscopy
ACS	American Chemical Society
AES	atomic emission spectroscopy
AL	action limit
ANOVA	analysis of variance
ANSI	American National Standards Institute
AOC	assimilable organic carbon
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
BLL	blood lead level
°C	degrees Celsius
CCT	corrosion control treatment
CFR	Code of Federal Regulations
CL	Chlorinated pH 8 extraction water
cm	centimeter
cm^2	square centimeter
CSL	copper service line
Cu##	copper service line section identification number
DBPs	disinfection by-products
DOC	dissolved organic carbon
DT	Dechlorinated pH 8 tap water
DWI	Drinking Water Inspectorate (UK)
ed.	edition
EDCs	endocrine (system) disrupting compounds
eds.	editors
EPA	United States Environmental Protection Agency
°F	degrees Fahrenheit
FD#	Fill-and-dump experiment (experiment number)
FLAAS	flame atomic absorption spectroscopy
FLSLR	full lead service line replacement
GC/MS	gas chromatography / mass spectrometry
GFAAS	graphite furnace atomic absorption spectrometry
HDPE	high density polyethylene
HPLC	high pressure liquid chromatograph (or chromatography)
ICP	inductively coupled plasma

ICP-MS	inductively coupled plasma – mass spectrometry
ICP-OES	inductively coupled plasma – optical emission spectrometry
ID	inner diameter
IQ	intelligence quotient
kg	kilogram
KU	University of Kansas
L	liter
LAN	local area network
LC	liquid chromatograph (or chromatography)
LCR	Lead and Copper Rule
LCRWG	Lead and Copper Rule Working Group (see NDWAC)
LP	low pH (pH 6.5) extraction water
LTLCR	long-term Lead and Copper Rule
LSL	lead service line
LSLR	lead service line replacement
M	molar
MCL	maximum contaminant level
MDL	method detection level
MDPE	medium density polyethylene
mg/L	milligram(s) per liter
mL	milliliter
MRM	multiple reaction monitoring
MS	mass spectrometer (or spectrometry)
MSDS	material safety data sheet
μg/L	microgram(s) per liter
N	normality
NDWAC	National Drinking Water Advisory Committee
NSF	NSF International (formerly the National Sanitation Foundation)
NSF 61	NSF/ANSI Standard 61 (and similarly for other NSF Standards)
Ω	ohm
PAC	Project Advisory Committee
PAE	phthalate ester
Pb##	lead service line section identification number
PET	poly(ethylene terephthalate)
PEX	cross-linked polyethylene
PLSLR	partial lead service line replacement
PTFE	polytetrafluoroethylene
PVC	polyvinylchloride
PUA	polyurea
PUR	polyurethane

PWS	public water system
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
QC	quality control
SA	surface area
SD	standard deviation
SOP	standard operating procedure
SS	stainless steel
TETA	triethylenetetramine
TOC	total organic carbon
TOF	time-of-flight
TOF-MS	time-of-flight mass spectrometer (spectrometry)
UK	United Kingdom
USB	universal serial bus
V	volume
W	watt
WRAS	Water Regulations Advisory Scheme
WRF	Water Research Foundation

ABBREVIATIONS OF COMMON CHEMICAL NAMES

BADGE	bisphenol A diglycidyl ether
BADGE-H2O	bisphenol A (2,3-dihydroxypropyl) glycidyl ether
BADGE-2H2O	bisphenol A bis(2,3-dihydroxypropyl) ether
BADGE-H2O-HCl	bisphenol A (3-chloro-2-hydroxypropyl) (2,3-dihydroxypropyl) ether
BADGE-HCl	bisphenol A (3-chloro-2-hydroxypropyl) glycidyl ether
BADGE-2HCl	bisphenol A bis(3-chloro-2-hydroxypropyl) ether
BBP	butyl benzyl phthalate
BFDGE	bisphenol F diglycidyl ether
BFDGE-H2O	bisphenol F (2,3-dihydroxypropyl) glycidyl ether
BFDGE-2H2O	bisphenol F bis(2,3-dihydroxypropyl) ether
BFDGE-H2O-HCl	bisphenol F (3-chloro-2-hydroxypropyl) (2,3-dihydroxypropyl) ether
BFDGE-HCl	bisphenol F (3-chloro-2-hydroxypropyl) glycidyl ether
BFDGE-2HCl	bisphenol F bis(3-chloro-2-hydroxypropyl) ether
BPA	bisphenol A
BPA-Cl	monochlorobisphenol A
BPA-2Cl	dichlorobisphenol A
BPA-3Cl	trichlorobisphenol A

BPA-4Cl	tetrachlorobisphenol A
BPB	bisphenol B
BPD	bisphenol D
BPE	bisphenol E
BPF	bisphenol F
BPS	bisphenol S
DEHA	Bis(2-ethylhexyl) adipate
DEHP	di ethyl hexyl phthalate
DEP	diethyl phthalate
DETP	diethyl terephthalate
DMIP	dimethyl isophthalate
DMP	dimethyl phthalate
DMTP	dimethyl terephthalate
DNBP	di-n-butyl phthalate
DNHP-D6	di-n-hexylphthalate-D6 (deuterated)
DNOP	di-n-octyl phthalate
IPA	isophthalic acid
PA	phthalic acid
PA-D4	phthalic acid (deuterated)
PANE-D10	phenanthrene-D10 (deuterated)
SMXL-D4	sulfamethoxazole-D4 (deuterated)
TPA	terephthalic acid