

**Addressing and Assessing Lead Threats in Drinking Water:
Non-Leaded Brass, Product Testing, Particulate Lead Occurrence and
Effects of the Chloride to Sulfate Mass Ratio on Corrosion**

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Abstract

Growing concern over adverse health effects resulting from low level lead exposure prompted reassessment of the lead-in-drinking-water issue. Initial efforts were directed at 1) considering complete removal of lead from new brass plumbing materials, and 2) testing of existing brass products. During the course of this thesis, disturbing cases of lead poisoning in North Carolina and Washington D.C. were attributed to contaminated potable water. Those discoveries prompted work into 3) deficiencies in testing of drinking water samples for lead, and 4) lead contamination of potable water resulting from changes in water treatment.

To reduce the threat of lead leaching from plumbing components used in water distribution systems, it is possible to make brass without adding lead, thereby producing products with < 0.25 percent lead by weight. An in-depth literature review and expert workshop confirmed that this type of brass mitigates the health risk from lead leaching, but legitimate concerns remain over corrosion resistance and longevity. Nonetheless, non-leaded brass products are attractive at slightly high cost.

For existing products containing leaded brass, anecdotal evidence suggests that even those certified as “safe” by ANSI/NSF 61 Section 9 testing may sometimes leach levels of lead to potable water well above the current 15 ppb EPA standard. As a possible explanation, the rigor of the test protocol was critically evaluated from the perspective of the water used during product testing. Results demonstrate that in waters with lower pH and alkalinity, problematic levels of lead could be leached from devices that pass the Section 9 test protocol, which uses a less corrosive test water (higher pH and higher alkalinity). Steps should be taken to tighten the standard in order to account for this limitation.

Several cases of childhood lead poisoning from contaminated drinking water were investigated during this research. Environmental assessments demonstrated that the lead poisoning was due to lead solder particles in water. Laboratory experiments proved that up to 80% of this particulate lead could be “missed” by standard sampling protocols, yet this lead would be rendered bioavailable in the presence of warm hydrochloric acid inside the stomach. Testing using water from the building of a lead poisoned child, demonstrated that these lead particles could cause severe lead contamination of foods such as pasta. Future environmental assessments should carefully consider this issue.

Each of the cases of lead poisoning in North Carolina occurred after the water utility changed both disinfectant chemical (from chlorine to chloramine) and coagulant type. Although authorities initially thought chloramine was the cause for the high levels of lead in the water, bench scale studies proved that the change in coagulant from aluminum sulfate to either ferric chloride or polyaluminum chloride was critical. The change in coagulant increased the chloride to sulfate mass ratio of the water, which in turn triggered

severe galvanic corrosion attack on lead solder used to join copper pipe. The galvanic corrosion dropped the pH at the lead solder surface and possibly had other important effects not yet identified, thereby increasing lead contamination of the water by orders of magnitude. This problem was not controlled by addition of phosphate corrosion inhibitors.

This thesis provides the water industry with a basis for improved prevention, detection and mitigation of lead in drinking water through literature reviews, case studies, bench-scale experiments and field sampling events. Although additional research is necessary to better understand the scope of these problems, a sound basis is provided for rational decision making by regulators, public health officials, manufacturers and water utilities.

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In addition, thank you to all the members of my research group for their help, advice and cooperation in various projects we have undertaken as a team. Thanks to Julie Petruska and Jody Smiley for sharing with me some of their expertise in analytical procedures. Last but not least I would like to thank my family. Their endless support equipped me to go on during some of the more challenging times of this journey, towards the Master's degree.

Author's Preface

All four chapters of this thesis are presented as separate manuscripts according to the specifications of Virginia Tech's journal article formatting. Chapter 1 is a literature review of non-leaded brass use in potable water applications. This work was undertaken as part of AWWARF project #3112 "Performance and Metal Release of Non-leaded Brass Meters, Components and Fittings", in collaboration with HDR Engineering and will be presented at the Water Quality Technology Conference (WQTC) in November 2006. The author of this thesis did approximately half the writing of this chapter and is appropriately listed as second author on the article which will be submitted to a journal for publication.

All remaining chapters were produced via collaboration between student and advisor, as is typical for an M.S. thesis. Chapter 2 critically evaluates the chemistry of the leaching solution of the NSF 61 section 9 product test. This study was presented at the AWWA Annual Conference in June of 2006 and part of it appears in the proceedings of that conference.

Chapter 3 addresses the important issue of particulate lead occurrence in drinking water, and the effectiveness of routine sampling procedures in assessing the true extent of that exposure. The work was prompted by environmental assessments of children, conducted during this thesis, who were poisoned by lead-contaminated drinking water. This work was also presented at the AWWA Annual Conference in 2006 and portions of it appear in the proceedings of that conference. Chapter 4 is the first experimental study to explicitly examine the relative effects of chloride and sulfate in lead leaching from solder and brass. Some portions of this study will be presented at the AWWA WQTC in November 2006 and will appear in the proceedings of that conference.

This research work has also been discussed in the following press releases, prompted by lead poisonings from drinking water in Durham, NC and Greenville, NC:

The Ones that Get Away (National Science Foundation on-line News)

http://www.nsf.gov/news/news_summ.jsp?cntn_id=107066

Lead in Water linked to Coagulant (Environmental Science and Technology on-line News)

http://pubs.acs.org/subscribe/journals/esthag-w/2006/aug/science/rr_lead.html

<http://pubs.acs.org/subscribe/journals/esthag/40/i17/html/090106news1.html>

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CHAPTER 1

CURRENT UNDERSTANDING OF NON-LEADED BRASS

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INTRODUCTION

In order to provide a current understanding of the issues surrounding the use of non-leaded, residential-sized components in the water distribution system and premise plumbing, a series of papers were developed on the following topics:

- Description of the Composition, Lead Content and Mechanical Properties of New Non-Leaded Brasses
- Potential Health Effects of Non-Leaded Brasses
- Potential of Non-Leaded Brasses to Release Lead, Copper, and other Metals (Bismuth and Selenium) into Drinking Water
- American Society for Testing and Materials (ASTM) Specifications for New Non-Leaded Brasses
- Summary of Current State Experiences with Non-Leaded Materials
- Utility Motivations and Experience with Non-Leaded Brass Components
- Potential Impacts to Manufacturers
- Plumbing Industry Issues
- Potential Impacts to Utility Operations and Maintenance Procedures
- Alternative Materials for Fittings and Components.

The purpose of these topic papers was to formulate an initial understanding of the issues surrounding the use of non-leaded, residential-sized components in the water distribution system and premise plumbing. In addition, these topic papers summarize the current knowledge on the performance of non-leaded brass alloys and their potential for leaching compounds (lead, copper, selenium, bismuth) in drinking water, information of particular value to utilities in their decision-making processes for developing non-leaded component replacement programs. These topic papers are included below.

DESCRIPTION OF THE COMPOSITION, LEAD CONTENT, AND MECHANICAL PROPERTIES OF NEW NON-LEADED BRASSES

Research has been undertaken in order to develop a new generation of reasonably priced alloys for plumbing hardware that contain no added lead (< 0.25 percent). Historically, lead has been added to brass alloys used in drinking water applications to improve the “pressure-tightness” of a product by sealing micro-pores (Showman 1994). Lead is also believed to reduce the corrosion of other metals in the alloy and result in longer product life (OECD

1994). In addition, lead is important in the machining of brass castings. It functions both as a “chip breaker” and a lubricant, resulting in cost-effective machining rates for intricate brass devices (Showman 1994).

The presence of lead in the alloy also increases the potential for contamination of water that contacts the device. Under at least some circumstances, the water flowing through the device can dissolve the “pockets of lead” that exist on the brass surface, and introduce lead into drinking water (Cassidy 1994). Elevated lead levels in drinking water have been attributed to lead containing products. For instance, in a survey that was conducted by the Association of Metropolitan Water Agencies for the promulgation of the LCR, lead leaching from new faucets and fittings was found to be, or suspected to be, the major reason for increased lead levels in water samples (Lytle and Schock 1996). Other researchers have drawn very strong circumstantial ties between lead in water and leaching from brass (Kimbrough 2001).

Composition

Currently, three families of non-leaded brass alloys are commercially available:

- The combined effort of the CDA, the Brass and Bronze Ingot Manufacturers (BBIM), the American Foundrymen’s Society (AFS), the Materials Technology Laboratory of CANMET in Canada, other foundries and water product manufacturers resulted in a series of non-leaded copper alloys available as Envirobrass[®] (SeBiLOY[®]). These alloys contain from 0.1 percent lead (Envirobrass III) to 0.25 percent lead (Envirobrass I and II), as an incidental impurity from the recycling of materials from which casting alloys are commonly made (i.e. no lead is intentionally added to them) (CDA 2000). In the place of lead, bismuth and selenium are added to the alloys to improve mechanical characteristics.
- The Federal Metal Company has also developed non-leaded alloys commercially available as Federalloy[®]. In these alloys, bismuth is added in the place of lead, which comprises up to 0.1 percent of the alloy in most cases (Table 1-1), due to incidental impurities. No selenium is added to the Federalloy series of brasses.
- Sambo Copper Alloy Co., Ltd developed a silicon brass with the trade name ECO BRASS[®]. The alloy was originally designed in Japan to meet the Japanese 7 ug/L lead leachate requirement for copper alloy drinking water components. The alloy contains silicon and phosphorus (Table 1-1) in a brass with a nominal 20 percent zinc content. There are two subsets of this alloy designed for sand and permanent mold casting, with each having a lead maximum of 0.1 percent to accommodate contaminants from scrap used as charge materials.

The compositions of Envirobrass, Federalloy and EcoBrass alternative brasses (Table 1-1) were developed so that products made from these alloys would be comparable to their leaded counterparts in terms of mechanical strength.

Mechanical Strength Properties

Mechanical properties such as ultimate tensile strength, yield strength, elongation and hardness have been determined for non-lead brass alloys, in order to evaluate their strength. The mechanical properties of Envirobrass I and Envirobrass II are in general similar to the standard leaded semi-red and red plumbing brasses. However, they are lower in elongation. Envirobrass III strength properties were not all directly comparable to those of leaded yellow brass (Table 1-2). For Federalloy brasses I and III tensile and yield strength, elongation and hardness approximate their leaded alloy equivalents. EcoBrass sand and permanent mold castings (C87851 and C87852 respectively) in general have higher tensile strength, yield strength and hardness when compared to the conventional leaded alloys (Table 1-2).

Machinability

Machining is used as the final shaping operation in all plumbing cast products and contributes significantly to the cost (CDA 2005). In assessing the machinability of an alloy, factors such as tool life, surface quality, chip form and cutting force are considered (Kuyucak and Sahoo 1996). The leaded alloy C36000 (free-cutting brass) has the maximum machinability of 100. Compared to this machinability rating, copper alloys are generally classified into three categories (Kuyucak and Sahoo 1996):

- Free-machining alloys, which have ratings between 70-100
- Readily machinable alloys, which have ratings between 30-70
- Difficult-to-machine alloys, which have ratings less than 30

Based on the above classification Envirobrass I, II and III alloys all fall within the free-machining range of 70-100. From the Federalloy family of alloys, and for those for which information was readily available, all types but one fall within the free-machining range. The exception is the (original) Federalloy I C89837, with a slightly lower machinability of 66. The alternative alloy EcoBrass falls within the free-machining range; it has a machinability of 70, at the lower end of that range (Table 1-2).

Table 1-1: Composition of some current non-lead brass alloys. (CDA 2005 and Federal Metal Company 2005)

ALLOY		RANGE OR MAXIMUM %													
		Copper (Cu)	Tin (Sn)	Lead (Pb)	Zinc (Sn)	Bismuth (Bi)	Selenium (Se)	Nickel (Ni)	Iron (Fe)	Antimony (Sb)	Sulfur (S)	Phosphorous (P)	Aluminum (Al)	Silicon (Si)	Manganese (Mn)
ENVIRO BRASS	Envirobrass I (C 89510)	86.0-88.0	4.0-6.0	0.25	4.0-6.0	0.5-1.5	0.35-0.75	1.0	0.2	0.25	0.08	0.05	0.005	0.005	-
	Envirobrass II (C89520)	85.0-87.0	5.0-6.0	0.25	4.0-6.0	1.6-2.2	0.8-1.1	1.0	0.2	0.25	0.08	0.05	0.005	0.005	-
	Envirobrass III (C89550)	58.0-64.0	1.2	0.1	32.0-38.0	0.6-1.2	0.01-0.1	1.0	0.5	0.05	0.05	0.01	0.1-0.6	0.25	-
FEDERALLOY	Federalloy I original (C89837)	84.0-88.0	3.0-4.0	0.10	6.0-10.0	0.70-1.2	-	0.50-1.0	0.30	0.25	0.08	0.05	0.005	0.005	-
	Federalloy I-836 Version (C89833)	87.0-91.0	4.0-6.0	0.10	2.0-4.0	1.7-2.7	-	0.50-1.0	0.30	0.25	0.08	0.05	0.005	0.005	-
	Federalloy I-836 Version Zero Lead	87.0-91.0	4.0-6.0	0.005	2.0-4.0	1.7-2.7	-	0.50-1.0	0.30	0.25	0.08	0.05	0.005	0.005	-
	Federalloy I-833 Version	92.0-94.0	1.0-2.0	0.10	2.0-6.0	1.2-1.7	-	0.1	0.10	Trace	Trace	0.05	0.005	0.005	-
	Federalloy I-844 Version (C89831)	87.0-91.0	2.7-3.7	0.10	2.0-4.0	2.7-3.7	-	0.50-1.0	0.30	0.25	0.08	0.05	0.005	0.005	-
	Federalloy I-844 Modified (C89844)	83.0-86.0	3.0-5.0	0.20	7.0-10.0	2.0-4.0	-	1.0	0.30	0.25	0.08	0.05	0.005	0.005	-
	Federalloy I 848-A Version	77.0-79.0	3.0-4.0	0.10	15.5-17.5	1.7-2.7	-	0.50-1.0	0.35	0.25	0.08	0.05	0.005	0.005	-
	Federalloy II (922 Version)	Balance	5.75-6.50	0.10	3.0-5.0	1.0-1.75	-	0.50-1.0	0.20	0.25	0.05	0.05	0.005	0.005	-
	Federalloy II (927 Version)	Balance	9.0-11.0	0.10	0.7	1.0-2.0	-	0.50-1.0	0.20	0.25	0.05	0.05	0.005	0.005	-
	Federalloy II (255 Ingot Version)	Balance	5.0-6.0	0.10	3.5-4.5	1.7-2.7	-	0.80	0.25	0.20	0.05	0.010-0.016	0.005	0.005	-
	Federalloy III (932 Version) (C89835)	85.0-89.0	6.0-7.5	0.10	2.0-4.0	1.7-2.7	-	0.50-1.0	0.20	0.25	0.08	0.05	0.05	0.005	-
	Federalloy III (937 Version) (C89325)	84.0-88.0	9.0-11.0	0.10	1.0	2.7-3.7	-	0.50-1.0	0.15	0.25	0.08	0.05	0.05	0.005	-
	Federalloy III (938 Version)	Balance	6.0-8.0	0.10	1.0	3.7-4.7	-	0.50-1.0	0.15	0.50	0.08	0.05	0.05	0.005	-
	Federalloy III (945 Version)	86.0-90.0	6.0-8.0	0.10	1.2	3.7-4.7	-	0.50-1.0	0.15	0.25	0.08	0.05	0.05	0.005	-

ALLOY	RANGE OR MAXIMUM %													
	Copper (Cu)	Tin (Sn)	Lead (Pb)	Zinc (Sn)	Bismuth (Bi)	Selenium (Se)	Nickel (Ni)	Iron (Fe)	Antimony (Sb)	Sulfur (S)	Phosphorous (P)	Aluminum (Al)	Silicon (Si)	Manganese (Mn)
Federalloy IV (B1 Version) Sand Cast Version	60.0-63.0	0.50-1.50	0.10	Balance	0.75-1.5	-	1.0	0.50	0.02-0.10	0.05	0.01	0.50-0.75	0.05	-
Federalloy IV (B2 Version) Permanent Mold Version	59.5-60.5	0.10	0.10	Balance	0.75-1.5	-	0.01	0.03	0.01	0.01	0.005	0.50-0.75	0.02	-
Federalloy V (973 Version)	63.0-67.0	1.50-3.0	0.10	13.00-17.00	1.0-2.0	-	11.00-14.00	0.75	Trace	0.08	Trace	0.005	0.005	0.5
Federalloy V (974 Version)	58.0-61.0	2.50-4.50	0.10	Balance	0.75-1.0	-	16.00-17.00	1.5	0.25	0.08	0.02	0.005	0.05	0.5
Federalloy V (976 Version)	Balance	3.50-4.50	0.10	3.0-9.0	0.75-1.0	-	19.00-21.50	1.5	0.25	0.08	0.05	0.005	0.015	1.0
ECO BRASS EcoBrass (C87850)	74.0-78.0	0.20	0.10	Balance	-	-	0.10	0.10	-	-	0.04-0.20	-	2.7-3.4	0.10

Table 1-2: Typical mechanical properties and machinability rating for some current non-lead brasses and for commonly used traditional lead brasses. The alloys were sand cast unless otherwise stated. (CDA 2000 and Chase Brass and Copper Co. 2006)

ALLOY		UTS-Ultimate Tensile Strength ksi (Mpa)	0.5 % YS-Yield Strength ksi (Mpa)	Elongation (%)	Hardness (500 kg) BHN**	Machinability Rating (-)
LEADED	C83600 (Red Brass)	37 (255)	17 (117)	30	60	84
	C84400 (Semi Red Brass)	34 (234)	15 (103)	26	55	90
	C85800* (Yellow Brass)	55 (379)	30 (207) (but at 0.2% offset)	15	60 (but as Rockwell hardness B)	80
ENVIRO BRASS	C89510 (Envirobrass I)	30 (209)	20 (136)	12	37	75
	C89520 (Envirobrass II)	31 (215)	21 (145)	10	54	85
	C89550 (Envirobrass III)	48 (330)	29 (200)	8	-	75 (with 0.7% Bi) 97 (with 1.1% Bi)
FEDERALLOY	Federalloy I (C89837)	37 (258)	17 (119)	32	60	66
	Federalloy I-836 (C89833)	37 (258)	17 (119)	28	60	81
	Federalloy I-844 (C89831)	34 (237)	15 (105)	20	55	85
	Federalloy I-844 Modified (C89844)	34 (234)	15 (103)	30	55	70
	Federalloy III-932 (C89835)	35 (244)	18 (126)	20	65	70
	Federalloy III-937 (C89325)	35 (244)	18 (126)	20	73	80
ECO BRASS	EcoBrass C87851	60 (379)	24 (165)	22	115	70
	EcoBrass C87852	69 (475)	35 (241)	21	135	70

*Die Cast

**BHN= Brinell Hardness Number

POTENTIAL HEALTH EFFECTS OF NON-LEADED BRASS ALLOYS

Non-leaded brasses can contain a variety of metals that may be released into the drinking water, including bismuth, selenium, copper, tin, nickel, antimony, zinc, and lead. The following sections summarize information on the potential health effects of these metals in drinking water.

Bismuth

Bismuth, a reddish white metal, is typically found in nature as bismite (Bi_2O_3), bismuthinite (Bi_2S_3), and bismutite [$(\text{BiO})_2\text{CO}_3$]. It occurs in two oxidation states, +3 and +5. Most health information on bismuth has focused on pharmaceutical applications (USEPA 2005b), probably due to the fact that the main applications of bismuth salts (such as bismuth subsalicylate, the active ingredient in Pepto Bismol and Kaopectate) are for the treatment of gastrointestinal problems like gastritis, peptic ulcer and diarrhea. The World Health Organization (WHO 2005) states that “acute poisoning with bismuth may cause renal damage, encephalopathy and peripheral neuropathy. Neurotoxicity may also occur after chronic treatment with bismuth salts, but is reversible if medication is stopped.” The USEPA is currently reviewing the health effects of bismuth to determine if a health advisory is warranted (USEPA 2005b), and NSF International is also conducting a risk assessment on bismuth (McClellan 2005). As part of the NSF International risk assessment, analytical tests will be performed to determine the form of Bi leached from brass, specifically its oxidation state and whether it is an oxide or chloride salt. These are being conducted primarily to confirm that Bi^{3+} is present as an oxide. There is also an issue related to the Bi form in the colloids that have been used in available toxicological studies. There is a need to establish the chemical relationship between the form of Bi from brass and the form of Bi in the colloids as well as the expected absorption of Bi from brass compared to the colloids (McClellan 2006). Bismuth is not currently regulated in drinking water and its occurrence in drinking water has not been documented.

Selenium

Selenium is a naturally occurring mineral element that is distributed widely in nature in most rocks and soils. In its pure form, it exists as metallic gray to black hexagonal crystals, but in nature it is usually combined with sulfide or with silver, copper, lead, and nickel minerals. Selenium is an essential nutrient at low levels. Recommended daily allowance for men and women is 0.055 mg/d (Agency for Toxic Substances and Disease Registry 2003a).

The USEPA has set a Maximum Contaminant Level Goal (MCLG) and Maximum Contaminant Level MCL of 0.05 mg/L for selenium because it can potentially cause the following health effects at levels above the MCL: hair and fingernail changes, damage to the peripheral nervous system, fatigue and irritability, damage to kidney and liver tissue, as well as the nervous and circulatory systems. Currently, there is no evidence that selenium has the potential to cause cancer from lifetime exposures in drinking water. In fact, based on human studies, lower-than-normal selenium levels in the diet might increase the risk of cancer (Agency for Toxic Substances and Disease Registry 2003b). Selenium is usually found at very low levels in drinking water (<0.01 mg/L). Higher levels may occur in drinking waters in areas where high selenium levels in the soil contribute to elevated levels in the water (USEPA 2005c).

Copper

Copper is a reddish metal that occurs naturally throughout the environment, in rocks, soil, water, and air. Copper is an essential nutrient at low levels, however toxic effects can occur at higher levels. Acute exposure can cause gastrointestinal disturbances, including nausea, vomiting, stomach cramps, or diarrhea, and intentionally high intakes of copper can cause liver and kidney damage and even death. Chronic exposure can cause liver or kidney damage and people with Wilson's disease may be more sensitive to the effects of copper contamination. USEPA does not classify copper as a human carcinogen because there are no adequate human or animal cancer studies." (Agency for Toxic Substances and Disease Registry 2004 and USEPA 2005d).

Copper levels in drinking water generally occur due to corrosion of copper premise piping. USEPA has set the MCLG and an action level of 1.3 milligrams copper per liter of water (1.3 mg/L), and a secondary drinking water standard of 1 mg/L. The MCLG for copper was set based on the potential for health effects at levels greater than 1.3 mg/L, and the action level was set based on the ability of present treatment technology to control copper levels at customers' taps. The secondary standard was established because of blue-green staining and metallic taste associated with copper levels above 1 mg/L. These secondary standards are federally non-enforceable guidelines, however some states (such as California) may have state statutes in place to enforce secondary standards.

Tin

Tin is a soft, white, silvery metal that is insoluble in water. Tin can combine with other chemicals such as chlorine, sulfur or oxygen to form inorganic tin compounds. Tin can also combine with carbon to form organotin compounds. Tin metal, as well as inorganic and organic tin compounds can be present in water. Organic tin compounds are mostly attached to particles in water or may settle out into sediments.

Because inorganic tin compounds usually enter and leave the body rapidly after ingestion, they do not usually cause harmful effects. However, humans who swallowed large amounts of inorganic tin in a research study suffered stomach aches, anemia, and liver and kidney problems. There is no evidence that inorganic tin compounds affect reproductive functions, produce birth defects, or cause genetic changes. Exposure to some organotin compounds has been shown to cause harmful effects in humans, but the main effect depends on the particular compound. There have been reports of skin and eye irritation, respiratory irritation, gastrointestinal effects, and neurological problems in humans exposed for a short period of time to high amounts of certain organotin compounds." (Agency for Toxic Substances and Disease Registry 2005a). There is no evidence that tin or tin compounds cause cancer in humans. There are no U.S. regulations for tin in drinking water.

Zinc

Zinc is one of the most common elements in the earth's crust. Zinc is found in the air, soil, and water and is present in all foods. "Zinc is an essential element needed by your body in small amounts. We are exposed to zinc compounds in food and it is also present in most drinking water. Drinking water or other beverages may contain high levels of zinc if they are stored in

metal containers or flow through pipes that have been coated with zinc to resist rust.” (Agency for Toxic Substances and Disease Registry 2003c)

The USEPA has not established a primary (health based) standard for zinc in drinking water. However, a secondary standard of 5 mg/L zinc has been established because of effects on the water’s taste (metallic). Zinc has not been classified for carcinogenicity due to incomplete information. (Agency for Toxic Substances and Disease Registry 2003d).

Nickel

Nickel is a silvery white metal that is hard, malleable, and ductile. It is found in natural ore deposits with other elements and is primarily used to make stainless steel and other alloys. “Eating or drinking large amounts of nickel has caused lung disease in dogs and rats and has affected the stomach, blood, liver, kidneys, and immune system in rats and mice, as well as their reproduction and development. However, exposures of the general population from other sources, such as foods and drinking water, are almost always too low to be of concern” (Agency for Toxic Substances and Disease Registry 2003e).

The USEPA promulgated an MCLG and MCL for nickel of 0.1mg/L. These were based on health effects associated with chronic exposure to levels above the MCL, which include decreased body weight, heart and liver damage, and skin irritation. However these regulations were remanded on February 9, 1995 and there is no current regulation for nickel in drinking water (USEPA 2005e).

Antimony

Antimony is a silvery-white metal that is found in the earth's crust. Antimony is not used alone because it breaks easily, but when mixed into alloys, it is used in lead storage batteries, solder, sheet and pipe metal, bearings, castings, and pewter (Agency for Toxic Substances and Disease Registry 1995). Because antimony is found naturally in the environment, the general population is exposed to low levels of it every day, primarily in food, drinking water, and air.

The USEPA has established an MCLG and MCL for antimony of 0.006 mg/L in drinking water because of health effects including nausea, vomiting and diarrhea. The Department of Health and Human Services (DHHS), the International Agency for Research on Cancer (IARC), and the USEPA have not classified antimony as to its human carcinogenicity (Agency for Toxic Substances and Disease Registry 1995).

Lead

Lead is a heavy, bluish-gray metal that occurs naturally in the Earth's crust, usually associated with ores containing other elements. Because of its physical properties (corrosion resistance, malleability) lead and lead alloys have historically been used in plumbing applications. Elevated lead levels in drinking water generally occur due to corrosion of lead pipe used for service lines and lead contained in household plumbing. A variety of health effects have been associated with lead exposure, including interference with red blood cell chemistry, delays in normal physical and mental development in babies and young children, slight deficits in the attention span, hearing, and learning abilities of children, and slight increases in the blood pressure of some

adults. Long-term effects of lead exposure include stroke and kidney disease, and cancer (USEPA 2005f).

Exposure to lead, especially in infants and young children, may cause permanent neurological damage leading to IQ reductions, attention deficit disorders, and aggressive behavior (Needleman and Gatsonis 1990; Schwartz 1994). Too much lead can also damage reproductive systems and the kidneys, and can cause high blood pressure and anemia (WHO 1993).

Kidney tumors have developed in rats and mice that had been given large doses of some kinds of lead compounds. The Department of Health and Human Services (DHHS) has determined that lead and lead compounds are reasonably anticipated to be human carcinogens based on limited evidence from studies in humans and sufficient evidence from animal studies, and the USEPA has determined that lead is a probable human carcinogen. The International Agency for Research on Cancer (IARC) has determined that inorganic lead is probably carcinogenic to humans. IARC determined that organic lead compounds are not classifiable as to their carcinogenicity in humans based on inadequate evidence from studies in humans and in animals.” (Agency for Toxic Substances and Disease Registry 2005b).

In light of these findings, the USEPA set a MCLG of zero for lead. The LCR lead action level of 0.015 mg/L at the 90th percentile is not a health-based action level but was derived based on the capabilities of corrosion control processes to adequately control lead concentrations at the tap (USEPA 2004a). The WHO has established a health guideline for lead in drinking water at 0.1 mg/L (WHO 1993)

The Centers for Disease Control and Prevention has set a level of 10 µg of lead per deciliter (dL) of blood as the level above which a child is to be investigated for lead poisoning. Very recent published research has documented measurable childhood IQ deficits at a blood lead level as low as 2.5 µg/dL, a level previously believed to be well below the threshold for observable neurological damage (Hertz-Picciotto *et al.* 2000; Lanphear *et al* 2000; Bettinger 2003). Canfield *et al* (2003) evaluated the relationship between blood lead levels and IQ in children using linear and nonlinear models and concluded that children in the U.S. may be more adversely affected by environmental lead than previously thought. Their results indicated that each 10 µg/dL increase in the lifetime average blood lead concentration was associated with a 4.6-point decrease in IQ. However, for a sub-sample of children with blood lead levels below 10 µg, the change in IQ associated with a change in blood lead concentration from 1 to 10 µg /dL was greater (7.4 points).

POTENTIAL OF NON-LEADED BRASSES TO RELEASE LEAD AND COPPER AND OTHER METALS (BISMUTH AND SELENIUM) INTO DRINKING WATER

The potential of non-leaded brasses to leach lead, copper and other metals into potable water has not been adequately examined. Preliminary tests studying the corrosion and dezincification behavior of non-leaded brasses have been aimed more at their practical performance in drinking water applications rather than their potential health effects.

More recently, and as the discussion on non-lead brass alternatives is gaining further attention, research studies were conducted that specifically addressed the leaching issues. However, it is

obvious at this point that more work needs to be undertaken in order to gain a better understanding of the leaching propensity of these alloys.

Leaching Studies

Among the few studies that have been conducted, the American Foundry Society (AFS) quantified leaching levels for two different experimental non-lead compositions in brasses (Table 1-3). Hollow cylinders 5” long x ¼” diameter were tested in the “as-cast” form. One sample of C84400 served as a control. Initial results were obtained at two pH levels of 5 and pH 10, purportedly following the NSF/ANSI Standard 61 Section 9 methodology (Table 1-4). There may be an editorial or other error in this report, since Section 9 does not use a pH 5 and pH 10 water. It is also uncertain at this time whether the pH 5 water and the pH 10 water had orthophosphate or were prepared fresh, which are two factors that can impact their aggressiveness towards lead. Despite these potential limitations, the results indicated that a 0.2 percent lead level in the alloy would be below the 11 ug/L maximum allowable level for the two test waters according to the Section 9 protocol. The leach levels for bismuth and selenium were also obtained at two different pH’s. Bismuth leaching was below the detection limit for every experimental condition and at both pH levels (Table 1-5). The selenium leach level was below the detection limit for every experimental composition at pH = 5, but there were detectable levels of selenium leaching in some of the experimental alloys at pH = 10 (Table 1-5) (Twarog 1995).

The verification leach test that followed as part of the study was conducted with a pH = 8 solution, so that results could be comparable to other leaching tests conducted at pH = 8 using the NSF/ANSI Standard 61 Section 9 methodology. The alloy control that was used in this run was C83600. Tube samples were cut and adjusted so that they could maintain a 50 mL water volume. Before the test, all samples were washed and conditioned as described in Section 9 of NSF/ANSI Standard 61 (Appendix A). The “Q” statistic in the case of lead and the 19th day normalized mean concentration for bismuth and selenium were reported (Table 1-6) (Twarog 1995). Lead leaching was reduced by a factor of about 3-5 for the non-lead alloys as compared to the C83600 control.

Table 1-3: Intended compositions of the two experimental non-lead brass alloys that were tested in the Twarog study (1995).

Experimental Alloy	Bi	Se	Sn	Zn	P	Ni	Pb	Cu
2%Bi/ 1% Se	2%	1%	5%	5%	0.15%	0.75%	0.2%	Bal.
1% Bi/ 0.5% Se	1%	0.5%	5%	5%	0.15%	0.75%	0.2%	Bal.

The compositions actually achieved when the multiple samples were fabricated, slightly deviated from the target values.

Table 1-4: Lead Leaching for Experimental Alloys (Twarog 1995).

Sample #	% Lead in Alloy	“Q” at pH=5 (ug)	“Q” at pH=10 (ug)
1	0.0	0.062	0.082
2	0.2	0.240	4.13
3	0.2	0.036	0.367
4	0.13	0.436	2.76
5	0.24	0.027	2.82
6	0.0	0.039	0.049
7	0.23	0.552	5.58
8	0.0	0.066	0.034
9	0.13	0.013	0.510
Control (C84400)	7.15	4.09	8.15

Table 1-5: 19th day Mean Normalized Leach of Selenium and Bismuth for the Experimental Alloys.* (Twarog 1995)

Sample Number	Bismuth pH=5	Bismuth pH=10	Selenium pH=5	Selenium (ug/L) pH=10
1	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	1.01
3	BDL	BDL	BDL	0.23
4	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	26.97
6	BDL	BDL	BDL	8.05
7	BDL	BDL	BDL	BDL
8	BDL	BDL	BDL	0.95
9	BDL	BDL	BDL	54.56
Control (C84400)	BDL	BDL	BDL	BDL

* BDL stands for Below Detection Limit levels

Table 1-6: Leach Verification Test Results in the Twarog Study (1995)

Alloy	Lead (ug/L) “Q” Statistic	Bismuth 19 th Day Mean Normalized (ug/L)	Selenium 19 th Day Mean Normalized (ug/L)
Control (C83600)	15.5	<0.1	<0.1
2% Bi/ 1% Se	5.6	1.6	1.7
1% Bi/ 0.5% Se	2.9	5.2	0.1

Other projects were undertaken on behalf of the CDA, which examined the leaching propensity of experimental alloys containing very small amounts of lead and bismuth (Peters 1995). Five brass alloys, including four alternative experimental alloys and the conventional leaded brass C84400 (Table 1-7), were tested according to an earlier version of NSF/ANSI Standard 61,

Section 9. The test specimens were in the form of cast spouts. Based on the results of that study, the standard alloy C84400, with the highest lead content, resulted in the highest lead leaching (Figure 1-1). Alloy 2, with the lowest lead content of 1 percent, resulted in the lowest lead leaching, whereas alloys 3, 4 and 5 with the intermediate lead contents fell in between (Figure 1-1) (Peters, 1995).

Table 1-7: Compositions of experimental alloys reported in the CDA study (Peters, 1995).

Alloy #	Composition (% wt)					
	Pb	Bi	Sn	Zn	P	Cu
1 (C84440)	6.9	0	2.6	9.5	0.012	79.8
2	1	3	3	11.9	0.1	80.3
3	2	0.65	3	13.3	0.1	80.3
4	3	1	3	11.9	0.1	80.3
5	4	1.3	3	9.8	0.1	80.3

Subsequent experiments reported in the same CDA study, examined bismuth and selenium leaching from experimental alloys with very low lead content. The test specimens were large faucet body castings. The bismuth and selenium leaching data that were reported (Figure 1-2) were not adjusted for the internal volume of the test specimens. According to the report, when the 19th day concentrations are adjusted for the internal volume, the USEPA requirement for selenium (50 ug/L) is met. (Peters 1995).

In a 1992 study performed by the International Copper Development Association (ICA) and the CDA, the corrosion behavior of alloys containing 0.5, 1.0, and 1.5 percent lead was examined and compared to a 5 percent lead alloy. The test method used in this study was based on a 1988 draft version of NSF/ANSI Standard 61, Section 12. This protocol is different than the one given in the current draft of the standard, therefore the data are not directly applicable to that test, but results are likely to give useful trends. The alloys were exposed to three potable waters at pH 5, 8 and 10 respectively, for 14 days at room temperature. Extracts from solutions exposed for 1, 2, 3, 4, 7, 8, 9, 10, 11 and 14 days, plus one final extraction were analyzed for lead using atomic absorption spectrometry. The effect of alloy lead content on lead leaching after a 14-day exposure period was reported for the pH 8 water (Figure 1-3). (Dresher and Peters 1992)

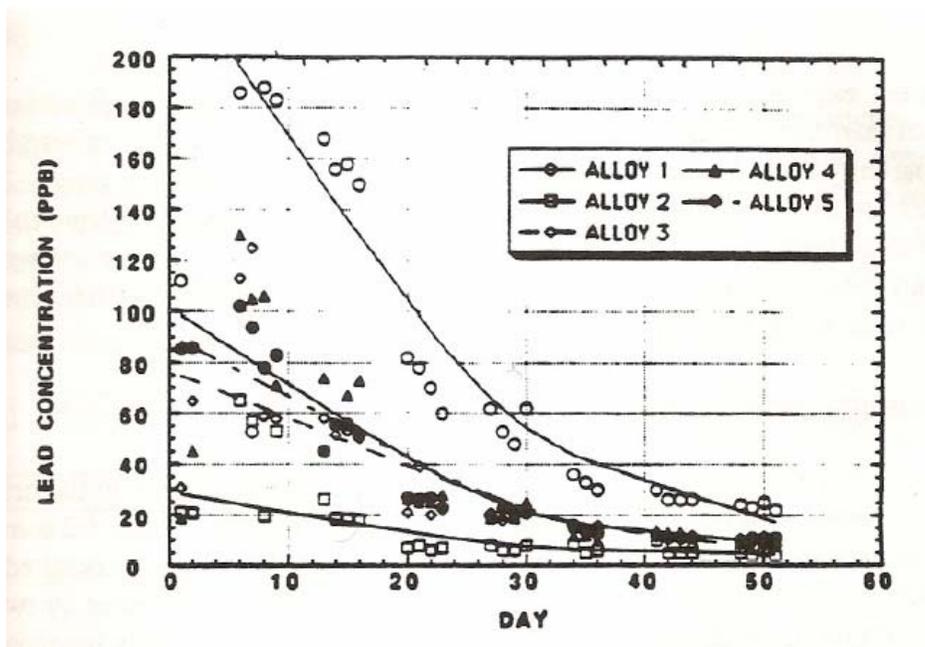


Figure 1-1: Lead leaching versus time in a pH 8.0 water, based on an earlier version of NSF/ANSI Standard 61, Section 9. (after Peters 1995)

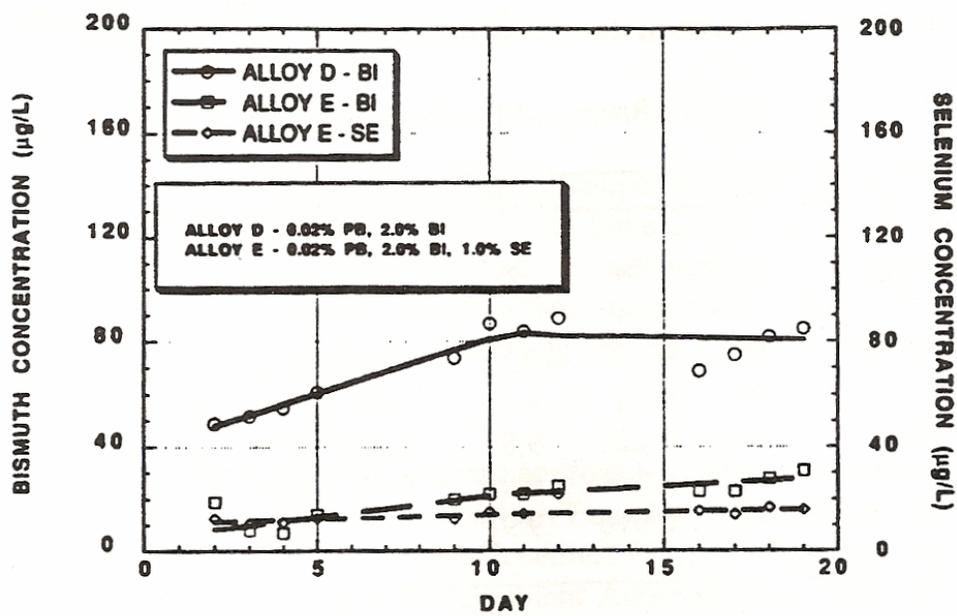


Figure 1-2: Bismuth and Selenium leaching in faucet body castings. (after Peters 1995)

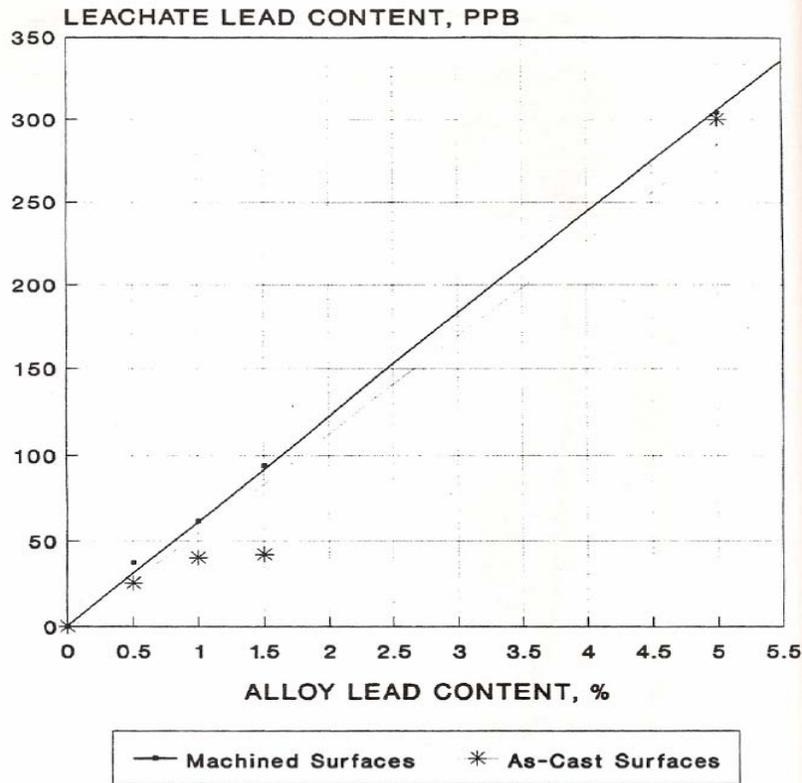


Figure 1-3: Effect of alloy lead content on lead leaching. Data were collected after a 14-day exposure in pH 8 water based on a 1988 draft of NSF/ANSI Standard 61, Section 12. This test protocol is no longer in use. (after Dresher and Peters 1992)

The Environmental Quality Institute performed laboratory studies in order to compare the leaching tendency of leaded (5-7 percent lead) versus non-leaded (<0.1 percent lead) individual plumbing components including curb stops, main stops, couplings and others. The components were exposed to a synthesized extraction water that closely matched the characteristics of average California public water supply. Although the parts were plumbed into a flow-through pilot apparatus and not “dumped and filled”, NSF/ANSI Standard 61 Section 9 protocol was otherwise followed. Total lead was quantified at time intervals mandated by Section 9 protocol during the three week test period. Additional samples were taken, more frequently than what the methodology of the test mandates.

Lead discharge was found to be low for the non-lead components. The overall mean lead concentration (adjusted to one liter) during the entire test period was below 5 ug/L for all non-lead components. For some of the conventional leaded components the mean was significantly higher and even exceeded the LCR Action Level. The corresponding “Q” statistic value was also higher than the LCR level for some of the leaded parts. In addition, lead discharge decreased by more than 50 percent over the three weeks of testing for the non-lead parts in the test water. The equivalent leaded components continued to leach about 70 percent of their initial lead discharge at the end of the test, indicating that the rate of decrease in lead dissolution was

more significant for unleaded parts. No copper, selenium or bismuth leaching data were reported in that study. (Maas and Patch 2004)

Previous work carried out by the Environmental Quality Institute had quantified lead discharge of non-lead water service products using Envirobrass II brass alloy. Non-lead ball valve curb stops and elbow couplings were examined, following a modified Section 9 protocol. The extraction water and pressurized manifold system were different than Section 9 procedures. The water samples were analyzed for total lead, but bismuth and selenium levels were also enumerated. Lead discharge for the parts tested was quite low. The one liter adjusted overall mean, for the whole testing period, was below 2.0 ug/L for all Envirobrass parts. Selenium discharge was reported as barely detectable, even at week one of the test, whereas bismuth discharge was also very low. (Maas 2002)

Recent “dump and fill” tests conducted by the Greater Cincinnati Water Works (GCWW) examined lead leaching from non-leaded brass meters and fittings versus their leaded counterparts (De Marco 2005). In the case of brass meters after six hours of stagnation, the Envirobrass leached 28 ug/L lead, which would correspond to a concentration of 4.9 ug/L if adjusted to one liter. The conventional brass meters leached as much as 1,240 ug/L, which translated to 94.7 ug/L if the contents were diluted into one liter. In tests of fittings containing between 0.2 and 8 percent leaded brass alloys and having the same water holding time of six hours, the non-lead materials showed significantly decreased lead dissolution into drinking water when compared to the leaded brass. Nonetheless in the case of curb stops, the lead released (adjusted to one liter) was above the LCR Action Level of 15 ug/L even for the 0.2 percent lead alloy (De Marco 2005). No copper, bismuth or selenium leaching data were presented.

Corrosion Propensity

Copper alloys, such as brass, are also subject to exotic modes of corrosion failure including intergranular corrosion, stress corrosion cracking or season cracking (Pugh *et al* 1966; Thompson and Tracey 1949) and dezincification (Lucey 1965). The likelihood of a brass device failing from any of these phenomena is a complex function of:

- 1) The alloy, including trace constituents such as arsenic at levels of 0.02 percent
- 2) How it is produced and in residual stresses within the metal
- 3) How it is installed, including mechanical stress on the device
- 4) Water chemistry.

There are standard test apparatus to investigate dezincification and stress corrosion cracking susceptibility of particular alloys (Lucey 1965; ATSM 1994). The water industry documented failures from chloramine attack on brass that were clearly inter-granular more than 50 years ago (Larson *et al.* 1956; Ingleson *et al.* 1949; anonymous 1951). It is noted that modern brass alloys in drinking water are also subject to this type of attack and failure. Depending on the aggressivity of the water and the alloy, the metal can essentially disintegrate with individual grains falling into the water from the device (Sundberg 2006; Sundberg *et al.* 2003). Ammonia is especially prone to causing stress corrosion cracking and intergranular attack (e.g. Guo *et al* 2002), but other nitrogen species and other constituents are clearly involved (Giordano *et al.*

1997; Rao and Nair 1998) These phenomena become more likely above about pH 7.0 and in one study they were maximized at pH 11.4.

For the case of non-lead brass alloys, the same concerns stand regarding potential for exotic failure modes. Research on the dezincification of bismuth containing alternative brasses (1-3 % Bi) showed that these alloys were more susceptible to dezincification than leaded brass, when evaluated in synthetic tap water using potentiostatic polarization, scanning electron microscopy (SEM) and electron probe microanalysis (Kim *et al.* 2001). In other experiments, Envirobrass I and II showed similar corrosion characteristics to leaded alloy C83600 when using potentiodynamic polarization and weight loss measurements (Sahoo *et al.* 1999). Both Envirobrass I and II (5 % Zn) were not prone to dezincification, as evaluated by procedures such as “ISO 6509” and the “Hanningfield” test. Envirobrass III (36 % Zn) had excellent corrosion resistance but was prone to dezincification (Sahoo *et al.* 1999).

With respect to stress corrosion cracking, one manufacturer states that cracking, either easily discernible (Figure 1-4a) or not visible to the naked eye (Figure 1-4b), has been observed during dry machining of copper-bismuth-selenium alloy surfaces of thin sections that were heated up. Heating can be caused due to excessive feeds and speeds or dull/ incorrect tooling. A conventional leaded alloy (C83600) exposed to the same machining process did not form cracks. However, the manufacturer reports that the same non-lead products could have been machined differently and not result in cracks. (Ford Meter Box Company 2005a).

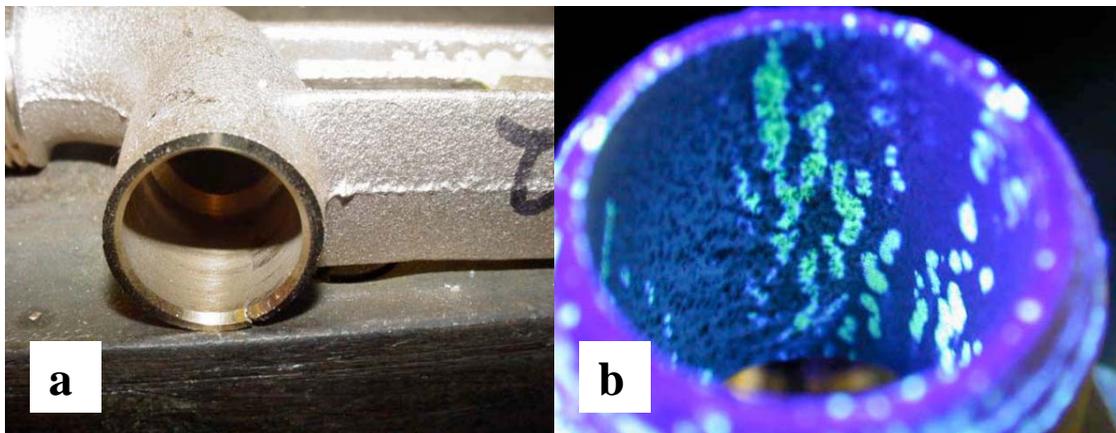


Figure 1-4: a) Envirobrass II (C89520) casting with presence of a visible crack in the bottom of the machined surface. b) Envirobrass II (C89520) casting, which did not show visible cracks to the naked eye. Cracks were revealed as light green areas during a fluorescence penetration test. (Ford Meter Box Company 2005a)

In a lead-leaching experiment conducted at Virginia Polytechnic Institute and State University as part of this AWWARF project, visible cracks in some non-leaded alloys were also observed after machining. During setup of the experiment, the alloys provided were cut with a lathe in order to obtain desirable sample shape and dimensions, based on the experimental design. This process caused cracks to form on a few unleaded brass specimens (Figure 1-5). The cracks were observed in a limited number of coupons and therefore do not constitute a generalized case. This may also be an isolated instance for the specific heat of material that was provided, or may have resulted from improper lathe use. Nonetheless, it does reinforce cause for concern. Results of this evaluation are contained in Appendix B of this report.



Figure 1-5: Unleaded brass coupon in the Virginia Tech leaching study. Cracks were observed after cutting of the original material to smaller coupons.

Other manufacturers assert that some alternative brass alloys possess excellent stress corrosion cracking resistance. More specifically, it is reported that “*the susceptibility of Ecobrass to stress corrosion cracking is one-thirtieth and below the usual materials according to the JIS ammonia test and CES ammonia test and solves the stress corrosion cracking problem that they have*” (Sambo Copper Alloy Company 2005). The JIS method involves soaking in an atmosphere of NH_4OH aqueous solution (concentration not less than 11.8 percent) for two hours at room temperature and identifying cracks by visual observation. The same manufacturer claims that the dezincification corrosion resistance of this alloy is also excellent, when evaluated using the “ISO 6509” test (Sambo Copper Alloy Company 2005). These issues are deserving of additional study.

ASTM SPECIFICATIONS FOR NEW NON-LEADED BRASSES

ASTM sets voluntary technical standards for materials, products, systems and services. These standards can theoretically draw on the wisdom of more than 30,000 technical experts including producers, users, consumers, government and academia from over 100 countries (ASTM International 2005). The specifications set by these standards offer detailed description as to how production should be made or as to how a process should be performed (NDT 2005).

ASTM standard specifications can play an important role in guiding design, manufacture and trade. They are developed by a large group of interested parties and are therefore widely accepted. From the manufacturers’ perspective, a standard of production results in a more uniform and consistent process or product (NDT 2005). In addition, the specifications provide a basis for comparison between products that helps companies compete in the global marketplace. From the consumers’ standpoint, ASTM specifications allow them to use products that have been tested and satisfy the requirements of the applicable standard.

ASTM Standard Specifications

No specifications have been developed by ASTM that focus specifically on non-lead brass alloys. Some of the new alternative alloys have already been listed in existing ASTM standards for copper alloy applications, whereas some others are currently under evaluation for ASTM listing.

From the Envirobrass family of alternative brass alloys, Envirobrass I (C89510) and Envirobrass II (C89520) are already listed in ASTM B30 Standard for copper alloys in ingot form, as well as in ASTM B584 Standard for sand castings (Table 1-8). From the Federalloy series of non-lead brass alloys, currently C89844 is approved for the same ASTM Standards (B30 and B584), as well as B763 (Table 1-8). EnviroBrass III (C89540) is expected to be included in 2006/2007 standards for Permanent Mold Castings (Sadayappan 2005a). Other alloys from the Envirobrass and the Federalloy series that are currently commercially available have not received ASTM accreditation so far. EcoBrass data is being collected for C87851 (sand casting) and C87852 (permanent mold casting) and the alloy is expected to be included in B30, B584 and B806 Standards in 2006/2007 (Chase Brass & Copper Co. 2006).

Table 1-8: ASTM specifications for non-lead brass alloys (CDA 2000).

Alloy	Form	ASTM Standard	Description
Envirobrass I (C 89510)	Ingot	B30	Copper base alloys in ingot form
	Sand	B584	Copper alloy sand castings for general applications
Envirobrass II (C89520)	Ingot	B30	Copper base alloys in ingot form
	Sand	B584	Copper alloy sand castings for general applications
Federalloy 844 Version (C89844)	Ingot	B30	Copper base alloys in ingot form
	Sand	B584	Copper alloy sand castings for general applications
		B763	Copper alloy sand castings for valve applications

ASTM Standard B30 sets the requirements for copper alloys in ingot form to be re-melted for the manufacturing of castings. ASTM Standard B584 sets the requirements (e.g. minimum mechanical properties and chemical composition) for copper alloy sand castings intended for general applications. ASTM Standard B763 sets the requirements for copper alloy sand castings intended for valve applications: materials and manufacture, chemical composition and mechanical properties of suitable alloys are specified by this standard.

The composition requirements for the three ASTM accredited non-lead brass alloys match their composition as presented previously in this chapter under the heading “*Description of the Composition, Lead Content and Mechanical Properties of New Non-lead Brasses*”. The minimum mechanical properties mandated by the relative standards are reported herein (Table 1-9).

Table 1-9: Minimum mechanical requirements for ASTM accredited non-lead brasses. No mechanical properties are mentioned in the B30 Standard as ingot is an intermediate product.

ASTM Standard	Alloy	Minimum Tensile Strength ksi (MPa)	Minimum Yield Strength ksi (MPa)	Minimum Elongation in 2 in. or 50 mm (%)
B584	C89510 (Envirobrass I)	26 (184)	17 (120)	8
	C89520 (Envirobrass II)	25 (176)	17 (120)	6
	C89844 (Federalloy Version 844)	28 (193)	13 (90)	15
B763	C89844 (Federalloy Version 844)	28 (193)	13 (90)	15

SUMMARY OF CURRENT STATE EXPERIENCE WITH NON-LEADED MATERIALS

Plumbing codes [including the International Plumbing Code (IPC) and the Uniform Plumbing Code (UPC)] have been adopted by most states. These codes cover water supply and distribution issues, among others. They do not specifically exclude the use of lead in drinking water system components. In the USEPA Simultaneous Compliance Workshop (2004b) it was proposed that plumbing codes be altered so that they provide true “lead-free” materials.

Action has been taken by different states in order to eliminate lead use in drinking water components (e.g. California) or to promote use of components with lower lead content (e.g. Massachusetts). Although there are potential limitations to each of these initiatives, they do provide a potential model to consider at the national level, and are discussed below.

California

California is widely considered to be one of the most active states in reducing lead in plumbing components through Proposition 65 (most commonly referred to as CA Prop 65). CA Prop 65 was adopted as the “Safe Drinking Water and Toxic Requirement Act of 1986” as a means to prohibit the discharge of toxic chemicals at levels that would cause significant health concerns into “any source of drinking water” (OEHHA 2005). Faucet water was also included in the interpretation of drinking water sources (Weil 2005). With respect to lead, CA Prop 65 set the “safe harbor exposure level” at 0.5 ug/day (OEHHA 2005). This lead level takes into account cumulative exposure from multiple sources. It is thought to be based on data (presented in Canfield 2003), according to which a 10 ug/L blood lead level results in a 10 point IQ deficit in children (Heumann 2005).

CA proposition 65 is entirely imposed through private citizen litigations (Weil 2005). In general, relatively few lawsuits go to trial, and settlements are often agreed upon by all involved parties. This statute has been utilized extensively, and as of 1998 (Heumann 2005):

- 950 Prop 65 notice letters had been sent to 3,710 businesses
- 200 lawsuits had been litigated
- \$25 million had been spent in enforcement payments
- \$250 million had been spent in reformulations/ process changes/ compliance.

Table 1-10 lists several lead-related Proposition 65 lawsuits that have been litigated.

Table 1-10: Major Proposition 65 Lawsuits, related to lead (from Weil, reported by Heumann 2005)

Product	Lawsuit Title	Court	Case Number
Faucets	People v. American Standard	San Francisco Superior Court	CGC-92-948017
Water Coolers	Mangini v. Haws Drinking Faucet Co.	San Francisco Superior Court	CGC-93-952872
Water Meters	Natural Resources Defense Council and Environmental Law Foundation v. Badger Meter	San Francisco Superior Court	CGC-97-984562
Galvanized Pipe Products	Mateel Environmental Justice Foundation v. Edmund Gray Co.	San Francisco Superior Court	CGC-00-309176
In-Line Plumbing Devices	As You Sow v. Conbraco Industries	San Francisco Superior Court	CGC-01-400568
Submersible Pumps	People v. Aeromotor Pumps	Alameda County Superior Court	733686-7

The issue of lead from brass devices was initiated in 1992, when elevated lead concentrations were measured in first-draw water samples from brass faucets. The State filed the “People of the State of California versus American Standard *et al.*” case in 1992 against twelve defendants. Five separate consent judgments were agreed upon in 1995 and 1996. All settlements establish the same lists of covered and excluded products. In most settlements, covered products must meet the lead testing requirements of NSF/ANSI Standard 61, Section 9 (1994 version) with the normal Q statistic of 11 ug. Residential kitchen faucets (all settlements), and covered products (in some settlements) are to be tested according to the same requirements, but with a more strict Q statistic of 5 ug. Compliance schedules that eventually reach 100 percent of covered products sold in California are provided in each settlement. Certain penalties and payments were also agreed upon. The use of subsequent versions of Standard 61 for testing is at the discretion of the settling defendants. In addition, all compliance documents remain confidential. (Heumann 2005)

CA Prop 65 is imposed through enforcement actions seeking injunctive relief and civil penalties that are initiated by private citizens, non-profit groups or government attorneys. In addition, government attorneys can join actions initiated by private citizens or groups. Since California is one of only a few states that have not adopted NSF/ANSI Standard 61, Prop 65 settlements are the only means of enforcement for toxic contamination from indirect additives to drinking water.

Plumbing components meeting the standard for CA Prop 65 have been utilized for other drinking water components such as check valves, drinking water fountains and water meters. It is believed that devices that meet this standard may have a competitive advantage in the marketplace, even outside of California (Weil 2005). Labels for plumbing devices in other states often list that the products are Prop 65 compliant.

Natural Resources Defense Council and Environmental Law Foundation v. Badger Meter was filed in 1997 against six defendants. Three defendants settled early and the others agreed to a consent judgment in 2000. The settlement covers residential water meters with spuds of $\frac{3}{4}$ inch or less. Lead testing of meters was to be done according to NSF/ANSI Standard 61, Section 9 (1999 version) with the California revised Q statistic of 5 ug. It also defined new alloys with lead content of 0.25 percent or less, and identified two (Federalloy I (836) and Sebiloy II) as meeting the definition of a non-lead meter. Certain penalties and payments were also agreed to. The use of subsequent versions of Standard 61 for testing is at the discretion of the settling defendants. In addition, all compliance documents remain confidential

Another settlement initiated the implementation of a non-lead program by the Los Angeles Department of Water and Power (LADWP). The LADWP and the California Attorney General (AG) joined an existing action (filed under seal by the Environmental Law Foundation) in 1999. A settlement was agreed to by the LADWP, the California AG and a defendant in 2000, and the LADWP and California AG exited the litigation. The terms of the agreement financially supported the project, which aims to substitute old leaded water meters, curb valves, and other service line components with non-leaded products. Replacements were begun in April 2001 and the program is expected to result in replacement of all installed water meters in a time period of approximately 15 years. The annual replacement goal was initially set at 40,000 meters. A more detailed description of the LADWP program is contained in this chapter under the heading entitled "*Utility Motivations and Experience with Non-lead Brass Components*".

The Proposition 65 settlements resulted in more rigorous lead reduction methods for certain products, and the development and deployment of alternative alloys. As non-lead meters and fittings have been installed in California, a population of these new materials has been created that can be tested in the field. In addition, due to distribution channel constraints, essentially all residential kitchen faucets sold or distributed by major manufacturers in the U.S. now meet the testing provisions of NSF/ANSI Standard 61, Section 9 with a restricted Q statistic of 5 ug. In total Proposition 65 has reduced lead in some products, and provided encouragement for further lead reduction in others (Heumann 2005).

Massachusetts

The State of Massachusetts does not require conformance to NSF/ANSI Standard 61 (Laprade 2005), however the Massachusetts Plumbing Code requires end-point devices to comply with

NSF/ANSI 61. This is done through a reference to ASME A112.18.1, which mandates NSF/ANSI Standard 61 compliance (Viola 2005). The state's plumbing code also sets a requirement with respect to the maximum allowable lead content in drinking water system components. This regulation focuses on the use of materials with lower lead content for drinking water applications, rather than the complete elimination of lead. More specifically, the Massachusetts State Plumbing Code (248 CMR) requires that pipes, valves, pipe fittings, aerators or faucets which are utilized in drinking water applications contain no more than 3 percent lead as of January 2, 1995 (Laprade 2005). Until very recently, the Massachusetts Plumbing Board accepted NSF/ANSI Standard 61 testing as proof of compliance with the 3 percent lead provision. After learning that NSF/ANSI Standard 61 compliance does not assure that products contain less than 3 percent lead, the Board no longer accepts NSF/ANSI Standard 61 data and strictly enforces the 3 percent lead provision (Viola 2005).

UTILITY MOTIVATIONS AND EXPERIENCE WITH NON-LEAD BRASS COMPONENTS

By installing non-leaded brass components, utilities can demonstrate “due diligence” or the prevention of foreseeable harm. In some cases, utilities have initiated lead source replacement programs in response to regulatory requirements such as lead service line replacement programs, or customer concerns about the health effects of lead exposure. In other cases, utilities have embraced current technological advances such as non-lead brass meters and have incorporated them into their contract specifications and maintenance programs (i.e. meter replacement programs). Some utilities have implemented rebate programs to motivate consumers to purchase non-lead faucets and other fittings. In California, money available from Proposition 65 and other legal settlements is used to support these programs.

For many utilities, the switch to non-leaded components may also be based on the potential for improvement in the utility's 90th percentile lead levels. For utilities located in warm climates, the meter is generally located outside the residence (Figure 1-6), while for cold climates, the meter is located either in the basement or in a meter pit (Figures 1-7 and 1-8). The mass of lead leached from a leaded meter and associated fittings may potentially have more of an impact on lead levels measured at the tap in cold weather settings. When compared to warm climate service configurations, cold climate service installations may exhibit a shorter distance to the faucet and therefore less dispersion of the lead mass.

In 2000, Asarco commissioned a survey of U.S. water utilities to identify utility plans for replacement of leaded components with non-leaded components. Asarco is a smelting and refining company that produces the bismuth selenide alloy used in making Envirobrass, and were part of a consortium that developed bismuth selenium compounds as replacements for lead in brass. They received responses from 301 utilities nationwide, with 50 percent of survey respondents representing small systems (defined as serving <5000 connections). Survey findings show that 20 percent of utilities (61 of 301 responses) currently have plans to replace their lead-containing brass components. Twenty-one percent of survey respondents indicated they were not aware that non-leaded brass options are available (Asarco 2000).

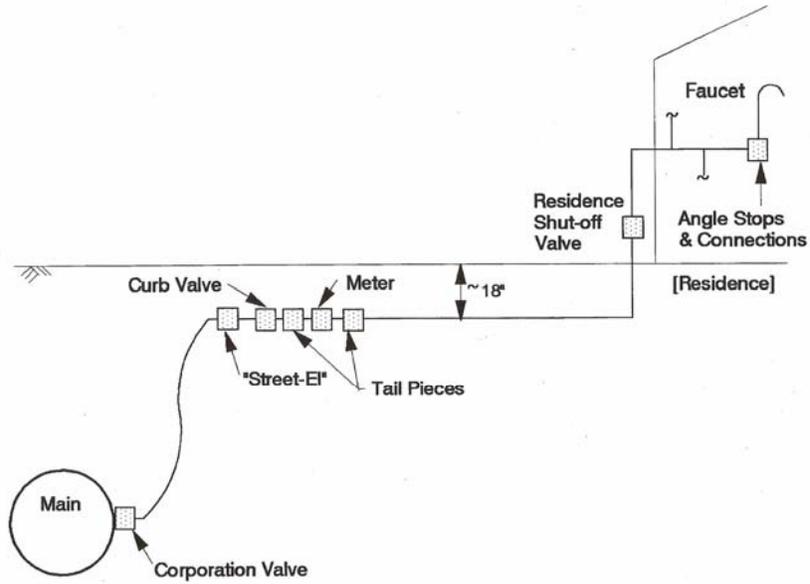


Figure 1-6: Diagram of Typical Warm Climate Residential Service (Provided by Heumann 2005)

Diagram of Typical Cold-Climate Residential Service

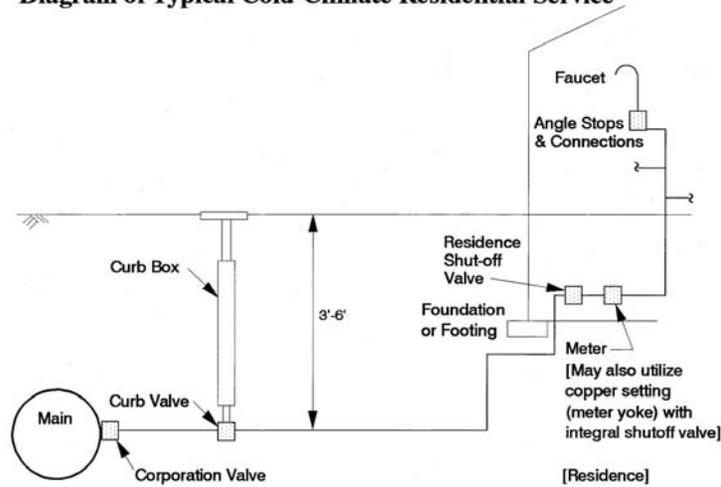


Figure 1-7: Diagram of Typical Cold-Climate Residential Service (Provided by Heumann 2005)

Diagram of Alternate Cold-Climate Residential Service

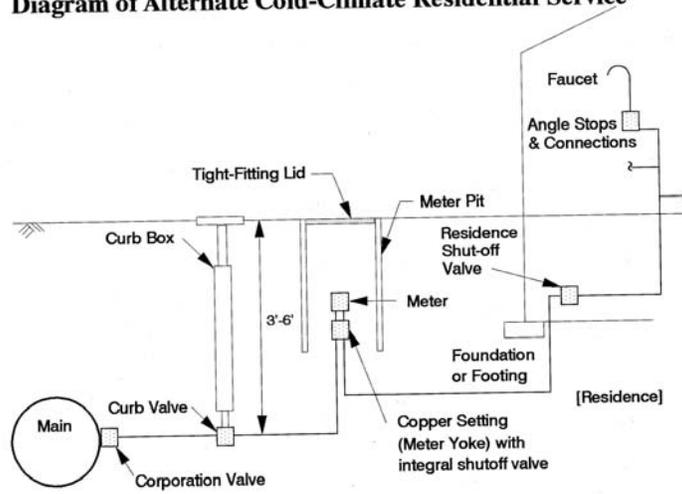


Figure 1-8: Diagram of Alternate Cold-Climate Residential Service (Provided by Heumann 2005)

A water utility survey conducted as part of AWWARF Project 3018, *Contribution of Service Line and Plumbing Fittings to Lead and Copper Rule Compliance Issues*, provides some insight into utility lead component replacement programs (HDR/EES 2005a). The survey captured utility knowledge on lead sources and the availability of utility data and information related to project objectives. Preliminary survey results applicable to this project (based on 30 responses) are summarized as follows:

- Three respondents have programs to install non-lead meters and other fittings.
- Ten of 30 survey respondents have developed their own specifications for either lead-free (<8 %) or non-lead (<0.25 %) components.

Table 1-11 provides examples of utility lead source replacement programs that utilize non-lead brass components.

Table 1-11: Utility Programs Utilizing Non-Leaded Brass

Utility	Program Description (Year Started)	Reference
Los Angeles Dept. of Water and Power	Replacement of substandard curb valves and meters as a result of legal settlement with supplier.	Maas, Patch and Lagasse 2002; Heumann 2005; HDR/EES 2005b
East Bay Municipal Utility District	Old meter and service line fittings replaced with non-leaded parts by attrition.	HDR/EES 2005c
Bangor Water District, Maine	Large meter replacement program; utility specified non-	Moriarty 2005

Utility	Program Description (Year Started)	Reference
	leaded brass components on new contracts.	
Greater Cincinnati Water Works	Meter replacement program	USEPA 2005b
Seattle Public Schools	Replacement of drinking water fountains, faucets, flexible connectors and shut-off valves.	Seattle Public Schools 2006 Pierson, 2006 Boyd <i>et al</i> 2005
San Francisco Public Utility Commission	Faucet rebate program; meter replacement program, specification of non-leaded curb stops.	HDR/EES 2005d

The following sections provide additional details on these utility lead source replacement programs.

Los Angeles Department of Water and Power

LADWP has long been active in efforts to reduce lead contamination in drinking water. Beginning in the early 1980s, studies were performed to determine corrosion rates on water system materials, including the development of weight-loss corrosion measurement methods and sampling protocols. In order to assess the effect on residential plumbing, an employee residence sampling program was conducted in 1985. This resulted in a change to lead-free solder for all LADWP activities in advance of federal regulations. Studies of lead-dispersion from lead goosenecks were also carried out, resulting in a program to identify and remove lead goosenecks (although not required by federal regulations). Removal of all known lead goosenecks from distribution system was completed in 2005. In addition, corrosion inhibitor effectiveness studies on LADWP water sources were performed, and a pilot scale corrosion control facility was constructed in 1990, which continues in operation. A demonstration scale corrosion control facility is pending. These activities have been pursued, even though all LCR residence compliance samples collected have been below the federal action levels for lead and copper.

The LADWP initiated a “Non-lead Brass” Program as a result of a legal settlement regarding substandard valves and other parts supplied to the utility. These components contained up to 40 percent more lead than allowed by contract specifications. In 1998 LADWP tested 195 parts supplied under contract and found that 68 percent failed to meet contract specifications. The measured lead levels in drinking water did not result in water quality problems to LADWP’s customers or violate any USEPA action levels for lead. Settlement funds were used to initiate the program.

LADWP uses two different alloys in the “Non-lead Brass” Program. The alloy used for waterworks fittings (curb valves, meter tailpieces, etc.) is Federalalloy I (version 836) with a 0.1 percent maximum lead content. LADWP testing of production pieces revealed a range of lead

concentrations from 0.07 percent to 0.09 percent. The alloy used in meters is SeBiloy II (a.k.a. Envirobrass), with a 0.25 percent maximum lead content. LADWP testing of production pieces revealed a range of lead concentrations from 0.12 percent to 0.18 percent. These testing results indicate that both Federalloy and SeBiloy could probably meet a 0.2 percent lead limit. LADWP testing results indicate that the percent elongation for Federalloy under failure testing more closely approximates the behavior of traditional brass than does Sebiloy. However, there have been no observed differences as regards failures of either non-lead alloy when compared to traditional brass over the past 4.5 years. This is true despite the fact that soils in the LA area are active, providing a relatively rigorous application environment.

LADWP began installing only non-lead meters in 2001 and intends to replace all meters (~700,000) by 2016, with an annual replacement goal of 40,000 meters. As of July 5, 2006, there were 723,250 service connections (88 percent of which are residential) and more than 171,000 meters have been replaced with non-lead meters. Meter replacement normally includes replacement of meter couplings (a.k.a. tail pieces Figure 1-6), so approximately the same number of tail piece pairs has also been replaced. In addition, when a meter is replaced, the curb valve is sometimes replaced. Since 2001, more than 70,000 curb valves have been replaced. This program will continue for the foreseeable future (Heumann 2005; HDR/EES 2005b; Maas, Patch, and Lagasse 2002).

With regard to the new non-lead meters that have been installed, the LADWP has not experienced failures or leaks at a higher frequency than that observed when old leaded meters were installed. At the same time however, failures early in the product life are expected to be rare. The LADWP has started to perform tests on the structural stability and leaching characteristics of the non-lead service line components that have been retrieved from the field after approximately 5 years of service. The retrieved meters have exhibited no evidence of structural weakening or dealloying. Testing for changes in leaching characteristics are in progress, and although that work is not yet complete, there have been no significant changes in leaching discovered. The results of testing will be published eventually (Heumann 2005).

East Bay MUD

Between 1985 and 1992, East Bay Municipal Utility District (EBMUD) in California proactively replaced known lead service lines. In 2002, EBMUD implemented a program to further reduce the potential sources of household lead through the replacement of brass meters and service line fittings. This is an attrition program that focuses on removing the oldest equipment from the system first. EBMUD replaces obsolete meters and fittings with California Proposition 65 compliant non-lead meters and fittings. Each year EBMUD issues contracts for the replacement of approximately 15,000 small water meters, 150 large water meters, and 15,000 curb stops. EBMUD uses non-lead materials specifications that require the installation of meters and fittings whose components, individually, do not exceed a lead content of 0.25 percent (HDR/EES 2005c). EBMUD's most recent 90th percentile level for lead was 5 ug/L.

Bangor Water District

In the year 2000, the Bangor Water District in Maine decided to start specifying non-lead brass meters (<.25 percent lead) as part of the planning process for replacing all large meters in the

system (Moriarty 2005; USEPA 2004b). The District serves approximately 10,000 services using a surface water source that is treated by disinfection with ozone and chloramines, and pH adjustment with soda ash. Although the District's 90th percentile samples have a lead concentration below the action level (June 2004 90th percentile value was 10 µg/L), the District is motivated to reduce sources of lead that could potentially leach into the drinking water. The District has no lead service lines but has identified meters as a potential source of lead. A limited meter testing program in year 2000 showed the value of using non-lead components. The utility's Materials Specifications (6-1-2004) include non-lead materials for corporation stops, curb stops and miscellaneous brass goods (Bangor Water District 2005).

Greater Cincinnati Water Works

The Greater Cincinnati Water Works (GCWW) recently started to specify non-lead materials in their bid documents (USEPA 2005b). Although GCWW's 90th percentile tap samples have never exceeded the lead action level (most recent 90th percentile value was 7.3 µg/L), GCWW is committed to reducing sources of lead in distribution system materials. With respect to leaded brass meters and components, the utility's approach is to change them out as part of normal replacement cycles. For example, the utility is currently replacing meters in order to implement automatic reading so they have specified non-lead meters.

Seattle Public Schools

The Seattle Public Schools includes 97 buildings (schools and related facilities), all are served with water from Seattle Public Utilities. Seattle Public Schools conducted a comprehensive testing program in 2004 to identify existing endpoint devices (i.e. water fountains, classroom sinks, kitchen taps) with elevated lead levels. Initially, the testing program was focused on meeting the USEPA guideline of 20 µg/L for lead in school drinking water from first draw and flushed samples, but the school system later established its own lead action level of 10 µg/L in December 2004. All non-compliant sources have been or will be either fixed or taken out of service. Prior to mitigation, extensive testing at more than 3,100 drinking water fountains and sinks showed that about 20 percent exceeded the USEPA guideline (Seattle Public Schools, 2006). Seattle Public Schools is currently completing remediation of endpoint components that exceeded the 10 µg/L action level. Remediation plans developed for each individual school include full or partial pipe replacement, replacement of drinking water fittings (i.e. water fountains, faucets), replacement of flexible connectors and shut-off valves, and in some cases installation of point-of-use filters that are NSF certified for lead removal. Where brass components were replaced, non-lead (≤ 0.03 percent lead) brass components were utilized. As of March 2006, 87 of 97 school buildings had completed remediation and confirmation sampling was performed to demonstrate that lead levels are less than the SPS-specified action level of 10 µg/L. These schools have resumed use of City water and have removed temporary supplies of bottled water. Remediation work is continuing at the remaining 10 schools and is anticipated to be complete by the end of 2007 (Pierson 2006; Boyd *et al* 2005).

San Francisco Public Utility Commission (SFPUC)

In 2001 and 2002, the SFPUC's Water Quality Bureau conducted bench-top lead leaching tests to better understand the sources of lead (consumer's plumbing vs. water system's plumbing) and

to assess the merits of switching to non-lead in-line fixtures. The testing program in 2001 focused on leaded and unleaded water meters (5/8-inch, 1-inch and 2-inch) and curb stops (1-inch to 2-inch). The 2002 program evaluated four types of unleaded faucets. Bench testing results indicate that (i) there are significant differences in the amount of lead leached between brands of unleaded meters; (ii) curb stops have similar or higher lead leach rates as meters; and (iii) some unleaded faucets leach more lead than the others.

In early 2003, the SFPUC initiated a pilot-scale program to test non-lead curb stops under field conditions to evaluate operations and maintenance issues. As part of the pilot program, twenty 1-inch lead-free curb stops were installed in new residential installations in the City. After 1-year of installation, these curb stops were reportedly functioning well.

In 1998, SFPUC's Water Quality Bureau submitted a California Public Health Goals Report to the SFPUC proposing several strategies for reducing lead exposure from drinking water. One of the proposed strategies was to implement a faucet replacement program. In 1999, a pilot faucet replacement program was implemented to reduce lead exposure from drinking water to young children at City preschools and daycare centers. In 2000, the SFPUC expressed an interest in continuing the giveaway program to daycare centers, high lead sites, schools, and recreation centers. Due to the success of the pilot faucet replacement program, SFPUC initiated a faucet distribution program for residential customers in 2001. Customers were given the opportunity to purchase a specific kitchen faucet chosen by the SFPUC for \$10, a savings of \$110. The program objective was to enhance the general public's awareness of the potential lead leaching problem from residential plumbing fittings. Since 2001, 2,653 lead-free faucets have been distributed to residential customers and 487 faucets have been given free to preschools/daycare centers. In 2002, SFPUC gave 505 lead-free faucets and drinking fountains to 47 City schools.

In December 2000, SFPUC adopted a resolution to modify the existing water meter replacement program by discontinuing the purchase of leaded brass water meters whenever a suitable unleaded substitute is available. In 2002, the SFPUC implemented a non-lead meter replacement program with a goal of replacing 7,000 to 8,000 meters annually over a 20-year period. As of October 2005, about 13,000 non-lead meters have been installed (HDR/EES 2005d).

POTENTIAL IMPACTS TO MANUFACTURERS

A number of new cast alloys were developed with little or no lead content specifically to meet NSF requirements. An industry consortium of the CDA, AFS, BBIM, and Materials Technology Laboratory of CANMET in Canada conducted research and developed a series of copper alloys which contain 0.1 to 0.25 percent lead (commercially available as EnviroBrass[®] also known as SeBiLOY[®]). The Federal Metal Company has concurrently developed an alloy containing 0.1 percent lead (commercially available as FederAlloy[®]). No lead is added to these alloys, and the minimal amount of lead present is due to the lead contained in recycled materials and ore that are used as the source metals. These alloys are formed by substituting selenium and/or bismuth for lead, to enhance the machinability and self-sealing characteristics that are the desirable consequences of lead addition. Bismuth is used because it behaves similarly to lead in the manufacturing process and selenium is used to enhance the effects of bismuth.

In addition to development of specific non-lead alloys and the issues related to their manufacture, there are impacts to manufacturers who utilize these alloys to create a variety of drinking water components as described below.

Supply and Demand for Bismuth and Selenium

Some studies are showing that bismuth and selenium could be in short supply with competing European and Japanese demands (USEPA 2005b). The result of a short supply would be price increases, as demonstrated by the recent increase in the spot price for imported selenium as illustrated in Table 1-12 below.

Table 1-12: United States Selenium Supply and Demand Statistics

	2000	2001	2002	2003	2004
Imports for Consumption (metric tons)	4760	4830	4220	3670	3900
Exports, metal, waste, scrap (metric tons)	820	410	850	2430	900
Price (\$/lb)	\$3.84	\$3.80	\$4.27	\$5.68	\$27.00

Source: Summarized by Weed (2005) from data sources: George 2003a; USGS 2005a.

Bismuth consumption in the United States has ranged between 1930 to 2410 metric tons (4.5 and 5.5 million pounds) for the last five years and historically, prices have been relatively stable (United States Geological Survey (USGS) 2005a, b). USGS believes that world demand for bismuth is increasing approximately 5 percent per year. International agreements to eliminate lead from solder in manufacturing processes by 2005 in Europe, Japan, and North America will tend to increase the demand for bismuth over the next several years.” (Weed 2005)

Bismuth is not produced domestically, so the U.S. relies on imported material to satisfy demand. Only a small amount of bismuth is obtained by recycling old scrap. Over the past 5 years, the U.S. has imported 40 percent - 50 percent of the world’s refining capacity for bismuth. Throughout most of the world, bismuth is a byproduct of processing lead ores; in China, it is a byproduct of tungsten ore processing. The Tasna Mine in Bolivia, the only mine that produced bismuth from a bismuth ore, has been on standby since the mid-1990s awaiting a significant rise in the metal price.” (USGS 2005b) Additional statistics on bismuth supply and demand for the period 2000 to 2004 are presented in Table 1-13.

Table 1-13: United States Bismuth Supply and Demand Statistics

	2000	2001	2002	2003	2004
Imports (metric tons)	2,410	2,220	1,930	2,320	2,100
Consumption (metric tons)	2,130	2,200	2,320	2,120	2,420
Price (\$/lb)	\$3.70	\$3.74	\$3.14	\$2.87	\$3.10
Imports as percent of Consumption	95%	95%	95%	95%	90%

Source: Summarized by Weed (2005) from data sources George (2003b); USGS 2005a and 2005b.

World production and consumption data for selenium is limited. Selenium is a rare element, widely distributed within the Earth's crust, but not in concentrations high enough to justify mining solely for its content. It is recovered as byproducts, mostly from the anode slimes associated with electrolytic refining of copper. World refinery production of selenium is estimated to have remained stable. The average global consumption of selenium during the past 4 years is estimated to have been about 2 million kilograms per year, 4 – 5 times the amount consumed in the U.S. More than one-half of the metallurgical selenium is used as an additive to cast iron, copper, lead, and steel alloys. The driving force behind the worldwide demand increases for selenium is the growing economy of China. In mid-2003, China started importing large quantities of selenium, which caused the price to soar as illustrated in Table 1-12. Currently, there is little to no selenium being sold because there is no supply. Additional statistics on selenium supply and demand are presented in the following table.

Processing Issues

Developers of the new non-lead alloys state that the foundry characteristics (melting and casting) and their mechanical properties are similar to existing lead alloys; however the new alloys may exhibit lower ductility (percent elongation) and lower impact strength. According to the CDA, all of these alloys have worked well in the appropriate applications (Weed 2005). Ford Meter Box (2005a) offers the perspective that the mechanical properties and manufacturability of the new alloys are somewhat inferior to the copper-lead alloys. Ford Meter Box is concerned about applications where the product is buried underground and failure would be difficult to detect.

The CDA (Weed 2005) states that there is no problem producing bismuth-copper alloys in foundries. However, some process changes may be required. If an operation produces both lead and bismuth brass alloys, it is possible to produce both in the same furnace, however the wash heats necessary to condition the furnace for "non-lead" can be expensive and difficult to control. This often leads to dedicating specific melting equipment just for non-lead alloys and may even require the purchase of new equipment. Brass scrap that contains bismuth must be isolated from other brass scrap. Bismuth makes hot rolling and hot forming nearly impossible in copper alloys so bismuth scrap must be either re-used or sent to a foundry casting bismuth alloys. All brass mills in the U.S. test scrap for bismuth content and will refuse any load that contains bismuth. Presently, bismuth containing brass scrap is well controlled and used as run-around scrap or returned to a foundry. There may be a concern in the future as more consumer scrap

enters the recycling stream and additional time and expense are required to identify and segregate bismuth alloys from other copper alloys.

Component Manufacturing Issues

The need to comply with NSF/ANSI Standard 61 is causing manufacturers to consider alternative strategies for production of brass water meters and other components in drinking water systems. The primary compliance strategies used to meet NSF/ANSI Standard 61 are to reduce the lead content of the brass alloy; reduce the surface area available for water contact; use a different material for water contact such as platings or coatings; or remove lead from the surface of the water contact component. (Weed 2005). The following section discusses some potential impacts of using non-lead alloys to manufacture drinking water components.

The machinability of various alloys is compared to a standard machinability rating of 100 set for alloy C36000 (free cutting brass). Machinability ratings range from 75 to 85 for EnviroBrass[®] and Federalloy, and decreases as the bismuth content of the alloy decreases. The Copper Development Association states that EnviroBrass[®] III can be machined using essentially the same practice as leaded yellow brass, but there might be higher tool wear with EnviroBrass[®] I and EnviroBrass[®] II when compared with C83600 or C84400 alloys, and machining fluids may be needed (CDA 2005; Sadayappan 2005a).

There may also be issues associated with larger scale production. From a manufacturing point of view, if bismuth is used as a replacement for lead in alloys, this change involves upfront costs, design changes, and practice modifications. This could have large capital implications for manufacturers. The machinability ratings are based upon the speeds (rpm of the brass material) and feeds (inches per second feed rate of the tools) compared to alloy C36000, which has a rating of 100. So while another alloy may fall into the "free machining" class with a rating of 75, that means that the speeds/feeds rate at which material can be removed is only 75 percent of that of alloy C36000. The labor and overhead cost of making a part may be higher for an alloy rated at 75, compared with the C36000. Also, the ratings relate to the ability to remove the material, but do not always reflect the ability to produce the smooth surface finishes. Therefore, before significant investment is made, manufacturers need to know USEPA's direction on possible health impacts of bismuth (USEPA 2005b).

In yellow brass, used for faucets and other fittings, the addition of bismuth can cause cracking issues. Like water, bismuth migrates into cracks and expands by 3 percent as it solidifies. There is concern about the impact in field use or machining. Ford Meter Box (2005a) raises a concern with the generally lower ductility of the no-lead alloys and their demonstrated propensity to crack. The "...low ductility gives rise to concerns of failure, especially in thin sections of products that may be stressed in installation or usage. Indeed, manufacturers have had to redesign products to remove thin sections in order to reduce concerns with the low ductility. The propensity to crack has been found in the copper-bismuth-selenium alloys. The cracking has normally been found to occur on dry machined surfaces of thin sections that were heated up due to any of several reasons including excessive feeds and speeds or dull or incorrect tooling. The cracking, in some instances, is easily seen and discernible." (Ford Meter Box 2005b). Ford Meter Box has decided to not use these alloys as a solution to meet lower lead levels and instead is utilizing a lead-removing wash system known as the Kunkel Process to meet the NSF/ANSI

61 standard (Ford Meter Box 2005c). The Kunkel Process is a patented process that exposes parts to a series of acid/caustic solutions in order to dissolve lead contained on the surface of the part.

The decision to utilize non-lead brass alloys to manufacture drinking water components involves a variety of criteria, not just the ability to meet lower lead levels. Ford Meter Box (2005b) provides perspective on the issues related to the manufacture of drinking water components, and the use of non-lead alloys: “The selection of alloys must be based on product line configuration, manufacturing capabilities, resources and customer needs as well as safety. Product performance characteristics such as durability, machinability, resistance to corrosion, functionality, and strength are just a few items that must be considered when selecting a material for use in a product.” Selover (2005) states that companies that manufacture components use several product performance criteria when selecting materials and developing their product design, including:

- Burst Strength/Water Hammer Resistance
- Bending/Torque Strength (mounting issues)
- Durability –500,000 on-off cycles
- Machinability –tolerances necessary to provide smooth, durable function
- Functionality in High Mineral Content Water
- Ability to Apply Decorative Finishes
- Abuse/Vandalism –Excessive Force
- Hot/Cold Water Temperatures

Presumably, non-lead alloys used for manufacturing components would be subjected to these criteria as well.

Health and Environmental Impacts

Manufacturers may be gaining a competitive advantage by meeting the California Proposition 65 standard (USEPA 2005b). As a result of this standard, there have been major changes in the lead content of sandcast brass. Side benefits to reducing lead content include reduced worker exposure, lower air emissions, and less production of hazardous waste. However, Ford Meter Box (2005b) points out that waste streams containing selenium may be considered hazardous.

When the non-lead brasses “...are machined dry (without cutting fluids), no significant lead-bearing particles enter the machine shop air. This means no special air purification equipment is needed, enabling a possible drop in insurance costs for manufacturers of plumbing fittings because their workers may not be exposed to lead. In addition, for sand casters, the costs for prevention of airborne lead and for reclamation and disposal of foundry sand should be lower.” (CDA 1996).

IMPACTS TO PLUMBING INDUSTRY

The impacts and implications of moving the plumbing industry towards use of non-lead brass components for drinking water involves a complex interaction among the groups involved: manufacturers of components, organizations that certify components and develop standards and codes for their use, inspectors that enforce those codes, and the installers of components (both utilities and private plumbers). There are several issues that can be considered including; development of non-lead components, code revisions and code enforcement (at the utility, local, and state level), coordination between federal, state and local regulatory agencies and code organizations, education and training of plumbing inspectors and component installers, and standardization of terminology between groups.

Plumbing Manufacturers

Issues related to the development and manufacture of non-lead components are contained in the previous section on manufacturing. In summary, they include:

- Increased manufacturing costs due to re-tooling, product redesign, reduced manufacturing efficiency and scale up of facilities to produce non-lead components
- Concerns about cracking due to lower ductility of some non-lead alloys, and the need to significantly re-design products
- Ability of non-lead components to meet consumer, regulatory and/or companies' product performance criteria.

Possible changes to drinking water regulations, material certification requirements, and standards and codes to incorporate non-lead brass alloys could all play a significant role in product development and the timing for implementing changes.

Standards and Plumbing Codes

In addition to the requirements found in the NSF/ANSI 61 standard, the occurrence of lead in materials that come in contact with drinking water is controlled by building codes such as the Uniform Plumbing Code, standards by the American Water Works Association (AWWA), the American Society of Mechanical Engineers (ASME), and ASTM. Plumbing products within buildings are generally regulated at the state or local level through plumbing codes. These local codes are normally based on Model Plumbing Codes such as UPC, IPC, and the National Standard Plumbing Code (NSPC). All plumbing codes require products to comply with an applicable product standard that contains minimum performance requirements and test procedures that impact product design, manufacturing process and cost (Viola 2002). The UPC, IPC and NSPC all reference NSF/ANSI Standard 61 for pipe, fittings, and faucets but do not reference NSF/ANSI Standard 61 for in-line valves. The ASME A112.18.1 standard for faucets and other end-point devices in the U.S. and CSA B125.1 standard for faucet and other end-point devices in Canada require end-point devices that convey drinking water to be in compliance with NSF/ANSI Standard 61. These standards are referenced in virtually all model and state- and locally-written codes. Most faucets sold at the retail and wholesale levels in the U.S. are certified to NSF/ANSI Standard 61 (USEPA 2005b).

Moving the plumbing industry towards the use of non-lead alloys and components will likely require that certification, standard specifications, and code revisions be implemented. Minimum performance standards and certification evaluation procedures would need to be developed using realistic time-frames and schedules for implementing changes. The same would be true for plumbing code changes at the national, state, and local level.

There is often little or no discussion between the State drinking water primacy agency and the people working on plumbing codes (USEPA 2005b). It would be helpful to strengthen this connection, but this can be difficult, particularly in some states that have many jurisdictions. There needs to be increased dialogue between those that develop plumbing codes and those that implement them.

Installation and Inspection

Installers of non-lead brass components (utilities as well as master and journeyman plumbers) will need to be educated about the availability of these components and any technical information needed for proper installation. There are several unknowns related to installation of non-lead components, such as what the impact of installation and workmanship may have on drinking water quality, and how non-lead components perform in the long-term when compared to historically used components that contain lead. Plumbing code inspectors may also need to be educated about revisions to plumbing codes in order to enforce code requirements for non-lead brass components.

There is also a terminology gap between the various groups. In plumbing industry terminology, a fixture is a receptor that receives potable water after discharge (USEPA 2005b). By definition, a fixture does not contain potable drinking water, and therefore is not subject to lead in drinking water regulations. Current drinking water regulations may need to be revised to reflect industry terminology and avoid further confusion.

IMPACTS TO UTILITY OPERATIONS AND MAINTENANCE PROCEDURES

Utilities participating in two AWWARF projects (Project 3018 Contribution of Service Line and Plumbing Fixtures to Lead and Copper Rule Compliance Issues and Project 3112 Performance and Metal Release of Non-lead Brass Meters, Components and Fittings) were contacted regarding their experiences with installing non-lead brass meters and components and any specific impacts on O&M issues. Because the installation of non-lead brass components has only taken place within the last 5 years in the water industry, there is a lack of detailed information available. Utility experiences with material performance and installation costs are detailed in the following sections.

Material Performance

LADWP staff prefers Federalloy because the product material is more ductile, approximating that of the lead brass that it replaced (Heumann 2005). Federalloy now has ASTM approval for two alloys: Federalloy I (836), which has been used by LADWP for fittings since 2001, and Federalloy I (844 MOD), which is designed for use in water meters. LADWP was also recently informed that the Sebiloy II, used in water meters purchased by LADWP since 2001, will be replaced by BiAlloy for water meters supplied under existing contract. This change was agreed

to by NRDC as fulfilling the California Proposition 65 requirements, and the provisions of the 2000 Consent Judgment that helped initiate the LADWP meter replacement program. LADWP testing of the new materials has not yet been completed. It is expected that competition among all non-lead meter materials will ensue in the near future.

Since LADWP began replacing residential water meters in 2001, the utility has not seen fracture failures or leaks at a frequency different from older brass meters. Failures are not expected in the early years of the program. Meters retrieved and tested after 4.5 years of service had no structural weakening. In early 2003, SFPUC initiated a pilot program to test unleaded curb stops under field conditions to evaluate operations and maintenance issues (HDR/EES 2005d). As part of the pilot program, twenty 1-inch lead-free curb stops were installed in new residential service connections. After one year of installation, these lead-free curb stops were reportedly functioning well. However, the testing will go on for another year before a decision is made on their serviceability.

In 2005, the SPS replaced more than 360 drinking fountains from 97 separate schools and administrative buildings as a result of a comprehensive testing program in 2004 that identified endpoints with elevated lead levels (Seattle Public Schools 2006). Initially, the testing program was focused on meeting the USEPA guideline of 20 ug/L for lead in school drinking water from first draw and flushed samples, but the school system later established its own lead action level of 10 ug/L in December 2004. The replacement bubbler heads are “non-lead” brass construction with less than 0.2 percent lead; however, the presence of surface residuals with lead contaminated dust and cutting oils is common (ASTM 2005). Flushing is typically used to remove the surface residuals. For Seattle schools, a bubbler head pre-conditioning rig was fabricated and installed at an SPS operations facility. All bubbler heads are pre-conditioned before installation in schools. The pre-conditioning involves a 1-minute flush at 2 gpm (to remove any small metal particles from the casting/machining process), followed by a cumulative flush for 24 hours at 0.5 gpm. Upon installation, the bubbler heads are flushed for 5 minutes on-site before placing the bubbler head into service.

Installation Costs

Several utilities have estimated the costs of using non-leaded meters and other components as compared to components made using leaded brass materials. These cost increases range from 2 percent to 100 percent as illustrated by the following case examples for EBMUD, LADWP, GCWW and SFPUC.

EBMUD estimates that the specification of non-leaded meter replacement materials resulted in a 7 percent increase (\$59,150) in program cost based on fiscal year 2005 figures (HDR/EES 2005c).

In 2001, LADWP compared meter replacement costs for both leaded and non-lead brass including the meter, curb valve and tailpieces as summarized in Table 1-14. The non-lead brass meter replacement costs were 30 percent higher than the leaded brass alternative, with installation done by the utility (Heumann 2005).

Table 1-14: Cost Comparison for High and No Lead Bronze Meters Installation at a Typical Service at LADWP (materials only)

Brass component (1 inch)	High lead bronze (85-5-5-5 bronze)	No lead bronze	Cost difference
Curb valve	\$17.46	\$19.17*	\$1.71
Tail piece 1	\$3.86	\$6.64*	\$2.78
Tail piece 2	\$3.86	\$6.64*	\$2.78
Water meter	\$18.04	\$23.80 ⁺	\$5.76
Totals	\$43.22	\$56.25	\$13.03 (30%)

* Federalloy + SeBiloy

The following table presents the average full costs (i.e. with overheads) for new 1-inch service line installations at LADWP, based upon over 800 installations from July 1, 2005 to March 31, 2006. Labor hours and tool expenses are the same for non-lead and leaded brass installations done in the past. Materials are broken down into categories for “non-lead materials” and “other materials”. LADWP is only allowed to charge customers for costs incurred, and the total service line cost corresponds to the current charge for a new 1-inch service line. The service line cost is also calculated for leaded brass, using a non-lead materials cost differential of 30 percent (as determined by LADWP on comparative bids in 2001). The service line cost increase attributable to the change to non-lead brass is 2 percent (see Table 1-15 and notes).

Table 1-15: Average Full Costs for Service Installations at LADWP

Cost Element	Total Cost+ Conventional Materials	Total Cost+ Non-leaded Materials
Labor	\$1,190	\$1,190
Materials (293)	254	293
Equipment	195	195
Construction Support	251	251
Miscellaneous [^]	52	52
Total Service Line Cost	\$1,942	\$1,981

Relative service cost line w/ non-lead:

102%

* Data from 827 new service line installations

+ Direct costs with overheads applied

[^] Other cost elements, not disaggregated

GCWW compared installation costs for leaded brass and 0.25 percent lead (non-lead) meters and fittings, and found that the materials cost would be 20 percent higher for the non-lead fittings installed by the utility and 27 percent higher for components typically installed by the homeowners (Table 1-16) (USEPA 2005b).

Table 1-16: Material Cost Comparison for Leaded and Non- Leaded Meter and Fittings at GCWW

Brass component (3/4 inch)	8% Lead	0.25% Lead	Cost difference
Costs to Utilities:			
Ferrule	\$20.60	\$24.72	\$4.12
Curb stop	\$33.09	\$39.70	\$6.61
Ins coupling	\$22.00	\$26.40	\$4.40
Total Cost	\$75.69	\$90.82	\$15.13 (20%)
Costs to Homeowners:			
DA Valve	\$14.98	\$28.08	\$13.10
PWA Valve	\$13.60	\$25.80	\$12.20
Expander	\$7.91	\$14.93	\$7.02
Meter	\$71.00	\$68.00	-\$3.00
Total Cost	\$107.49	\$136.81	\$29.27 (27%)

SFPUC has provided cost information on non-leaded curb stops and faucets. In 2003, SFPUC initiated a pilot-scale program to evaluate non-leaded curb stops in residential service connections. Based on installation of twenty 1-inch non-leaded curb stops, the cost was reportedly twice the cost of existing curb stops used by the SFPUC (HDR/EES 2005d).

Summary

There is little documented information on the material performance of non-leaded components that have been installed in the field, however limited information indicates no observed differences in structural performance. Costs of non-leaded components are currently higher than their leaded counterparts (20% - 30%), but when material costs are evaluated in perspective to the entire cost of the service installation, the overall increase in costs is significantly less (2% - 5%). As more utilities install non-leaded components and the market expands, the material cost differentials should decline.

ALTERNATIVE MATERIALS FOR FITTINGS AND COMPONENTS

Possible approaches to reducing human exposure from lead in brass drinking water fittings and components include: a) use of alternatives to lead to fabricate those components and b) design changes to existing manufacturing procedures (i.e. modifications to current procedures) in order to eliminate lead leaching.

From the standpoint of consumers and regulators, getting the lead out is viewed more favorably, as it would address the lead leaching problem directly and with high certainty. As a general rule with many exceptions, it has been shown that higher lead content in brass results in higher lead leaching to potable water (e.g. Lytle and Schock 1996). Systematic attempts to identify substitutes for lead resulted in identification of selenium and/or bismuth containing brasses as the most promising solution. Although non-leaded bismuth and selenium-containing brass alloys are the main focus of this study, other materials are discussed as well.

Design changes, including coating and selective leaching of surface lead, might allow use of the existing capital equipment used for manufacturing without expensive modifications or replacements. This alternative is therefore attractive to manufacturers and price sensitive consumers. While this is a relatively painless solution short-term, in the end, the long-term performance of such leaded brass is less certain as the integrity of coatings and surface lead leaching has not been studied in detail. One manufacturer asserted the following about the potential merits of non-leaded cast valves and fittings: “The biggest potential benefit would be a reduction in health hazards to the typical homeowner. While it is difficult to determine a monetary estimate, the regulatory community gives this a very high value. For manufacturers the associated costs may become the cost of staying in business (Showman 1994).”

Consequently, given the stakes to various stakeholders, the feasibility of alternative non-leaded brass and design changes are described in the sections that follow.

Other Materials for Fabrication

Faucets made of plastic or faucets with plastic water channels could be considered (Lytle and Schock 1996). Plastics as an alternative were also discussed in the Organisation for Economic Co-operation and Development (OECD) Workshop on Non-Lead Products and Uses (OECD 1994). Based on one manufacturer’s perspective however, the use of plastic would not provide an economically viable solution for the industry; products would have to be redesigned and the tooling costs for plastic parts could be very high (Anderson 1994).

Considering options for metallic brasses, besides bismuth and selenium, other elements are known to improve machinability of copper alloys including indium, phosphorous and uranium. In the case of indium, the world supply is rather limited in relation to the new demand that would arise. Phosphorous in high concentrations would react with the water that is present in the green sand molding system. Finally uranium, a radioactive element, can be summarily rejected (Sadayappan *et al.* 2003).

Phosphorous and indium would probably not offer viable solutions as sole substitutes for lead in brass. However, they could be added to improve mechanical properties of copper alloys in which another substitute for lead (e.g. bismuth) was being used. Laboratory scale studies were conducted at AT&T Bell Laboratories, in which bismuth (and not lead) containing alloys were coupled with phosphorous or indium (among other elements). The machinability of the resultant alloys was equal to that of leaded-alloys (Lytle and Schock 1996).

Other types of alloys that could be used include silicone cast alloys, lead-free tin bronze, aluminum-bronze and copper-sulfur alloys (OECD 1994). According to Sadayppan (2005b) copper alloys such as silicon brasses and bronzes offer exceptional casting characteristics in sand and permanent molding operations and they could be considered potential candidates for potable water applications. But the above mentioned are not conventional plumbing alloys, and in order to replace lead-containing materials in drinking water applications they would have to possess acceptable mechanical properties relative to those using lead. Their toxicity would also have to be more thoroughly examined.

In a feasibility study that was performed by the Metals Technology Laboratories of CANMET in 1993, the machinability of tin-bronze, copper-sulfur and silicone brass unleaded alloys was examined. The study concluded that of these alloys copper-sulfur had the best machinability. On the other hand, it was stated that copper-sulfur may not have as much structural strength as the brasses, which could be a drawback in plumbing applications. Silicon brass had moderate machinability and could also have good strength (Sahoo *et al* 1993).

In addition, for some of these alloys, contamination would have to be rigidly controlled. Silicon contamination of red brasses and tin bronzes can produce excessive leaks in products, whereas in the case of copper-silicon lead is a contaminant of potential concern (Sadayappan 2005b). Avoiding potential contamination of lead-free alloys during storage and recycling is therefore a concern, and scrap brass might no longer be a suitable source. Scrap brass would have to be used for non drinking water applications (OECD, 1994), unless the removal of lead from scrap was pursued using processes like vacuum distillation (Lytle and Schock 1996). Lead would also be a contaminant of concern in the case of bismuth copper alloys.

Design Changes

Products could be redesigned in order to reduce internal surface area in contact with drinking water (Lytle and Schock 1996, OECD 1994). Design changes would involve considerable re-tooling costs, depending on the available design options. In the case that new manufacturing methods were to be adopted however, the capital investment could prove to be significant (OECD 1994).

Chemical treatment has been employed to existing lead components and fittings in order to reduce lead dissolution. The basic approach is to expose the brass surfaces to an aggressive metal extraction solution that removes surface lead from the product (Lytle and Schock 1996). Research conducted at the University of Florida, where cast products were exposed to a liquid solution of sodium acetate/acetic acid, indicated that such an approach could be feasible (Anderson 1994). However, based on pilot plant studies that followed, the sodium acetate wash was considered impractical for commercial use (OECD 1994). In another laboratory study by Paige and Covino (1992) pretreatment with acetic acid did not significantly reduce the amount of lead leached from commonly used alloys, under the conditions of that specific experiment.

But recent results have been more successful (Ford Meter Box Company 2005c), and chemical lead removal is currently available in the U.S. and in Europe. There is little doubt that the approach reduces lead leaching over the short term, but the question is whether or not long term leaching is reduced significantly. Research conducted by the Environmental Quality Institute in the 1990's indicated that the various acetate compounds examined were "relatively effective in quickly removing the initial high lead on the inside surface area of a leaded-brass part after sand-casting in a permanent-mold manufacture" (Mass 2003).

Permanent coatings could also be applied to the internal surface area of a product (OECD 1994, Lytle and Schock 1996, Sadayappan 2005b). The coating could be either organic or inorganic and many of the coating methods have received product approvals from NSF (Sadayappan 2005b). In the event that these coatings maintain their integrity long term and effectively isolate

the brass from the water, the lead performance characteristics would be identical to those of unleaded brass.

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APPENDIX
**EVALUATION OF THE LEACHING POTENTIAL OF NON-
LEADED BRASSES**

INTRODUCTION

During the Expert Workshop that took place as part of AWWARF project 3112, specific research needs were identified. The consensus opinion emphasized the need to *“identify key water quality characteristics in drinking waters that are aggressive to metal release and impact performance in brass”* and *“conduct performance testing with various water qualities and treatments to take into account chloramines and other identified water quality constituents”*.

In an effort to address some of these high priority needs on a preliminary basis, Virginia Polytechnic Institute & State University (VPI) conducted laboratory experiments that examined the leaching potential of seven different alternative brasses. Representative types of Envirobrass and Federalloy alternative alloys, as well as Ecobrass were examined (Table A-1).

Table A-1: UNS number and commercial name for the alternative brasses tested in this study.

UNS Number	Trade Name
C89510	Envirobrass I
C89520	Envirobrass II
C89837	Federalloy I Original
C89831	Federalloy I-844
C89844	Federalloy I-844 Modified
C89833	Federalloy I-836
C69300*	Ecobrass

*Ecobrass rod. The Ecobrass casting alloy, with the same composition as the rod used in this study, has the UNS number C87850

MATERIALS AND METHODS

For each alternative alloy, brass rods of 0.64 cm (or else 0.25 in) diameter and 0.97 cm (or else 0.38 in) height were epoxied to the bottom of a 46 mL glass vial (Figure A-1). This vial was filled all the way to the top with test water and air was excluded. The brass surface area to water volume ratio achieved was $8.0 \times 10^{-3} \text{ in}^2/\text{mL}$. This ratio is at the lower end of those typically encountered in NSF testing, assuming $\frac{3}{4} \text{ in}^2$ surface area is typical for a brass faucet (Weed 2005) and that a typical brass faucet can hold a water volume of 100 mL (Gardels and Sorg 1989). A lower surface area to volume ratio would tend to decrease the final concentration of metals in the water.

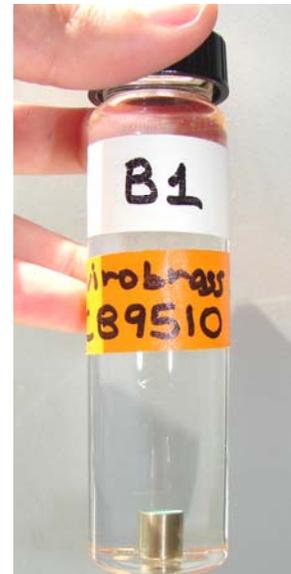


Figure A-1: Experimental setup.

All glass vials were kept out of light during the 4-week exposure of alternative alloys to two different leaching solutions. The first leaching solution was the NSF/ANSI Standard 61, Section 9 synthetic test water. This water has alkalinity of 500 mg/L (\pm 25 mg/L) as CaCO₃, pH of 8.0 (\pm 0.5) and free chlorine dosed at a concentration of 2.0 mg/L (\pm 0.05 mg/L). The second leaching solution, also synthetic, had been identified as aggressive in terms of lead leaching from brass in previous VPI studies. This water has a significantly lower alkalinity of 10 mg/L as CaCO₃, a lower pH of 7.4, and chloramines dosed at a concentration of 4.0 mg/L as Cl₂, consistent with changes in U.S. disinfection practice and lower pH and alkalinity water supplies.

The experiment was conducted following a static “dump and fill” protocol. Water was changed inside the glass vials three times a week. At the end of each week water samples were collected for metals analysis. Metals dissolution was quantified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In all cases, triplicate samples were tested, to allow for satisfactory Quality Assurance/Quality Control and to give the results statistical power. Since two different water conditions were examined in triplicate for seven alternative brasses, $2 \times 3 \times 7 = 42$ tests were conducted overall, for the non-lead alloy.

RESULTS

Lead Leaching

Lead leached from all seven alternative brasses was less than 1 ppb throughout the 4-week testing period, and in many instances was below the detection limit (Table A-2). Leaded brass (3% lead) however, which was included in the study for comparison reasons, released much higher lead to the water. In fact, lead dissolution for the conventional alloy was above the Lead and Copper Rule action level of 15 ppb throughout the testing period, with only one exception during week two (Table A-2). For the lead alloy, the modified water of low pH, low alkalinity and chloramines, was more aggressive towards lead leaching compared to the standard section 9 test water (Table A-2). This observation is consistent with previous tests conducted at Virginia Tech. The lead alloy tested in this study was not treated to remove surface lead, as is sometimes practiced to meet the NSF 61 and California Proposition 65 requirements.

Table A-2: Lead release for the non-leaded brass alloys used in the Virginia Tech study, versus a conventional leaded alloy. The values reported are the average of triplicate samples.

Brass Type	Pb %	Pb Release (ppb)							
		NSF/ANSI 61/ Section 9 Test Water				Low pH, Low Alkalinity, Chloraminated Water			
		Week 1	Week 2	Week 3	Week 4	Week 1	Week 2	Week 3	Week 4
C36000	3.0	23.24	12.63	20.50	21.88	34.96	31.36	37.28	40.46
Envirobrass I	0.25	0.21	BDL	0.38	BDL	BDL	BDL	0.14	0.11
Envirobrass II	0.25	BDL	BDL	0.37	0.38	BDL	0.85	0.18	0.72
Federalloy I Original	0.1	0.36	BDL	0.27	0.24	BDL	0.85	0.16	0.41
Federalloy I 844	0.1	0.76	0.41	0.26	0.31	BDL	BDL	0.07	0.24
Federalloy I 844 Mod.	0.2	0.86	0.16	0.47	0.43	BDL	BDL	BDL	0.15
Federalloy I 836	0.1	0.60	0.15	0.73	0.34	BDL	BDL	0.05	0.19
Ecobrass	0.1	0.36	0.16	0.38	0.39	0.05	0.09	0.27	0.35

BDL stands for Below Detection Limit levels. The detection limit for lead was DL (Pb) = 0.04 ppb

Bismuth Leaching

Bismuth levels were mostly below the detection limit throughout the monitoring period, for both the Section 9 test water, as well as the modified leaching solution (Table A-3).

Table A-3: Bismuth release for the non-leaded brass alloys used in the Virginia Tech study. The values reported are the average of triplicate samples. Ecobrass does not contain bismuth, therefore no bismuth data are presented herein for that alloy.

Alternative Brass Type	Bi %	Bi Release (ppb)							
		NSF/ANSI 61/ Section 9 Test Water				Low pH, Low Alkalinity, Chloraminated Water			
		Week 1	Week 2	Week 3	Week 4	Week 1	Week 2	Week 3	Week 4
Envirobrass I	0.5-1.5	BDL	BDL	0.71	BDL	BDL	BDL	BDL	BDL
Envirobrass II	1.6-2.2	0.76	BDL	0.97	1.84	BDL	BDL	BDL	BDL
Federalloy I Original	0.70-1.2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Federalloy I 844	2.7-3.7	0.72	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Federalloy I 844 Mod.	2.0-4.0	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Federalloy I 836	1.7-2.7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ecobrass	-	-	-	-	-	-	-	-	-

BDL stands for Below Detection Limit levels. The detection limit for bismuth was DL (Bi) = 0.70 ppb

Selenium Leaching

Envirobrass I and II contain selenium. Throughout the study, selenium release from these alloys was below the detection limit of 2.98 ppb for both the Standard 61, Section 9 test water as well as the modified version of that test water.

Copper Leaching

Copper release to the water was below the 1,300 ppb action level for all non-leaded brasses tested, for both exposure to the Section 9 test water (Figure A-2), as well as exposure to the modified water (Figure A-3).

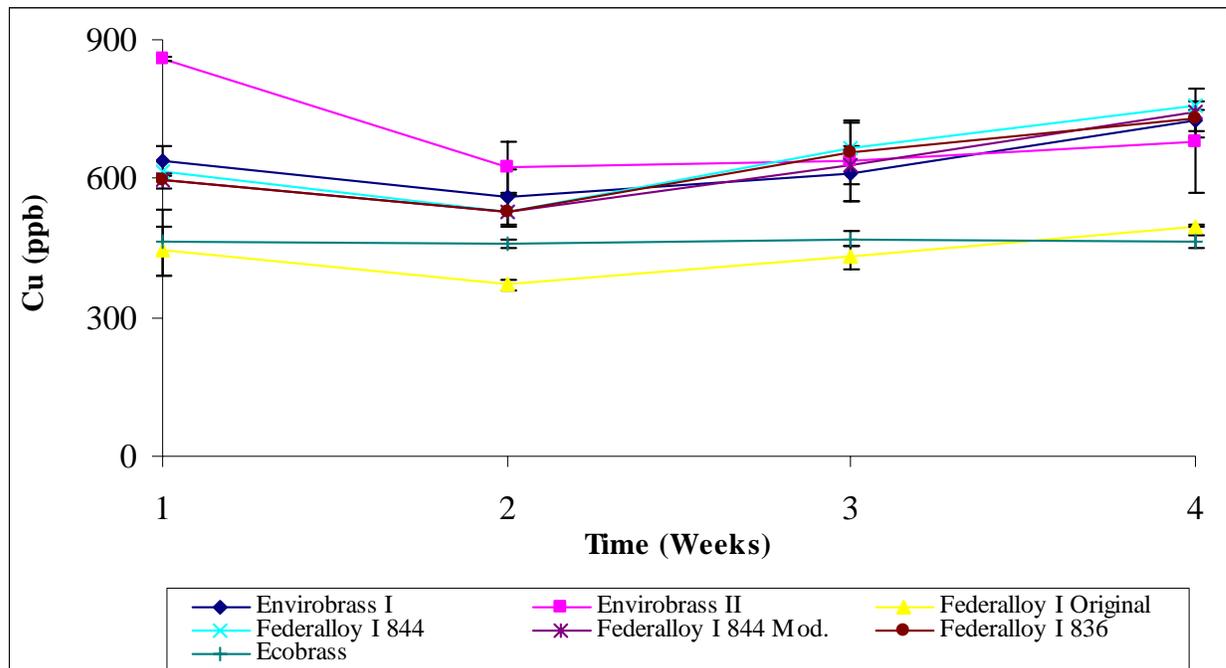


Figure A-2: Copper leaching for the non-leaded brasses, when exposed to the standard section 9 test water. The error bars represent 95 percent confidence intervals.

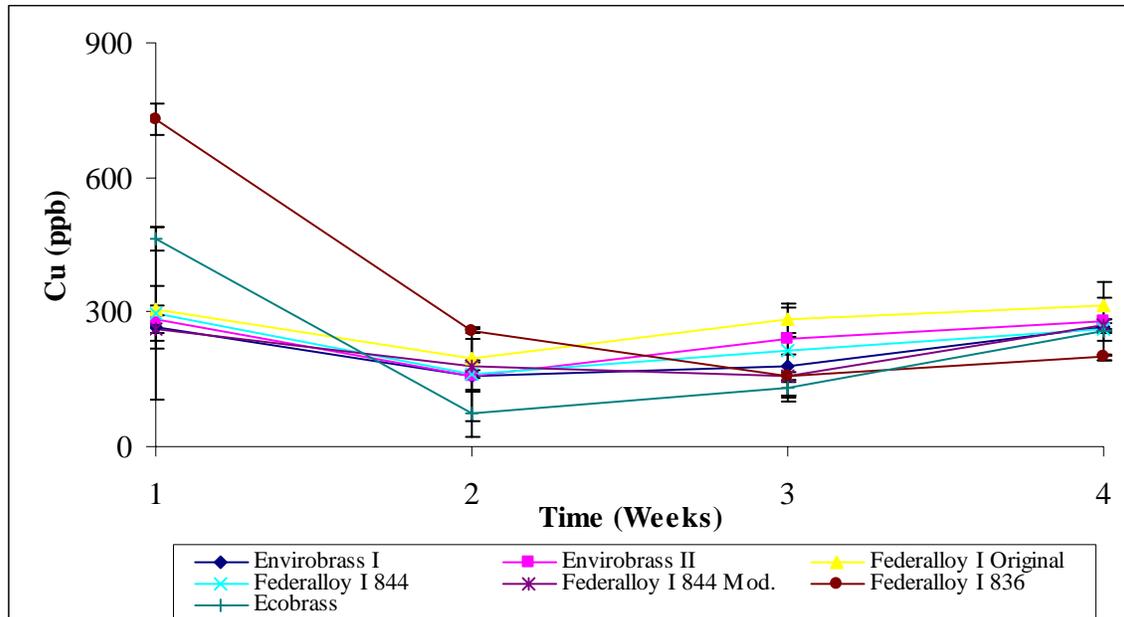


Figure A-3: Copper leaching for the non-leaded brasses, when exposed to the low pH, low alkalinity, chloraminated water. The error bars represent 95 percent confidence intervals.

Zinc Leaching

No primary MCL (maximum contaminant level) applies for zinc in drinking water and there is no zinc leachate limit in Standard 61. It is however related to dezincification, a common type of brass corrosion, and as such it was also enumerated in this study. Zinc dissolution for the alternative alloys was in general lower or about the same under exposure to the Standard 61, Section 9 test water (Figure A-4), compared to the modified water (Figure A-5).

Other Elements

Due to the unusual problem of “carry-over” contamination for antimony via ICP-MS, antimony detection limits were relatively high. When a majority of samples were re-run to minimize this problem, in every sample antimony levels were below the MCL of 6 ppb. Silicon levels leaching from brass were below 500 ppb in all cases.

Visual Differences

Visual differences were observed between the coupons exposed to the Standard 61, Section 9 test water, versus the modified water, for the same alloy. For instance, after completion of the experiment, Envirobrass II coupons had distinct visual differences between the two waters tested (Figure A-6). In addition, Federalalloy I Original and Ecobrass appeared more uniformly corroded when exposed to the standardized test water (Figures A-7 and A-8).

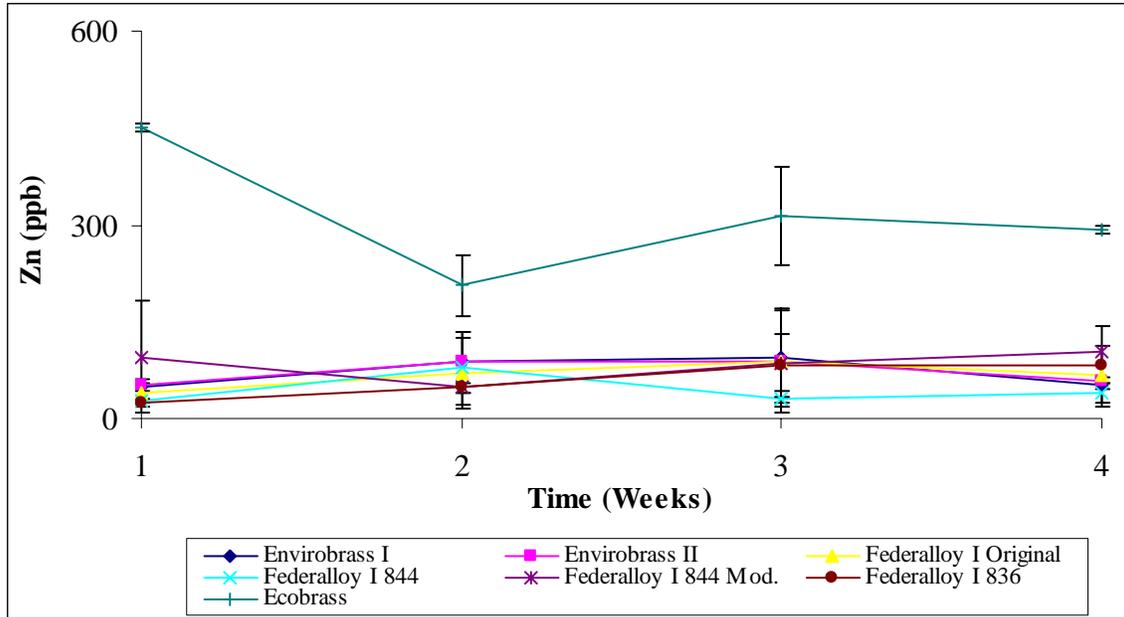


Figure A-4: Zinc leaching for the non-leaded brasses, when exposed to the standard section 9 test water. The error bars represent 95 percent confidence intervals.

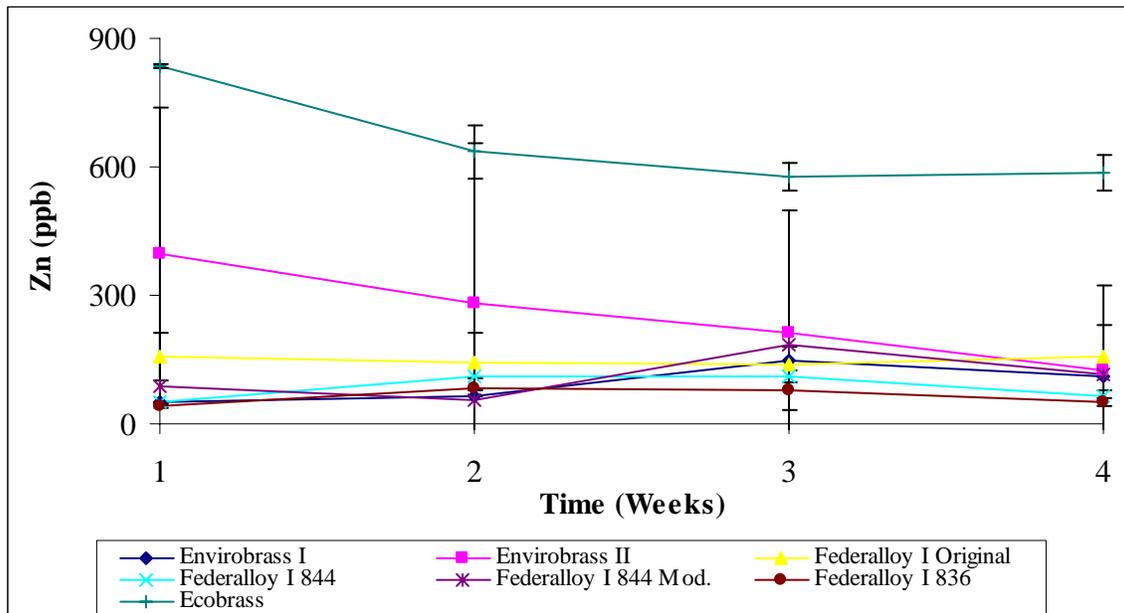


Figure A-5: Zinc leaching for the non-leaded brasses, when exposed to the low pH, low alkalinity, chloraminated water. The error bars represent 95 percent confidence intervals.



Figure A-6: Untested Envirobrass II coupon (far left). After exposure to standard Section 9 test water (middle). After exposure to low alkalinity, low pH, chloraminated water (far right).



Figure A-7: Untested Federalloy I Original coupon (far left). After exposure to standard Section 9 test water (middle). After exposure to low alkalinity, low pH, chloraminated water (far right).



Figure A-8: Untested Ecobrass coupon (far left). After exposure to standard Section 9 test water (middle). After exposure to low alkalinity, low pH, chloraminated water (far right).

CONCLUSIONS

The leaching potential of seven non-leaded brasses which are currently commercially available was evaluated in this laboratory study. Lead release from all non-leaded coupons was below 1 ppb throughout the 4 weeks of testing. Bismuth, selenium and antimony were below detection limits. Zinc release into the water tended to depend upon the zinc content of each alloy and copper was below the action limit. Based on these preliminary results, in terms of leaching and contamination concerns, non-leaded alloys provide an attractive alternative for fabrication of drinking water components. Nonetheless, further understanding of their leaching characteristics is needed.

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- The Copper Development Association for providing the 2 percent leaded brass samples

CHAPTER TWO

A CRITICAL EVALUATION OF THE NSF STANDARD 61/ SECTION 9 TEST WATER

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ABSTRACT. The ANSI/NSF Standard 61/ Section 9 protocol is critically evaluated from the perspective of test water chemistry and lead leaching propensity. Overall, the test water is roughly representative of a typical water supply. However, some lower pH and lower alkalinity, chloraminated waters can be more aggressive than the existing section 9 water, especially at longer exposure times, which might cause problems with first draw compliance for lead even for products that are section 9 certified. For public water supplies, the aggressiveness of the lower pH and lower alkalinity waters is often countered by addition of orthophosphate corrosion inhibitors. However, Section 9 devices are also recommended for use in the approximately 16% of private water supplies and cistern-type systems, which can include waters that are much more aggressive than tested herein. To account for these issues, it is recommended to tighten the Section 9 pass/fail criterion, and to add product information about limitations in corrosivity of the products relative to private water supplies.

KEYWORDS: ANSI/NSF 61 Section 9, brass, lead leaching

INTRODUCTION

ANSI/NSF Standard 61 was developed in order to “*establish minimum requirements for the control of potential adverse human health effects from products that contact drinking water*” (NSF, 2001). It was intended for use by utilities, regulatory agencies, and/or manufacturers as a basis of providing assurances to consumers that adequate health protection exists for certified products.

Section 9 of NSF 61 Standard is aimed at protecting the public from harmful levels of contaminants derived from plumbing devices installed in the last one liter of water volume in plumbing systems. These plumbing materials are termed “end-point” devices and can include kitchen faucets, stop valves, and drinking water fountains. The one liter demarcation is of particular interest, because this is the volume of water collected after an overnight stagnation under the United States Environmental Protection Agency (US EPA) lead and copper rule (LCR). Plumbing components covered in Section 9 are those that might contact the water collected during stagnation in the LCR and the Lead Contamination Control Act (LCCA) to determine compliance with lead standards for potable water. Any leaching of lead (or copper) from endpoint devices can strongly impact compliance with these regulations.

Lead, amongst other contaminants that are considered in the NSF 61 standard, poses great concern due to increasing evidence of harm from low-level lead exposure. Lead and copper are also the only contaminants which have drinking water standards determined at the tap after overnight stagnation. Moreover, lead leached from brass to first draw water samples collected under the LCR and LCCA is often considered a significant cause for action level and LCCA exceedences. There is anecdotal evidence that in at least some rare cases, new devices passing Section 9 can still leach lead to potable water at concentrations above the standards of 20 ppb Pb for the LCCA (200 mL sample first draw) and 15 ppb Pb for the LCR (1 liter first draw). This work examines possible reasons why the section 9 test might be failing to perform as expected in some of these situations.

The evaluation of products covered by Section 9 requires their exposure to one synthetic extraction water under a specified protocol, followed by statistical analysis of the lead leaching results which allows “safe” products to pass the test and be certified (Figure 2-1). Products above the standard pose a potential public health or regulatory concern and do not get the certification. The corrosivity of the test water is of obvious concern, since some waters have a high propensity to leach lead from end-point devices and other waters have a low propensity to leach lead. If devices were to be tested in a water that had a low propensity to leach lead, the values might be lower than those which would occur in real waters, and the test would not be protective of public health.



Figure 2-1: Certification label for end-point devices passing the Section 9 protocol (NSF, 2006)

When examining the test water chemistry used for Section 9 certification, the relatively high alkalinity, high pH and free chlorine level are of concern due to their influence on lead leaching propensity. Specifically, the test water has high alkalinity of 500 mg/L (\pm 25 mg/L) as CaCO_3 , a relatively high pH of 8.0 (\pm 0.5) and free chlorine at a concentration of 2.0 mg/L (\pm 0.05 mg/L). Due to the addition of hydrochloric acid (HCl) for pH adjustment, the extraction water also contains chloride (Cl^-) at an estimated concentration of about 3.5 mg/L. The source of the high alkalinity is sodium bicarbonate, which adds dissolved inorganic carbon (DIC) at a concentration of 120 mg/L (\pm 5.0 mg/L).

In a practical study of 90%’ile lead levels at about 400 large US water utilities, Dodrill and Edwards (1995) found that waters with alkalinity above 174 mg/L and pH above 7.81 had a 0% frequency of exceeding the lead action limit (Figure 2-2). This is consistent with known benefits of higher pH and higher alkalinity (or DIC) in reducing lead leaching propensity (Schock, 1989). The highest alkalinity for utilities in the Dodrill study was 433 mg/L as CaCO_3 (median alkalinity was 60 mg/L as CaCO_3). Therefore,

use of a test water with 500 mg/L alkalinity at pH 8.0 in the Section 9 testing is not representative of aggressive conditions encountered in practice. For example, the Dodrill study found that waters of pH 7.4-7.8 and alkalinity below 30 mg/L had a 65% likelihood of exceeding the 15 ppb lead action limit (Figure 2-2).

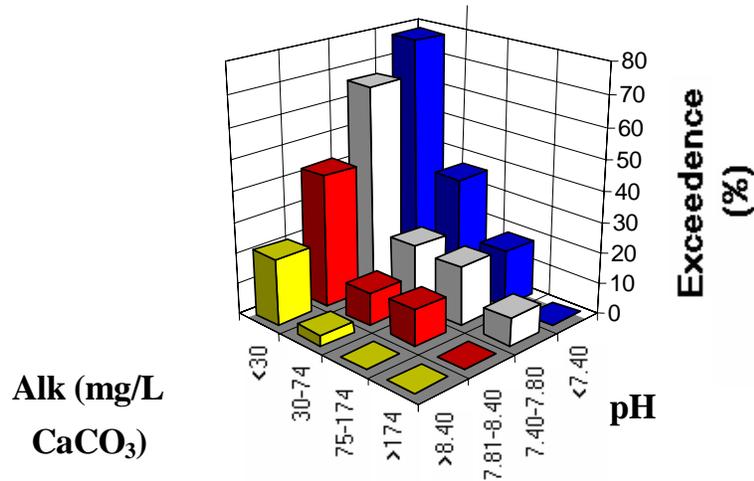


Figure 2-2: Percentage exceedence of the action level for lead, as a function of pH and alkalinity for utilities without phosphate inhibitors. Data gathered from large utilities under the initial sampling round for EPA’s Lead and Copper Rule. After Dodrill and Edwards (1995)

The importance of pH on lead release from brass was also emphasized upon in other studies. An in-depth laboratory investigation of several brass types with varying lead content determined that lowering the water pH from 8.5 to 7.0 always increased lead leaching, in some cases to as much as 100 ppb more (Lytle and Schock, 1996). That study also assessed the effect of orthophosphate on lead leaching from brass and concluded that when the inhibitor was dosed at 3.0 mg/L it caused lead levels to drop rapidly and stabilize for all brass types tested (Lytle and Schock, 1996).

Recent work (Dudi, 2005) has also heightened concern regarding other factors that might increase lead leaching. Specifically, chloramine is often slightly more aggressive in relation to lead leaching from brass than chlorine (e.g., about 15% higher lead), and chloramines can cause much more lead leaching from certain types of brass. It was recently suggested that the presence of fluoride and chloramine was a particularly aggressive combination for lead leaching from brass (Allegood, 2005). Galvanic connections between copper and brass were also demonstrated to increase lead leaching from brass in some cases. In addition, recent studies by Korshin *et al.* (2000) demonstrated that the presence of natural organic matter (NOM) in water can increase lead leaching from the surface of leaded brass, over both the short and long-term. But other studies with NOM have shown the opposite effect. The Section 9 water does not contain any NOM, fluoride or chloramines (instead it contains chlorine). Likewise, galvanic connection of the products to copper is not required in the NSF Section 9 test protocol.

In terms of other possible factors that might influence the difference in aggressiveness of real waters versus the Section 9 test water, the Cl^- level and the $\text{Cl}^-:\text{SO}_4^{-2}$ ratio might also be important. The effect of chloride has been studied with respect to the dezincification of brass, a typical form of brass corrosion. When the chloride concentration is high, dezincification can more readily occur under some conditions (Lytle and Shock, 1996). Dezincification is sometimes correlated to lead dissolution from the brass surface (Kimbrough 2001, USEPA 1993, Mariñas *et al.*, 1993). The ratio of $\text{Cl}^-:\text{SO}_4^{-2}$ also plays a poorly understood role in lead leaching (Edwards *et al.*, 1999). In general, higher $\text{Cl}^-:\text{SO}_4^{-2}$ ratio can increase difficulties in meeting the EPA Lead and Copper Rule Action limit. Dudi (2005) demonstrated that increasing the $\text{Cl}^-:\text{SO}_4^{-2}$ ratio causes increased corrosion and lead leaching from galvanically connected lead bearing materials and copper. The NSF water has Cl^- levels that are about 90% lower than terrestrial waters in the US (Davies and DeWiest, 1966) and the chloride to sulfate ratio is infinite. These factors might also play a role in either increasing or decreasing lead leaching from brass in the test.

The goal of this research was to examine leaching of lead from one common type of brass under a range of circumstances, in an attempt to isolate key factors that might be desirable in a standardized test to make it more representative of aggressive conditions that can be encountered in practice. Other work examined other types of brass and the role of phosphate inhibitors.

MATERIALS AND METHODS

Evaluation of the leaching solution for C36000 Brass. One of the most common types of brass used in faucets is C36000 (60% Cu, 3% Pb, 37% Zn). In this test small C36000 coupons were exposed to the Section 9 test water, as well as to eight modifications of that water. With exceptions that are detailed below, all tests were performed following Section 9 procedures, with metals leaching evaluated over the 19-day test.

Machined brass rods of 0.64 cm (0.25 in) diameter and 0.97 cm (0.38 in) height were epoxied to the bottom of a 46 mL glass vial. This vial was filled all the way to the top with test water and air was excluded. For testing of galvanic connections between brass and copper, the small brass sample was connected to the inside surface area of a copper pipe using lead-free solder. The bottom of the brass in this case was covered with epoxy, as occurred in the case without the connection to copper pipe. The C36000 brass samples were in an “as extruded” form and were provided by the Copper Development Association (CDA).

The brass surface area to water volume ratio achieved was $8.0 \times 10^{-3} \text{ in}^2/\text{mL}$ in the case of the samples not galvanically connected to copper. This ratio is at the lower end of those typically encountered in NSF testing, assuming $\frac{3}{4} \text{ in}^2$ surface area is typical for a brass faucet (Weed, 2005) and that a typical brass faucet can hold a water volume of 100 mL (Gardels and Sorg, 1989). The exposed surface area to volume ratio was decreased by only about 15% in the case of galvanic connections to the copper, due to the solder used

to attach the brass coupon to the copper pipe. A lower surface area to volume ratio would tend to decrease the final concentration of lead in the water.

The nine different test water chemistries were as follows:

- A) NSF Section 9 test water. This water has high alkalinity of 500 mg/L (\pm 25 mg/L) as CaCO₃, pH of 8.0 (\pm 0.5) and free chlorine dosed at a concentration of 2.0 mg/L (\pm 0.05 mg/L).
- B) NSF Section 9 test water modified with 0.5 mg/L natural organic matter. The NOM is reference Suwannee River material obtained from the International Humic Substance Society.
- C) NSF Section 9 test water with 4.0 mg/L chloramine (Mass ratio Cl₂:NH₃ of 4:1) instead of chlorine.
- D) NSF Section 9 test water with 4.0 mg/L chloramine and 1 mg/L fluoride added as NaF.
- E) NSF Section 9 test water with a solder connection to a small piece of 1/2" copper tube.
- F) NSF Section 9 test water but with lower alkalinity of 10 mg/L as CaCO₃ and pH of about 7.4.
- G) NSF Section 9 test water with additional 30 mg/L chloride added as NaCl.
- H) Water with the galvanic connection and all modifications from B to G.
This condition examined the cumulative result of all modifications.
- I) Real Blacksburg tap water, which is considered non-aggressive.

In addition, control conditions were run, including 1) Epoxy control (a drop of epoxy glued to the bottom of the glass vial without the brass), and 2) Galvanic Control (copper with the solder inside the glass vial but without the brass).

The brass samples were exposed to the different water chemistries following the Section 9 test protocol. That is, they were exposed for 19 days using a static "fill and dump" procedure. Water samples were collected after 16-hour dwell times on days 3, 4, 5, 10, 11, 12, 17, 18 and 19 and analyzed for metals. Lead, zinc and copper dissolution were quantified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Each test was conducted in triplicate to support statistical analysis of the results. With the 9 different water conditions and 2 sets of controls, 33 tests were conducted for the C36000 brass.

Evaluation of the Leaching Solution for Brasses of Different Lead Content and Using Different Inhibitors. Evaluation of tests from the preceding section raised new questions that were addressed in a separate phase of experiments. Three brass types with

a lead content of 2% (C35300), 3% (C36000) and 5% (C83600) were tested, using the same general procedures as in part 1 for a limited range of waters.

In addition, galvanic samples were prepared by physically squeezing brass into a hole machined in the side of a copper tube, thereby eliminating the need for solder.

The experimental conditions tested in part 2 are as follows:

- A) NSF Section 9 test water, with high alkalinity of 500 mg/L (± 25 mg/L) as CaCO_3 , pH of 8.0 (± 0.5) and free chlorine dosed at a concentration of 2.0 mg/L
- B) Synthetic water with lower alkalinity of 10 mg/L as CaCO_3 , lower pH of about 7.4 and monochloramine instead of chlorine dosed at a concentration of 2.0 mg/L (± 0.05 mg/L)
- C) Water B but with 3.0 mg/L PO_4^{-3}
- D) Water C but with added zinc at 0.5 mg/L Zn^{+2}

Exposure of the brasses to water was via a static “fill and dump” protocol three times per week (Monday/Wednesday/Friday), for four weeks. The water from each test condition was collected every Friday, after a 48-hour dwell time, and the sample was analyzed for metals. Even though the exact exposure protocol of Section 9 was not followed in part 2, the results of this analysis allow for drawing conclusions about the Section 9 water’s aggressiveness, as it is compared head to head with other water chemistries and under similar exposure conditions. All glass vials were kept out of light throughout the testing period and each test was performed in triplicate. Metals analysis was performed via Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

RESULTS

Evaluation of the leaching solution for C36000 Brass. Lead dissolution was much higher for the low alkalinity-low pH water compared to the standard Section 9 water. Though absolute levels should be viewed with caution due to the very low surface area to volume ratio, the levels in the low alkalinity and low pH water were above the LCR Action Level of 15 ppb for most of the exposure period (Figure 2-3). Moreover, lead leaching was on an uptrend with time in this more aggressive water, contrary to the trend observed for the other conditions. For the condition at low alkalinity, zinc dissolution was also significantly higher compared to the standard extraction water (Figure 2-4). The brass sample that was exposed to the low alkalinity water became more red in color by the end of the 19-day testing (Figure 2-5), consistent with higher dezincification.

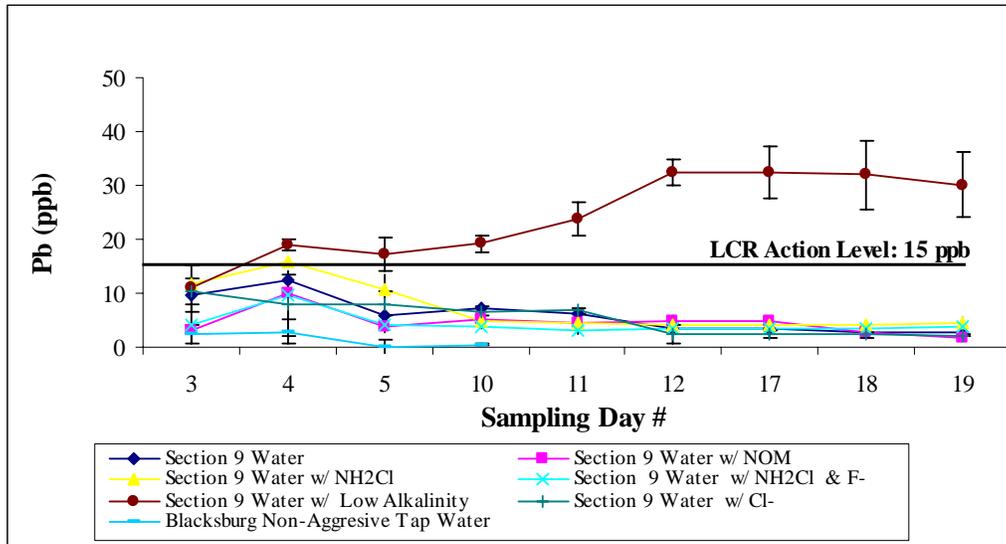


Figure 2-3: Lead dissolution following the standard Section 9 sampling protocol, for the non-galvanic samples. The error bars denote 95% confidence intervals.

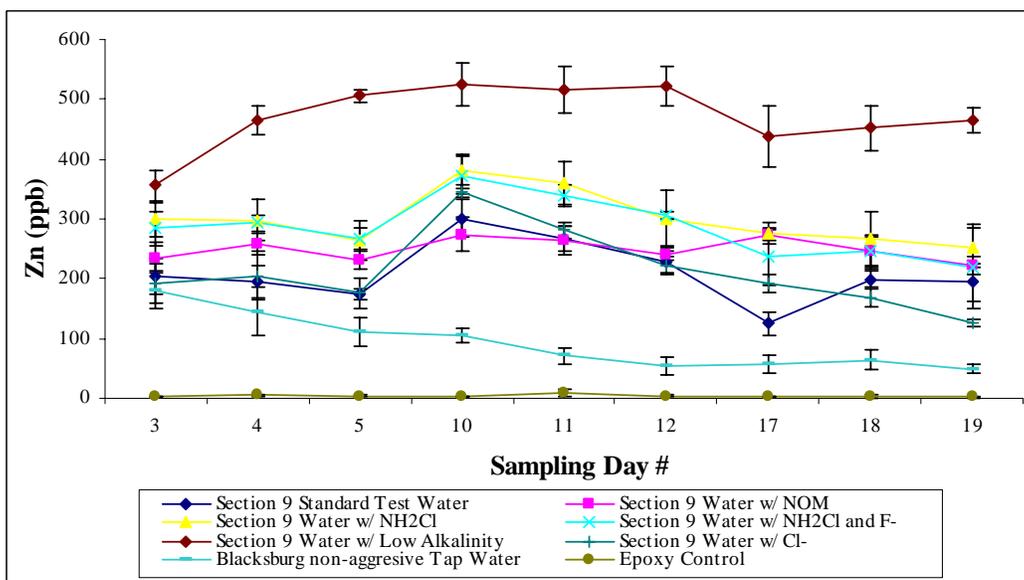


Figure 2-4: Zinc dissolution for the non-galvanic samples. The error bars denote 95% confidence intervals.

Although no primary (health-based) MCL exists for zinc in drinking water, higher zinc could be indicative of general brass corrosion and is also partly responsible for higher lead. That is, as the zinc in the alloy dissolves, more of the trace lead in the alloy is likely to dissolve or detach to the water. Kimbrough (2001) and various researchers (US EPA, 1993) also suggest that lead is mobilized along with zinc during the dezincification process, and that lead leaching might be reduced if dezincification is controlled.

In the case of the low alkalinity-low pH water, copper released to the water from brass was low, and at the same time zinc and lead released were the highest (Figure 2-3, 2-4, 2-6). The reddish color of the low alkalinity-low pH brass coupon due to enrichment of

copper in the brass as zinc and lead were selectively leached out (Figure 2-5) is also characteristic of dezincification.



Figure 2-5: New brass coupon (far left). After exposure to low alkalinity water (middle). After exposure to standard section 9 test water and also typical of all other synthetic water conditions examined (right).

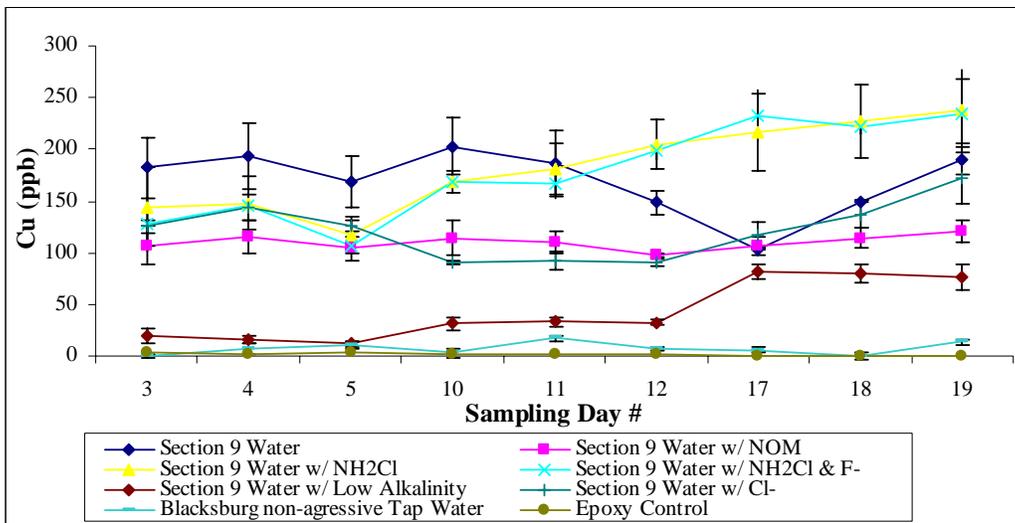


Figure 2-6: Copper dissolution for the non-galvanic samples. The error bars denote 95% confidence intervals.

At first glance, lead dissolution was either not significantly different, or was even lower, for all other water conditions examined (besides the low alkalinity-low pH case), compared to the standard extraction water (Figure 2-3). However, by pooling the 17, 18, and 19-day data for lead for each test condition and applying a t-test at 95% confidence, statistical comparisons can be made (Figure 2-7). The addition of NOM did not make a significant difference in lead leaching at 95% confidence. However, the presence of chloramine instead of chlorine in the water resulted in a 48% increase in lead. The combined effect of chloramine and fluoride was a 19% increase versus the standard water, although this difference was not significant at 95% confidence. If anything, addition of fluoride tended to decrease lead leaching in this particular instance, since the combination of chloramine and fluoride leached 29% less lead than did chloramine alone. Chloride addition to the standard water decreased lead leaching by about 20%. The highly non-aggressive tap water from Blacksburg, VA leached 80% less lead than the section 9 water (Figure 2-7).

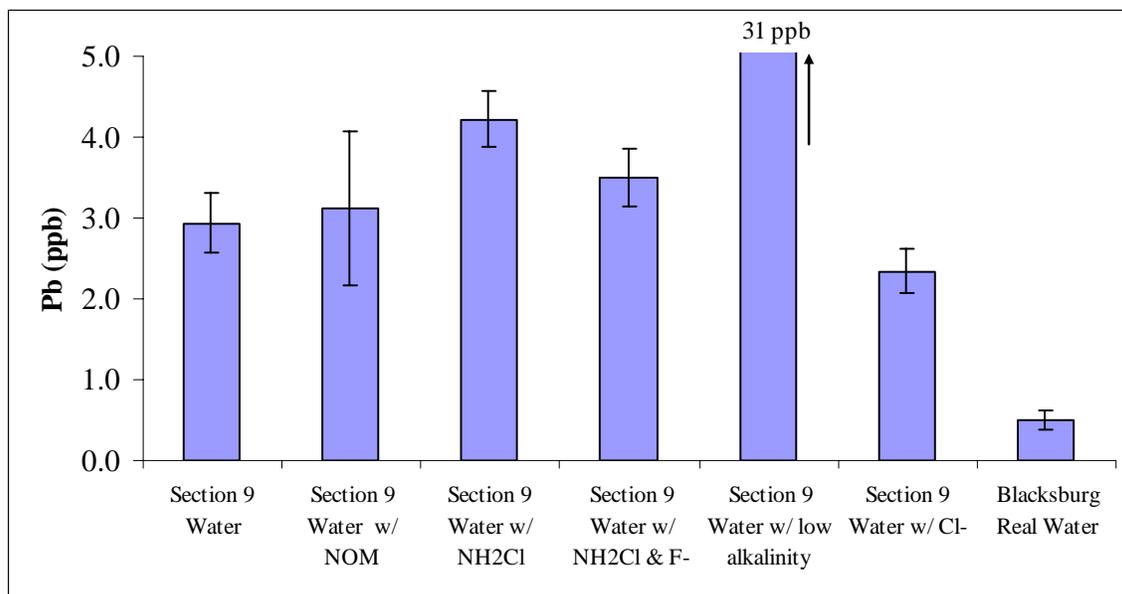


Figure 2-7: Average lead from samples of days 17, 18 and 19 and for the non-galvanic cases. The error bars denote 95% confidence intervals.

For all conditions examined, the copper leached to the water was significantly lower than the LCR Action Level of 1,300 ppb for the non-galvanic samples (Figure 2-6). For the galvanic connections, the copper leached in the standard section 9 condition, was higher and close to that level (Figure 2-8). It is uncertain whether most of the copper came from the brass or from the copper pipe.

The non-aggressive real tap water using a zinc orthophosphate inhibitor leached much lower lead, copper and zinc compared to the section 9 test water (Figure 2-3, 2-4, 2-6 and 2-7). While there are many other differences between the real water and the section 9 water, it is possible that the presence of a zinc orthophosphate inhibitor has a dominant effect. Nationally, about 56% of public water utilities currently add phosphate-based corrosion inhibitors to counter the corrosivity of water (McNeill and Edwards, 2002).

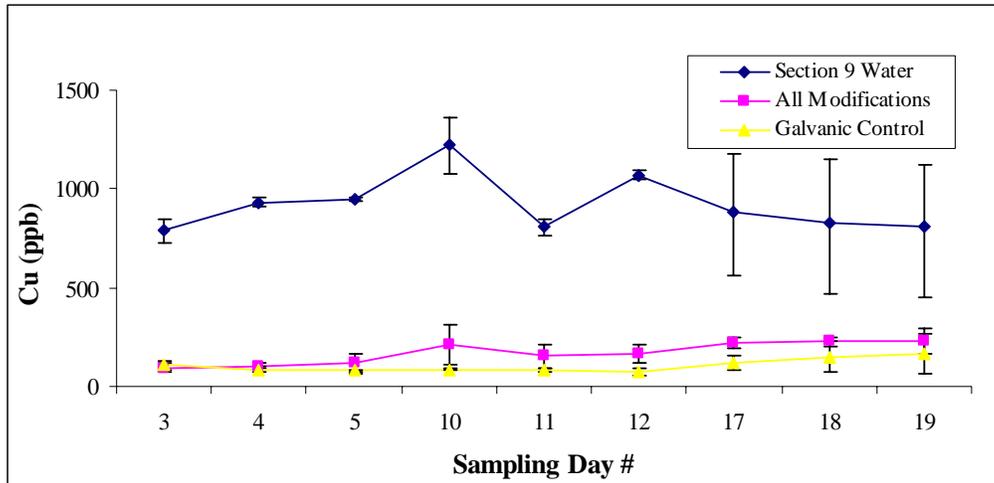


Figure 2-8: Copper dissolution for the galvanic samples. The error bars denote 95% confidence intervals.

Surprisingly, the samples in which brass was galvanically connected to copper were either not significantly different or even lower in lead leaching, relative to the same sample without galvanic connection (Figure 2-3, 2-9). The galvanic samples also had high variability of results between triplicates for the same water condition. The lower lead using a galvanic connection was surprising, since earlier work by Dudi (2005) demonstrated that galvanic connections to copper tended to increase lead leaching, which is expected given that brass is typically anodic to copper. One tentative important difference between this study and that of Dudi (2005), is that this work used a 95% tin and 5% antimony solder to attach the brass to the copper pipe. It is possible that the small amount of tin solder used to connect the copper to the brass may have been a major influence. Tin is anodic to both copper and brass, and if it were sacrificed, it would reduce corrosion of both copper and brass. In some cases the water in the test vials was white with a solid (Figure 2-10) and there were very high concentrations of tin detected by ICP-MS. This supports the idea that tin solder was being sacrificed. The amount of white solid in the water was highly variable, depending on the test water chemistry.

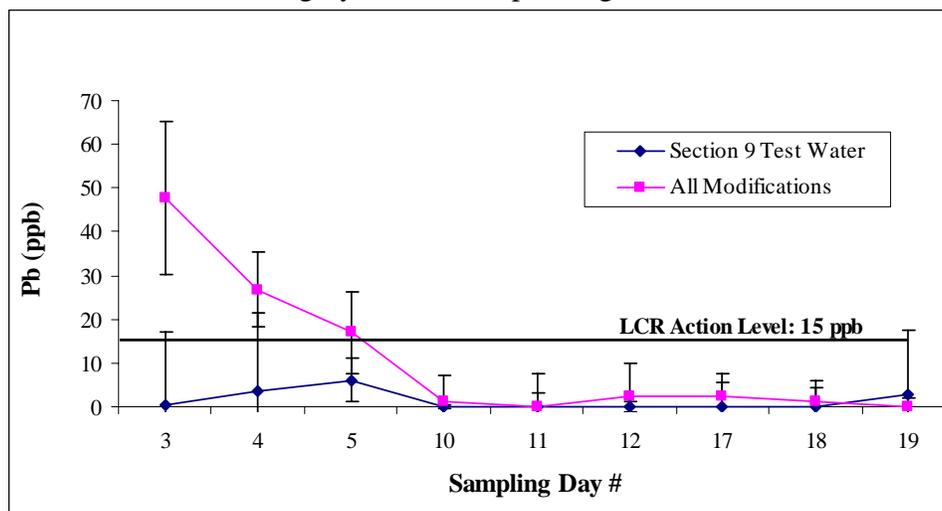


Figure 2-9: Lead dissolution for the galvanic samples. The error bars denote 95% confidence intervals.

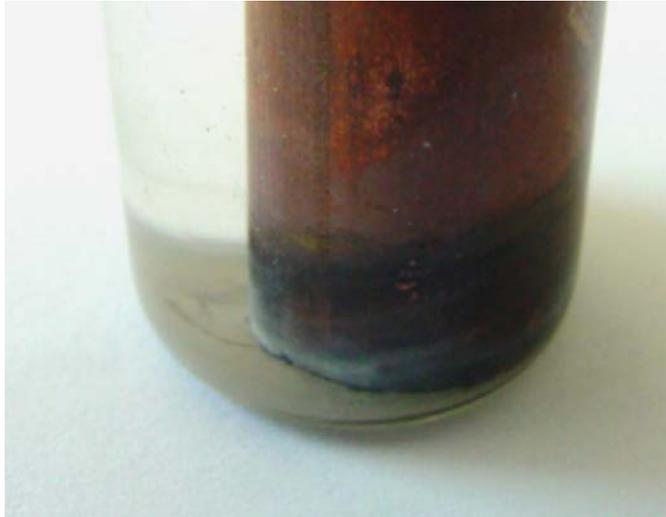


Figure 2-10: Galvanic sample in “all modifications” water (case H). A white precipitate is present at the bottom of the vial, which might be tin. The white precipitate was not present in the galvanic samples exposed to the standard section 9 test water (case E).

Effect of Brass Lead Content and Inhibitors. The tests aiming at understanding the role of lead content and inhibitors involved changing the water 3 times per week and used a 48 hour stagnation event before quantifying metals. Using this modified protocol, the lower pH, lower alkalinity chloraminated water was still more aggressive than the Section 9 water by a factor of about 2 times at the end of a 4 week exposure period (Figure 2-11). This difference was not as large as was observed for the same brass type during the earlier test rounds, due to the modified sampling protocol followed here compared to the standard section 9 protocol followed in the earlier rounds.

Addition of orthophosphate at a concentration of 3.0 mg/L to that water, was able to counter the negative effects of low alkalinity, low pH and chloramines, consistent with the observations of others (e.g. Lytle and Schock, 1996). Addition of zinc orthophosphate was also effective in reducing lead leaching (Figure 2-11). In fact, by the fourth week of the experiment, ortho-P reduced lead leaching by a factor of almost 70 times, and zinc ortho-P by a factor of 40 times for the 3% leaded brass (Figure 2-11).

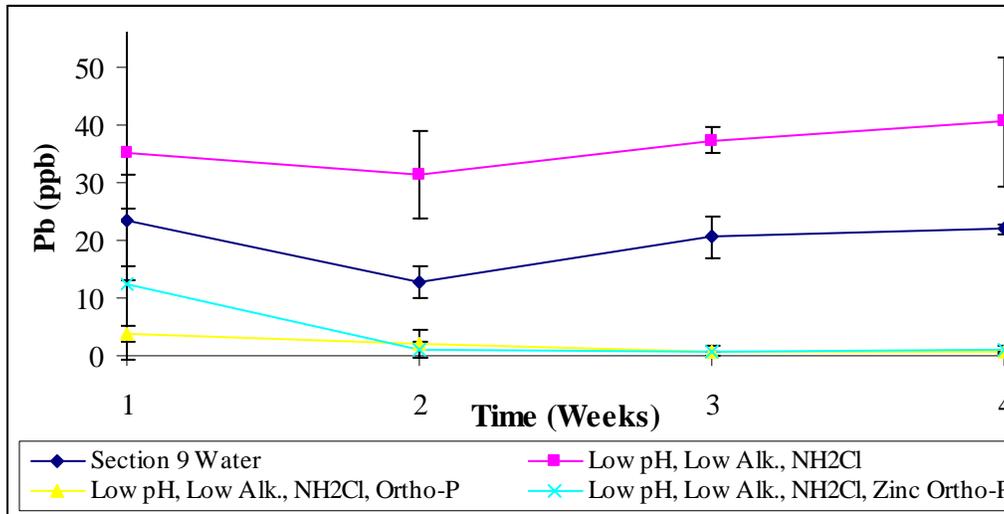


Figure 2-11: Lead release versus time for the 3% leaded brass non-galvanic samples. The error bars denote 95% confidence intervals.

The brass alloy with the highest lead content (5%), released the highest amount of lead to the water. The 3% leaded alloy was the second most likely to leach lead and the 2% alloy was least likely (Figure 2-12). This confirms the common sense notion that the amount of lead leached from brass alloys is often dependent on the percentage of lead in the alloy, even in short-term experiments. For all three brass types, addition of orthophosphate to the water, alone or combined with zinc, significantly reduced lead leaching (Figure 2-12). Use of orthophosphate did not alter the relative leaching propensity of the brass based on lead content.

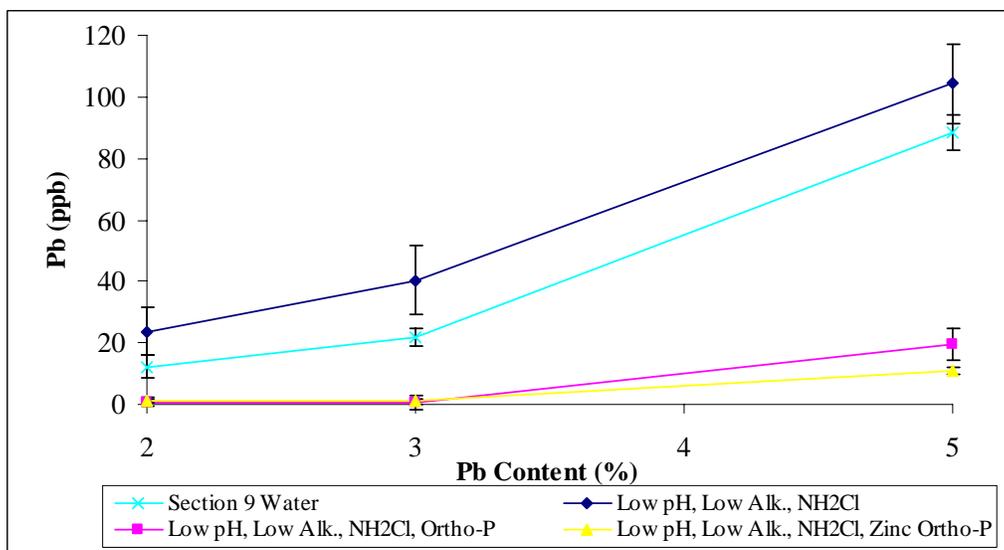


Figure 2-12: Lead release versus lead content of brass, for the non-galvanic samples and after four weeks of exposure to the different waters. The error bars denote 95% confidence intervals.

Visual observations of the coupons after exposure to the different waters verified that addition of zinc and/or orthophosphate to the aggressive water inhibited corrosion. In the case of exposure to the aggressive water without a corrosion inhibitor, the coupon turned red (Figure 2-13, middle), consistent with higher dezincification, as was also observed in part 1 of this study. When zinc and/or orthophosphate was added to that water however, the brass surface was visually less corroded (Figure 2-13, right) compared to the reddish coupon, instead it looked more similar to a new coupon surface, prior to exposure (Figure 2-13, far left).



Figure 2-13: 3% leaded brass coupon new (far left), after exposure to Section 9 test water, after exposure to “aggressive” water (middle), after exposure to aggressive water with ortho-P, and after exposure to aggressive water with zinc ortho-P (far right).

When evaluating the effect of the galvanic connection on lead release from brass, the results were again surprising. Brass would be expected to be anodic compared to copper and therefore should be sacrificed (i.e. corroded) if a connection between the two metals was established, resulting in increased lead leaching to water. While this was sometimes observed in the initial samples, at times thereafter lead leached from the brass as if it were cathodic to copper, since lead release was reduced by connection to copper pipe (Figure 2-14, 2-15). As visual support for this observation, in the cases where lead leaching was decreased by connection to copper, the copper was rapidly covered with a greenish colored scale, suggesting that the copper might be sacrificed instead of the brass (Figure 2-14 matches Figure 2-16 left, and Figure 2-15 matches Figure 2-16 right). The magnitude of the decrease in lead leaching and the possible reversal of the brass from anode to cathode is highly deserving of future study.

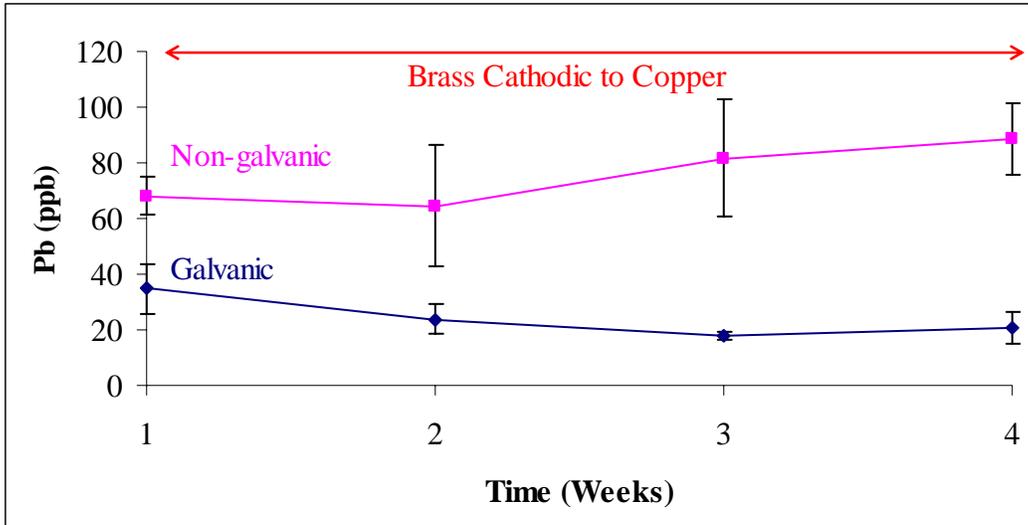


Figure 2-14: Lead release versus time for the 5% leaded brass, exposed to the Section 9 test water. Comparison between galvanic and non-galvanic connections to copper tube. The error bars denote 95% confidence intervals.

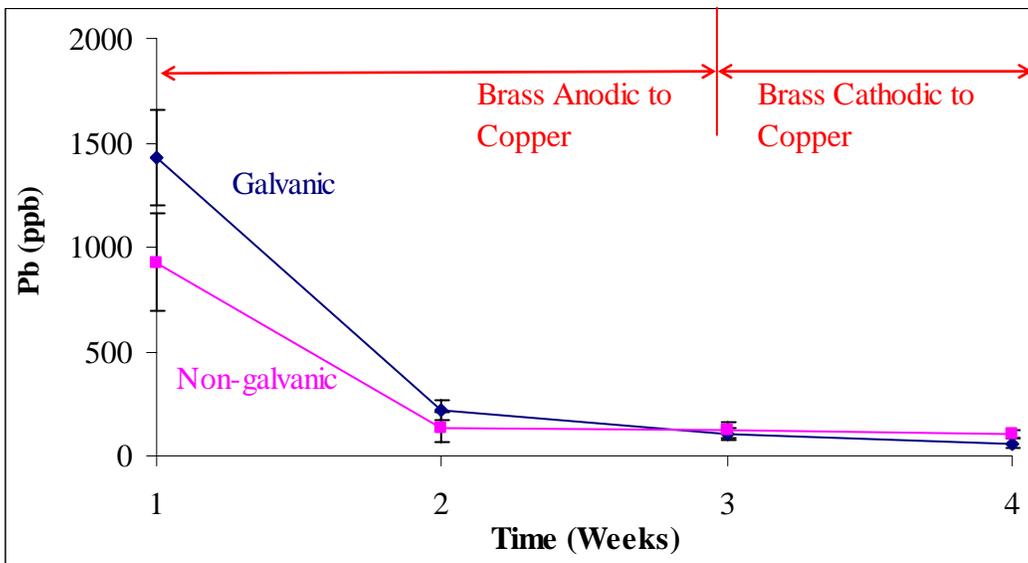


Figure 2-15: Lead release versus time for the 5% leaded brass, exposed to the low pH, low alkalinity, chloraminated water. Comparison between galvanic and non-galvanic connections to copper tube. The error bars denote 95% confidence intervals.



Figure 2-16: Galvanic sample of 5% leaded brass, after exposure to the section 9 water (left), and after exposure to the low pH low alkalinity, chloraminated water (right).

DISCUSSION

The results indicate that the Section 9 water is less aggressive than many drinking waters. This difference is expected to become more important at longer exposure times, since lead leaching from the Section 9 waters passivates quickly, whereas lead leaching is sustained or can even increase in waters that support dezincification. The relatively low leaching propensity of the Section 9 water could therefore explain how certain certified Section 9 devices are sometimes leaching high lead to drinking water.

For public water supplies, the discrepancy is likely to be problematic in a minority of households, because of widespread use of phosphate corrosion inhibitors in low alkalinity and lower pH waters. However, about 16% of US households do not use water from public supplies, but rely on well water or other surface water (USEPA, 2006). In addition, cistern water is highly aggressive to lead as it has relatively low pH and low alkalinity (e.g., pH 5.4 and alkalinity of 0), and studies of water quality in rainwater indicate that lead is high (Yaziz, 1988). Section 9 devices can be used in these unusual applications as well (NSF, 2006), and might be expected to leach harmful levels of lead in some situations.

The pass/fail criterion for Section 9 is currently set at a Q statistic of 11 ppb lead. Allowing 11 ppb as a passing threshold for a relatively non-aggressive water in the Section 9 test seems unacceptable. Concerns about lead leaching in public water supplies could be addressed by applying an additional safety factor to the pass/fail criterion. For unusual situations that are likely to be encountered frequently in non-public water

supplies, educational materials should be available highlighting concerns about lead leaching and the desirability of using plumbing system components without lead.

CONCLUSIONS

Based on both parts of this study:

- The NSF Section 9 water is roughly representative of a typical water supply, but some other waters encountered in practice may be more corrosive, in terms of lead release from end-point plumbing devices
- Of the factors present in real waters that might cause increased lead leaching relative to the Section 9 water, lower pH and lower alkalinity are deemed the most important. Use of chloramine also increased lead leaching from one type of brass by 40% versus chlorine, whereas fluoride tended to decrease lead leaching
- Most public utilities with low pH and low alkalinity water supplies counter the water corrosivity by addition of orthophosphate inhibitors. However, Section 9 devices are also recommended for use in the approximately 16% of private water supplies and cistern-type systems, which can include waters that are much more aggressive than the synthetic water used in the Section 9 certification protocol
- It is recommended to tighten the Section 9 pass/fail criterion, which is currently set to a Q statistic of 11 ppb, by a safety factor in order to account for reasonable ranges in corrosivity of real waters, compared to the synthetic test water
- When brass is galvanically connected to copper, it is sometimes cathodic to copper and sometimes anodic. This depends on the alloy and the water chemistry and has major implications for lead leaching in practice as cathodic brass would tend to be protected from corrosion, whereas anodic brass would leach much higher lead to the water
- Lead release was found to be dependent on the lead content of the alloy, for the three brass alloys tested in this study

ACKNOWLEDGEMENTS

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CHAPTER THREE

PARTICULATE LEAD IN DRINKING WATER

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ABSTRACT

The occurrence of particulate lead in drinking water deserves increased scrutiny since human exposure models, sampling protocols, analytical methods and environmental assessments are often based on the presumed dominance of soluble lead in drinking water. Recent cases of childhood lead poisoning from drinking water were tied to solder particles detaching into and contaminating the water supply--it is argued that similar cases could be occurring elsewhere but are not being detected with existing protocols. Specifically, approved sample handling procedures can “miss” particulate lead that is present in samples, leading to situations in which the actual lead present in drinking water is at least five times higher than obtained with approved protocols. The presence of chloride, warmer temperatures and lower pH of the stomach render a large fraction of this particulate lead bioavailable when ingested. The net result is that undetected lead can be bioavailable.

KEYWORDS: particulate lead, sampling protocol, bioavailability

INTRODUCTION

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

Recent events have highlighted disturbing instances where childhood lead poisoning was belatedly tied to lead in drinking water. Specifically, instances of lead poisoning in Greenville, North Carolina were tied to elevated particulate lead in water after a year passed, in which no other sources could be identified (Allegood, 2005; Bachelor,

2005). In several instances in Washington DC in 2003, it also took nearly a year of investigations until tap water was considered a possible source for children's elevated blood lead (Copeland, 2004; Renner, 2006). In all of these cases blood lead continued to rise while authorities focused on lead paint, dust and other possible sources such as toys. After North Carolina passed a policy requiring sampling of the drinking water in cases of childhood lead poisoning, another case was detected in Durham, NC (Gronberg, 2006). Durham was in compliance with the EPA LCR.

Routine sampling under the Lead and Copper Rule involves homeowners, and as a result, samples are typically collected in plastic bottles without acidification. After sitting for an unspecified time in the bottle unacidified, the water is later reduced to pH < 2.0 in the laboratory by addition of 0.15 percent nitric acid (v/v) (Figure 3-1). A minimum holding time of 16 hours is required from the time of acidification, at which point samples can then be analyzed for lead. Only water samples having turbidity > 1 ntu must be subjected to an additional heated-acid-digestion step, to assure that particulate lead (and copper) completely dissolve (US EPA, 1994; Lytle *et al.*, 1993).

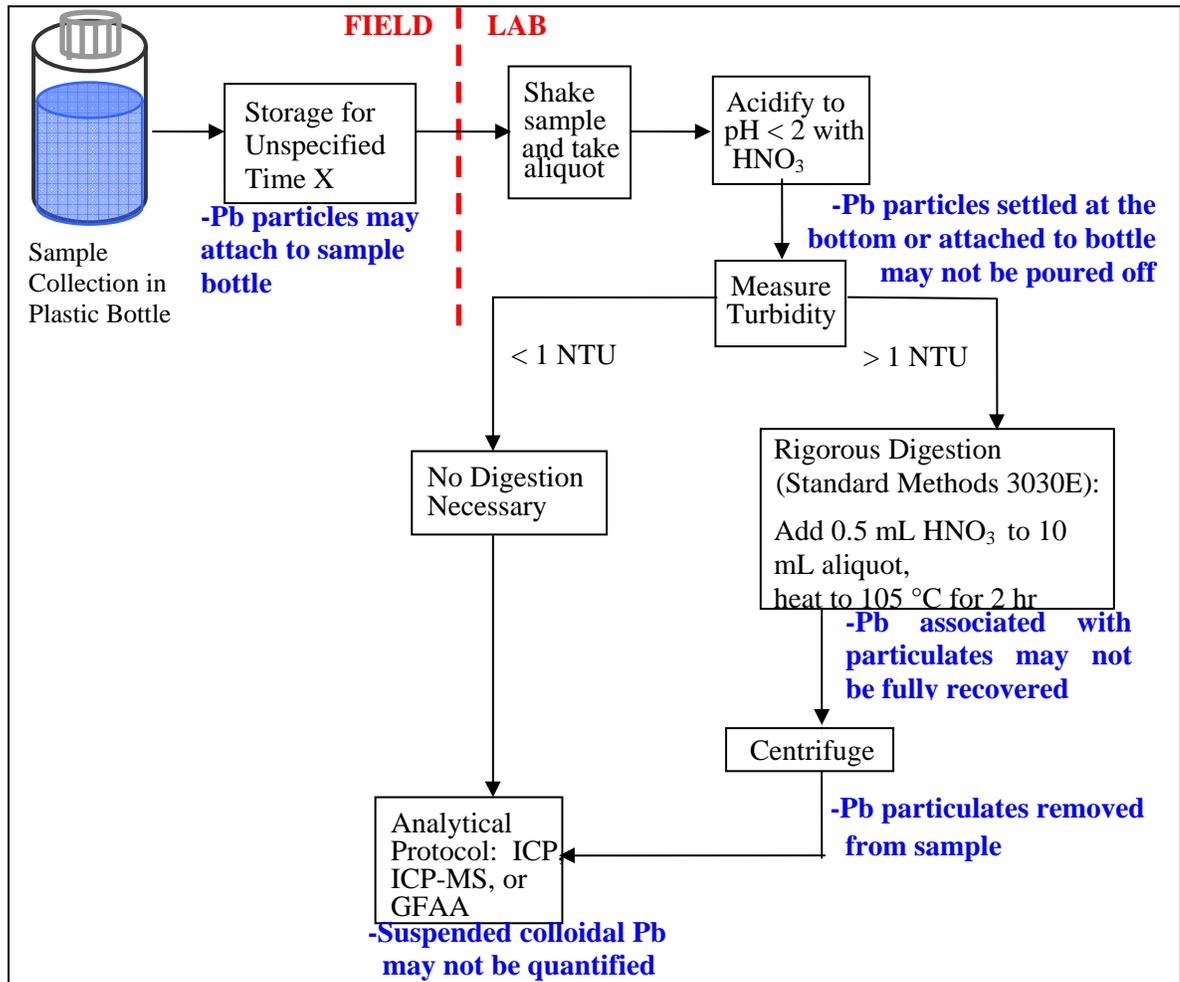


Figure 3-1: EPA Sampling Protocol for Total Lead and Potential Problems. (Modified from Parks *et al.*, 2004)

Parks *et al.* (2004) highlighted how this protocol could miss up to 100% of the particulate Cr (III) that was actually present in potable waters. Several obvious problems were caused by particulates settling in the bottle and attaching to plasticware—these attached particles do not contribute to measured turbidity. Indeed, field samples that originally contained high turbidity often measured less than 1 ntu when measured in the laboratory after storage and did not require full digestion. Moreover, even if a full digestion was undertaken, undissolved particles attached to the sample bottle are not poured out into the glassware in which full heated digestion occurs. The net result is that any Cr (III) not completely dissolved in 0.15 percent nitric acid at pH 2.0 could be completely “missed” by the analysis. In order to recover the Cr (III) present in the samples, Parks *et al.* (2004) recommended an in-the-bottle digestion that overcame the issue of particles attaching to the container.

Similar recovery problems are logically expected for any lead particles present in drinking water that do not dissolve in 0.15 percent nitric acid (Figure 3-1). While there are no reports of serious problems in older research, a 1993 study by Lytle *et al.* assessed the adequacy of the standard EPA sampling procedure for a case where 60:40 tin:lead solder powder was introduced to deionized water. In that study, the authors concluded that the typical nitric acid procedure recovered 100% of the lead in a solder powder used for laboratory simulation of the problem. However, the text of the article qualified this conclusion by noting that “*particle size and the time of acidification relative to the time of analysis also control the degree to which lead dissolves in the preservative. Lead or solder particles assumed to be present in the US EPA field study samples prior to acidification were given adequate time to dissolve and were not large enough to exceed the capacity of the acid to dissolve them*”. Moreover, the article noted that for some actual water samples collected in the field that prompted the investigation, lead concentrations were found to increase with longer holding times. This demonstrates that the standard protocol with 16 hours of sample holding time is sometimes inadequate.

A much more disturbing problem with standard analytical procedures was reported by Edwards *et al.*, (2004) for drinking water samples collected in Washington DC. Specifically, reddish colored particles were observed on the bottom of sampling bottles even after three months exposure to 0.15 percent nitric acid (Figure 3-2). The red particles did dissolve using 5 percent nitric acid and 100 °C digestion in the bottle after 24 hours. The red/brown particles were found to be comprised of lead oxides, and their color and recalcitrant nature was consistent with tetravalent lead (Pb (IV)) oxides found on lead pipe in Washington DC (Renner, 2004). After a full in the bottle digestion, lead levels were 500% higher than measured using standard EPA protocol. The implication is that acid resistant reddish colored Pb (IV) oxides were detaching from the piping and sticking to the sampling bottles. These Pb (IV) particles could have been consumed in the drinking water but would have been missed during routine sample collection, resulting in greater potential consumer exposure to lead and misclassification of some waters as “safe” when they were not.

Similarly, later study identified lead solder particulates on aerator screens in Washington DC (Edwards, 2005).



Figure 3-2: Red/brown lead (IV) oxides stuck on the bottom of plastic sampling bottles in Washington DC (Edwards *et al.*, 2004)

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

The Greenville incident, along with previous observations of particulate lead in Washington DC not detected by routine analytical procedures, prompted careful re-consideration of all aspects of lead in drinking water as it relates to public health. The current study emphasizes the extent to which standard EPA sample handling could miss human exposure to particulate lead and assesses bioavailability of various types of particulate lead. A companion study is underway that addresses concerns with water sampling instructions.

MATERIALS AND METHODS

A well-defined laboratory study of particulate lead occurrence was undertaken, followed by an examination of various real-world sampling results.

Laboratory Simulation of Particulate Lead Occurrence in Drinking water. The objective of part 1 of this work was to simulate conditions known to occur in Greenville, NC and Washington DC drinking water. That is, situations in which lead particles, small enough to pass through a medium faucet aerator screen, are present in drinking water samples. The goal was to evaluate the effectiveness of standard EPA method 200.8 (US EPA, 1994) in recovering the lead from representative particles that might be present in drinking water. As part of that evaluation, potential bio-availability of the same particles was examined in simulated gastric fluid (SGF) as well.

Lead dissolution was investigated in water samples to which representative leaded particles were added. The particles to which the water was exposed and the methods of preparing them are as follows:

a) Pure lead. The practice of using pure lead pipe in home plumbing systems was eliminated in 1986 (Lytle and Schock, 1996). It can however, still be present in older residencies and in the publicly owned distribution system. Pure lead particles can also be formed in water systems by cutting of lead pipe during partial service line replacements. Simulated pure lead particles used in this experiment were shaved off the external surface area of pure lead pipe.

b) Lead in the (IV) oxidation state (tetravalent lead). In the presence of strong oxidants such as chlorine, lead from the plumbing can be oxidized from the (II) to the (IV) oxidation state. Transition to the (IV) oxidation state has been shown to reduce lead solubility (Schock *et al.*, 2001; Edwards and Dudi, 2004). Lead (IV) particles were obtained by completely oxidizing lead (II) in a lead chloride solution to lead (IV) solids, with the addition of the appropriate amount of HOCl. After stirring for 30 minutes, the red-brown solids that formed were collected on a 0.45 micron pore size filter.

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

d+e) Red brass and Yellow brass. Leaded brass is considered a major source of lead leaching from newer faucets and fixtures (Lytle and Schock, 1996). Small grains of brass with lead have been observed to detach into water in some cases of corrosion (Sundberg, 2006; Sundberg *et al.*, 2003). For the needs of this experiment, leaded brass particles were filed off the external surface of red and yellow brass faucets.

The particles created as described above were sieved through a medium sized faucet aerator screen with mesh openings of 1.0 mm x 1.0 mm (Figure 3-3).

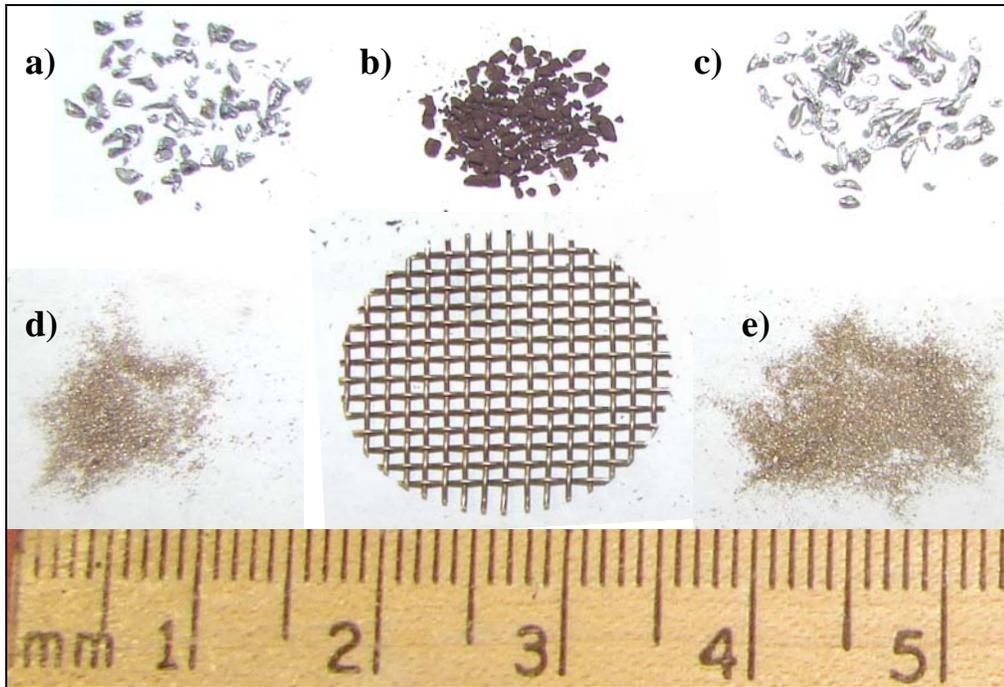


Figure 3-3: Particle types examined in the experiment: a) Pure Lead, b) Lead (IV), c) Solder (50:50 lead:tin), d) Red Brass and e) Yellow Brass. These particles were small enough to pass through the 1.0 mm x 1.0 mm openings of a faucet aerator screen (low middle).

Fifteen mg of each particle type was added to 250 mL water samples using plastic bottles. This is high, but in Washington DC samples of water were collected that contained as much as 48 mg of pure lead per liter of water (Edwards and Dudi, 2004). The brass particles (both red and yellow) differed from the rest of the particles examined in that they were in the form of filings and of smaller size (Figure 3-3). Four different experimental conditions were examined for each particle type (Table 3-1). Samples were prepared in triplicate, including blanks (water without the leaded particles) for Quality Assurance/ Quality Control (QA/QC) reasons.

Synthesized Potomac water was used to simulate Washington DC water (Rushing and Edwards, 2005). Synthesized Potomac water without (Case I) and with (Case II) phosphorous was tested following standard EPA Lead and Copper Rule sample handling procedures. The water samples were acidified with nitric acid to pH < 2.0 at room temperature. After a minimum holding time of 16 hours, the samples were analyzed for total lead using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Simulated gastric fluid (SGF) without (Case III) and with (Case IV) phosphorous was tested. The SGF (Table 3-1) consisted of sodium chloride, pepsin and hydrochloric acid (US Pharmacopoeial Convention, 2005; Yu *et al.*, 2006).

Table 3-1: Experimental Conditions Examined for each Particle Type.

	I. Water in EPA Digestion	II. Water with P in EPA Digestion	III. SGF*	IV. SGF* with P
Simulated Potomac Water Constituents	82 mg/L CaCl ₂ .2H ₂ O 89.6 mg/LCaSO ₄ .2H ₂ O 84.1 mg/L NaHCO ₃ .3H ₂ O	82 mg/L CaCl ₂ .2H ₂ O 89.6 mg/LCaSO ₄ .2H ₂ O 84.1 mg/L NaHCO ₃ .3H ₂ O	82 mg/L CaCl ₂ .2H ₂ O 89.6 mg/LCaSO ₄ .2H ₂ O 84.1 mg/L NaHCO ₃ .3H ₂ O	82 mg/L CaCl ₂ .2H ₂ O 89.6 mg/LCaSO ₄ .2H ₂ O 84.1 mg/L NaHCO ₃ .3H ₂ O
Simulated Gastric Fluid Constituents	N/A	N/A	0.2% NaCl 0.32% Pepsin 0.7% HCl	0.2% NaCl 0.32% Pepsin 0.7% HCl
NOM (Lake Pleasant Fulvic Acid)	0.3 mg/ L as C			
P	N/A	1.0 mg/L as P	N/A	1.0 mg/L as P

* SGF stands for Simulated Gastric Fluid.

The SGF samples were exposed to pH of about 1.2 with the hydrochloric acid addition and they were heated at 37 °C (body temperature) with gentle mixing, in contrast to the mild nitric acid at room temperature and without mixing in the EPA-method (Table 3-2). Results of this test simulate dissolution of lead from the particles in the stomach if they are ingested. In order to compare SGF results with those at the minimum EPA holding time of 16 hours, a typical stomach retention time of 3 hours could be accounted for (Table 3-2). This holding time inside the stomach is within the typical range of a few hours determined for solid meal types (Hellmig *et al.*, 2006; Singh *et al.*, 2006). Lead recovery in the SGF samples was also quantified via ICP-MS analysis.

Table 3-2: Comparison of the standard EPA preservation protocol versus Simulated Gastric Fluid.

	EPA Preservation	Simulated Gastric Fluid (SGF)
Constituents	HNO ₃ at 0.15% (v/v)	HCl at 0.7% (v/v) NaCl Pepsin
Typical pH	1.9	1.2
Temperature (°C)	20-22 (Room Temperature)	37 (Body Temperature)
Mixing Pattern	Stagnant	Gentle Motion
Holding Time	16 hours (Minimum)	3 hours (as per typical stomach holding times for solid food)

Real World Results. Recovery of lead using EPA sampling protocols versus complete strong acid in-the-bottle digestions are compared in several water systems. Likewise, the dissolution behavior of lead particles involved in two cases of lead poisoning is also carefully examined.

RESULTS

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

Behavior of Simulated Particles in EPA Sampling Protocol and Simulated Gastric Fluid

For all particle types, lead dissolution (%) was calculated at specified time intervals, using the following simple mathematical formula:

$$\% \text{ Lead Dissolution} = \frac{\text{Measured Lead Concentration in Water Sample}}{\text{Known Lead Concentration in Water Sample}} \cdot 100 \quad (\text{Equation 1})$$

The measured lead in the water sample refers to that quantified by ICP-MS. The known lead concentration in the water sample refers to that which would occur based on the measured mass and percentage of lead in each metal. For purposes of this paper we did not distinguish between soluble and colloidal matter. Therefore dissolution is defined as the fraction of lead recovered from the particles and suspended in the water, which could be soluble or colloidal.

Less than 20% of the pure lead particles dissolved after a 16 hour holding time and slightly more than 20% dissolved after 48 hours for all four conditions examined (Figure 3-4). If samples had been collected that contained these lead particles at the tap, the measured lead concentration would have been about 20% of the actual, since the particulate lead would not typically be poured into a sample tube for quantification by graphite furnace or inductively coupled plasma. The measured turbidity of the water in this sample is also much less than 1 ntu, since the heavy particles quickly settled to the bottom of the turbidity meter or container. After 3 hours in SGF, 6% of the lead was dissolved. Thus, the SGF was about 5% more aggressive than 0.15 percent nitric acid when compared at a common time of 16 hours, but about 4% less aggressive after 3 hours in SGF versus 16 hours in 0.15% nitric acid.

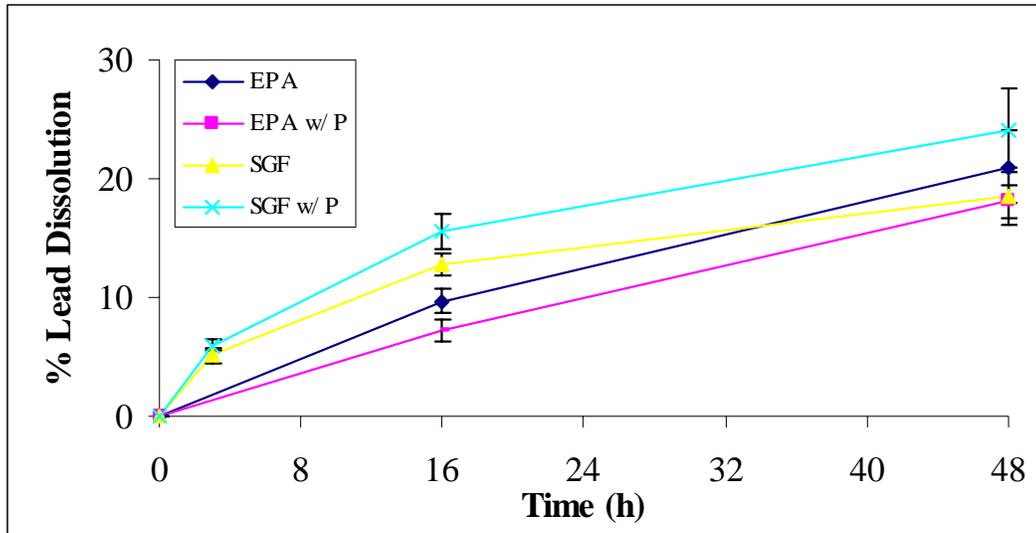


Figure 3-4: Lead Dissolution versus Digestion Time of Pure Lead Particles. The error bars denote 95% confidence intervals.

Only about 20% of Pb (IV) dissolved in the samples at pH < 2.0 in 16 hours. Three times more Pb (IV) dissolved in the simulated gastric acid after 16 hours (Figure 3-5). Even after just 3 hours in SGF, 10% more lead dissolved than in the 0.15 percent nitric acid after 16 hours. This suggests that the Standard EPA methods would miss most of the lead that was present in water with these particulates, but much of the Pb (IV) is readily bioavailable after just a few hours in the stomach. The 20% recovery of Pb (IV) particulates in these samples is consistent with earlier reports by Edwards *et al.* (2004) for the reddish lead discovered in samples of Washington DC drinking water.

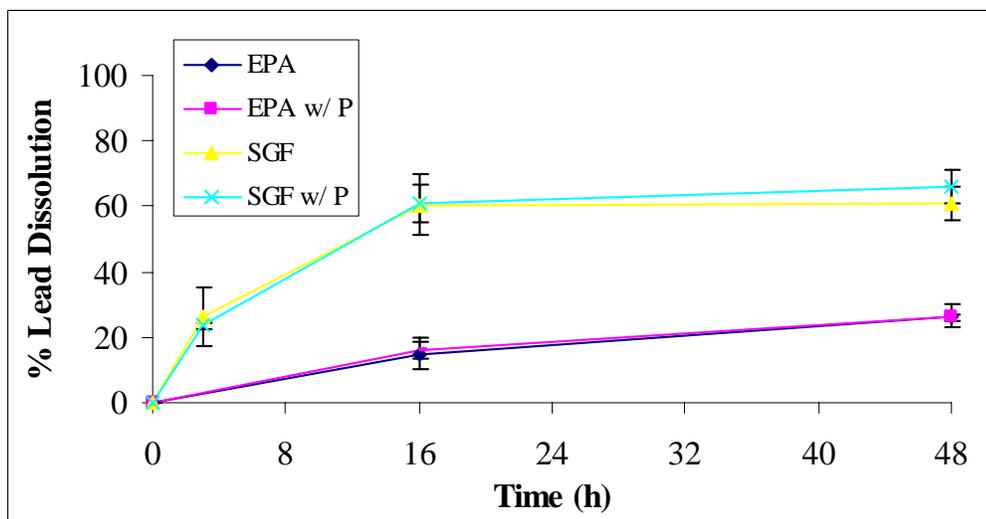


Figure 3-5: Lead Dissolution versus Digestion Time of Lead (IV) Particles. The error bars denote 95% confidence intervals.

The solder particles dissolved more readily in the 0.15 percent nitric acid than in the simulated gastric fluid. Even so, after 16 hours of sample holding time, less than 20% of the lead was recovered using the EPA method (Figure 3-6).

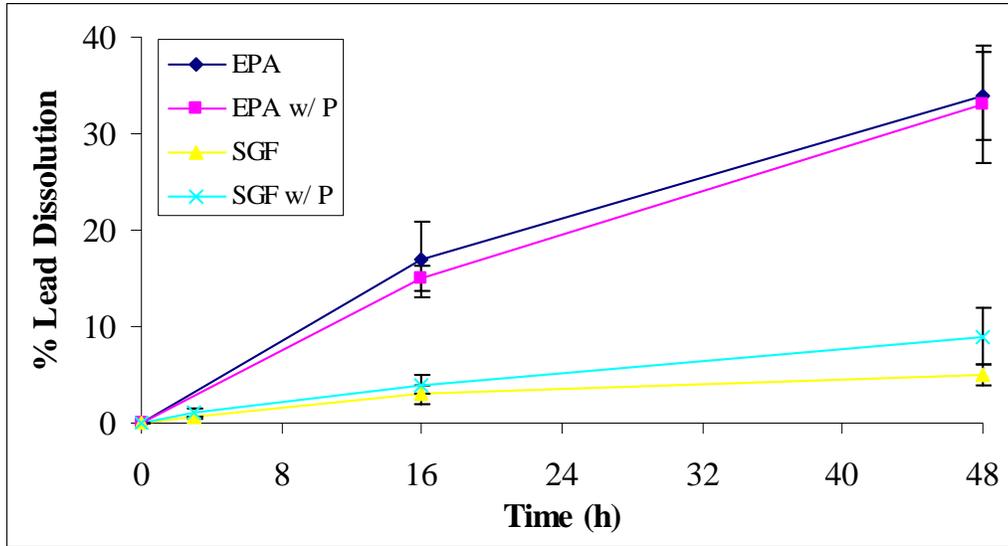


Figure 3-6: Lead Dissolution versus Digestion Time of Solder Particles. The error bars denote 95% confidence intervals.

The lead in red brass fillings dissolved slightly more readily in the SGF than in 0.15 percent nitric acid after 16 hours. Indeed, virtually all the lead dissolved after 3 hours in SGF, versus 90% after 16 hours in the 0.15 percent nitric acid (Figure 3-7). The much smaller size of brass particles relative to pure lead is also a factor to consider when attempting to compare results in Figure 3-7 to Figure 3-4. It is quite possible that use of larger leaded brass particles would have given much lower recoveries. However, the relative aggressiveness of the 0.15 percent nitric acid versus SGF is compared using the same size of particles in each case.

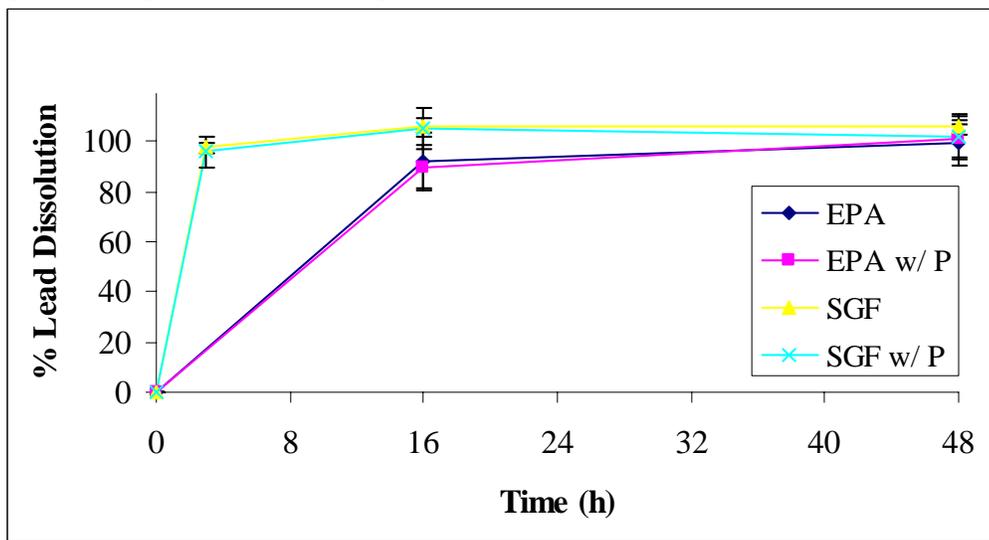


Figure 3-7: Lead Dissolution versus Digestion Time of Red Brass Filings. The error bars denote 95% confidence intervals.

Taking into account that a 3 hour sample was not collected in the sample with 0.15 percent nitric acid, there is no significant difference between dissolution of lead from yellow brass in the two solutions. After 16 hours about 80% of the lead had been recovered in all cases, using the small yellow brass filings (Figure 3-8).

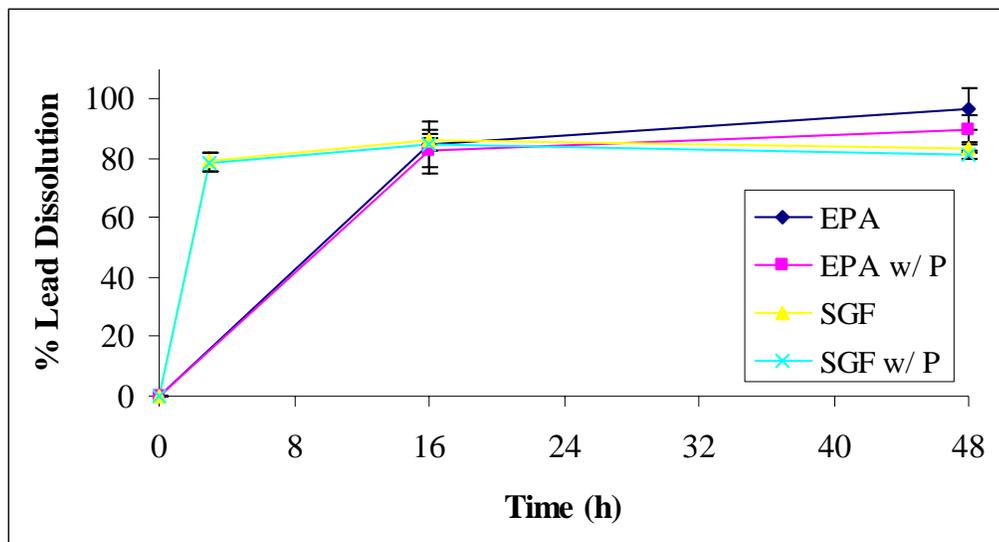


Figure 3-8: Lead Dissolution versus Digestion Time of Yellow Brass Filings. The error bars denote 95% confidence intervals.

The presence of phosphorous in the water did not affect lead dissolution in any of the cases examined (Figures 3-4 to 3-8). Phosphorus was included in the present study because many utilities in the US use phosphorus-based corrosion inhibitors, and previous research had suggested that phosphate in soils could make lead less bioavailable (Hettiarachchi *et al.*, 2001; Lambert *et al.*, 1997). However, under the conditions of the test there was no effect of phosphate at a level of 1.0 mg/L as P.

Real World Sampling Results

Montgomery County, Virginia. Sampling at ten representative schools did not suggest any problem with standard EPA sampling procedures. That is, the EPA preservation at pH < 2.0 recovered the same amount of lead as did a more aggressive digestion of 2% HNO₃, in 10 out of 10 water samples (Nicholson and Edwards, 2005). In all samples, lead levels were below the action level of 15 ppb. The water supply for this system is extremely non-corrosive and the utility, which successfully implements zinc orthophosphate corrosion control, has historically easily met the LCR action level for lead. This likely reflects the fact that in most instances where (particulate) lead occurrence in drinking water is not an issue, typical procedures are adequate.

Tellico Village, Tennessee. In other systems however, where the presence of lead in drinking water is more prevalent, the EPA method was only partly effective.

Sampling at homes of Tellico Village, TN showed a systematic inability of the EPA method to recover all the lead present in multiple drinking water samples. Specifically, lead release was always higher when the more aggressive digestion was implemented, typically by 20-50% but up to 250% in one case, compared to the EPA preservation method (Figure 3-9). Visual observations verified that in some cases, particles were still present (had not fully dissolved in the bottom of sampling bottles) after the EPA preservation (Figure 3-10). Along with higher recoveries for lead, the more aggressive digestion allowed for much higher recoveries of other elements, including copper, zinc and tin. This is expected based on prior work of Parks *et al.* (2004) and the earlier data with synthetic particles presented herein.

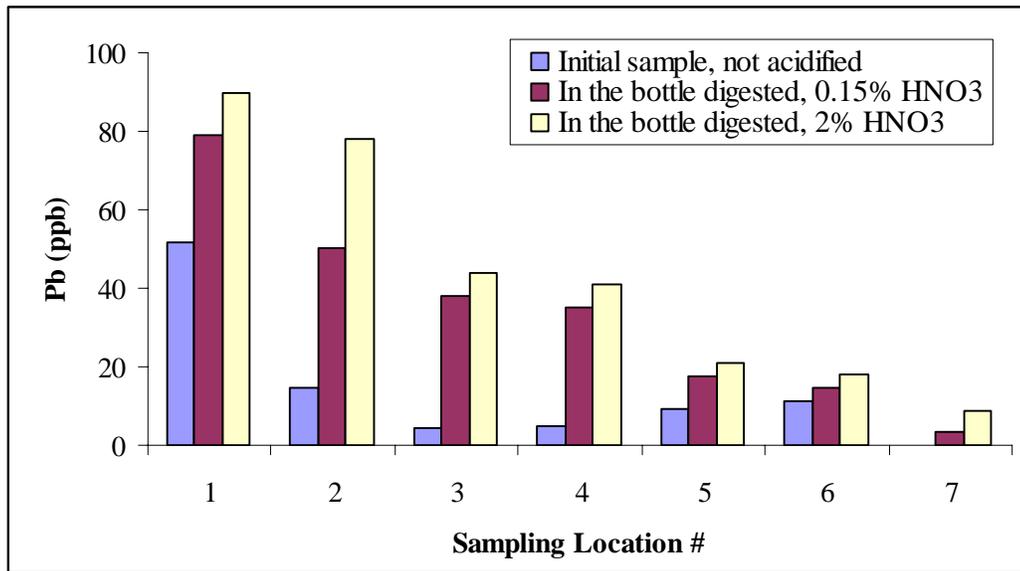


Figure 3-9: Lead release in water samples collected at homes of Tellico Village, Tennessee, following different preservation protocols.



Figure 3-10: Undissolved lead-containing particles at the bottom of plastic sampling container, after preservation of the water sample to pH < 2.0, according to standard EPA protocol. Water sample collected at Tellico Village, Tennessee.

Behavior of Lead Particles Involved in Childhood Lead Poisoning from Greenville NC and Durham NC

Extensive sampling in Greenville, NC demonstrated that the problem of particulate lead in drinking water can directly cause lead poisoning. Lead particles were found to be trapped in the faucet aerator screen of the affected child and elsewhere in the apartment building (Figure 3-11). Six similar particles weighing 5.0 ± 0.3 mg were collected from the screen and used in experiments. Each particle was exposed to 1 liter of simulated Potomac water without phosphorus in plastic containers. Three of the particles were exposed to standard EPA protocol, whereas the remaining three were exposed to simulated gastric fluid (Table 3-1). Percent lead dissolution was enumerated at specific time intervals, using Equation 1, and total lead was determined after a full heated digestion at 85-90 °C at the end of the experiment.



Figure 3-11: Particles trapped on faucet aerator screens, collected in the apartment building of lead poisoned child, in Greenville NC. Six of these particles were used in the experiment.

After the minimum EPA holding time of 16 hours, the particles exposed to simulated gastric fluid dissolved at a level of 47% versus the 27% lead dissolution of particles in the EPA preservation. The difference was significant at a confidence level > 90% (Error bars on triplicate samples plotted, Figure 3-12). Lead release in SGF after 3 hours was slightly lower than release in the EPA solution after 16 hours (21% versus 27%). After 48 hours the lead dissolution was 66% and 40% in SGF and EPA solutions, respectively (Figure 3-12). The results clearly demonstrate the bioavailability of the lead particles present in the faucet aerator, and lack of complete dissolution in the EPA protocol.

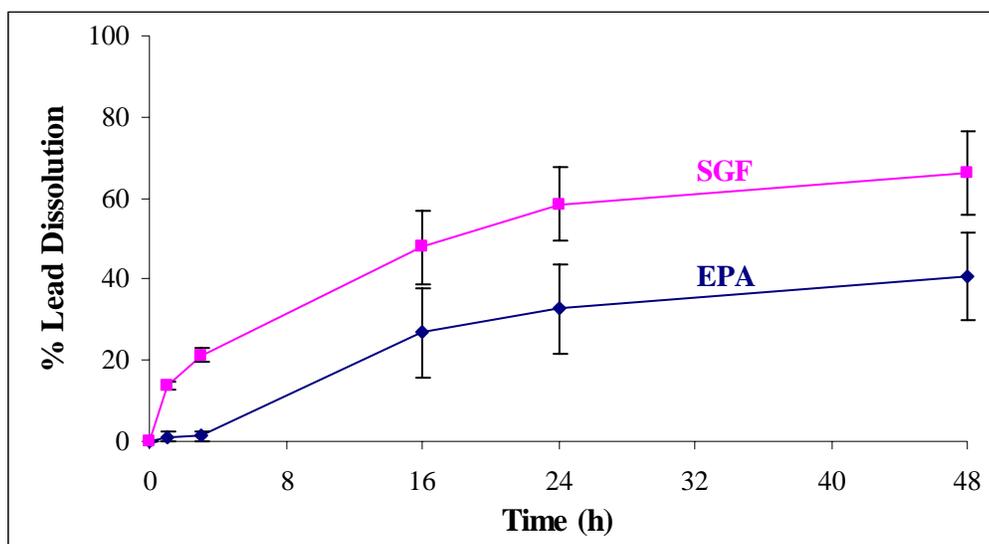


Figure 3-12: Lead Dissolution versus Digestion Time of real leaded particles collected from a home faucet in Greenville, NC. The error bars denote 90% confidence intervals.

Along with the lead, the dissolving particles released significant amounts of tin but did not release copper or zinc, suggesting that they originated from lead/tin solder (Figure 3-13). It is noted that these real lead:tin solder particles from the aerator behaved differently than did the new simulated solder. Even though they exhibited

the same behavior in the EPA sample handling protocol, the real particles dissolved much more readily in the SGF (Figure 3-12 versus 3-6).



Figure 3-13: Poorly crafted soldered joint in drinking water plumbing in Greenville NC. Even though the solder covers the outside surface, excess solder can flow down the interior of the pipe, contact drinking water and contaminate the water supply.

A similar experiment was conducted with actual particles collected from the apartment complex where lead poisoning of the child in Durham had occurred. Six leaded particles, with weight of 5.0 ± 0.5 mg, were exposed to EPA versus SGF as in the case for Greenville.

After the minimum EPA holding time of 16 hours, particles in SGF released about the same lead as did particles in the EPA preservation. By the end of 48 hours, lead dissolution was 24% and 21% in SGF and EPA respectively (Figure 3-14), a difference not statistically important at 90% confidence. As with the particles collected in Greenville, a final full heated digestion verified that the Durham solids originated from leaded solder. This is consistent with identification of lead solder joints in the plumbing during the site investigation.

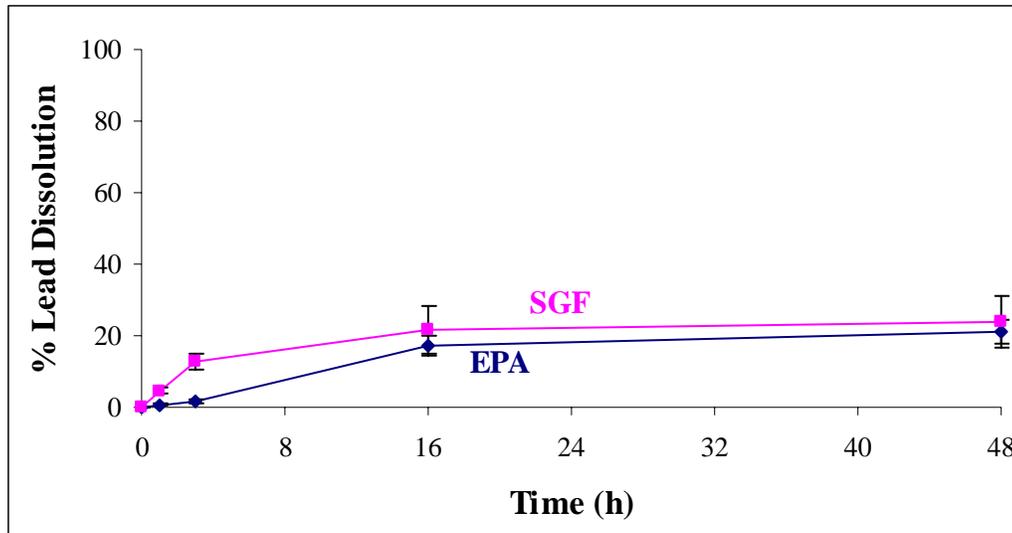


Figure 3-14: Lead Dissolution versus Digestion Time of real leaded particles collected from a home faucet in Durham, NC. The error bars denote 90% confidence intervals.

The actual Durham particles did not dissolve at a level higher than 24% after 48 hours (Figure 3-14). In the case of Greenville real particles, dissolution had reached almost 70% in SGF after 48 hours (Figure 3-13). When comparing the behavior of the two sets of real particles involved in the lead poisoning cases, it becomes clear that lead particles in drinking water exhibit variable behavior. Nonetheless, the study confirmed that a substantial fraction of particulate lead is bioavailable.

DISCUSSION AND SYNTHESIS

It is worthwhile to discuss some potential implications of the above research data in relation to public health. First, many faucets do not have an aerator, and as a result it is quite possible that particles larger than those studied herein are occasionally present in water collected from taps. The authors have collected lead-containing particles as large as 4 mm in diameter from faucets without aerators. In such cases, the potential limitations of the 0.15 percent nitric acid in recovering lead were even greater.

In the present study particles were not allowed to sit before acidification. If we had done so, and they stuck to the surface of the sample bottle, they might be more resistant to dissolution in the EPA method, since a lower surface area would be exposed to the water.

In addition, all metallic particles tested in the laboratory investigation were new. Actual particles derived from distribution systems might be somewhat less readily dissolved in the EPA preservation, since they sometimes are “aged” and may have developed a passivating layer as a result of exposure to drinking water. It is uncertain how this factor would alter the experimental results of part one for each type of representative lead-bearing metal, but the experiments with real solder particles from

Greenville and Durham proved it could be important. That is, using the new solder particles in the laboratory simulation, lead release in SGF was lower than in the EPA method, a trend that is of lesser public health concern since poor recovery of lead with the EPA test was still higher than bioavailable lead. But using the actual solder particles, lead release in SGF was either the same (Durham solids) or higher (Greenville solids) compared to lead release with the EPA method, indicating that lead “missed” in the EPA method would be largely bioavailable. We speculate that the relative difference between new and actual solder particles could arise from factors that include: 1) greater surface area of the real particles as was obvious based on SEM analysis, 2) enrichment of tin in a surface layer on the real particles, 3) oxide surface coatings on the old particles, and/or 4) more rapid dissolution of tin in the HCl of SGF than in the HNO₃ of the EPA protocol. Future research should examine these factors in greater detail.

In relation to human exposure, it is quite possible that the results reported herein for 3 hours exposure to SGF may be a lower bound to actual. Specifically, cases have been reported in which lead particles have been retained within the human digestive system, as was the case for small lead shot ingested from ducks which was believed to lodge in the folds of the intestine. In such cases, the shot could serve as a source of lead for much longer than 3 hours. Nonetheless, the bioavailability of the metallic lead particles tested in this study was already quite high in simulated gastric acid. Overall, the evidence in this work indicates that a large fraction of the particulate lead in drinking water would be bioavailable.

For all the particles examined in this study, lead was finally recovered at a level of 90-100%, under a 2% nitric acid (v/v) in-the-bottle digestion at 85-90 °C after about one week. This method is easy to use and is therefore recommended for water utilities who want to accurately quantify particulate lead in drinking water, versus the much less aggressive 0.15 percent standard method currently in use. On the other hand, in no instance did real or simulated samples with high particulate lead measure less than 15 ppb after the standard EPA method. The 15 ppb EPA Action Level therefore has use in indicating a potential hazardous condition at a faucet, which could be explored in more detail in follow up sampling, or the hazard could be mitigated by use of bottled water or filters.

Attention was then turned to determining how the lead poisonings could have occurred from tap water, since interviews suggested that in some cases direct consumption of water by the affected children had not occurred. A similar paradoxical case of lead poisoning from water that was not consumed had been reported in Washington DC, where it had been suggested that the exposure occurred via boiling of pasta, rice and potatoes in tap water (Copeland, 2004). Early research conducted on this possibility, using soluble lead during cooking, suggested that lead exposure via this pathway could be significant in some instances. In that study adsorption of lead from the water onto the surface of vegetables during cooking reached 80% in some cases (Little *et al.*, 1981). A more recent study also asserted

that lead accumulation in boiled potatoes derived primarily from lead in tap water that had been used for cooking (Baxter *et al.*, 1992).

To test the hypothesis in the apartment of the lead poisoned child in Greenville, where lead in the water was mostly particulate, tap water was collected at a high flow rate from a faucet in that apartment. The high flow rate typically used for pasta preparation (but atypical for sampling under the LCR) tended to abrade more particles on the aerator screen and introduced high concentrations of lead to the water supply. In this instance the 1.5 L of water collected contained 535 ppb lead. These particles were not readily visible to the naked eye, but could be observed sinking to the bottom of the pot. During cooking, the lead remained insoluble, since less than 5% of particulate lead was poured off after cooking. The 95% of lead from the water remained in the pasta (testing indicated it did not stick to the pan), resulted in more lead per serving of pasta than would be consumed by eating a dime-sized paint chip (Figure 3-15). This simple test demonstrates the very real public health threat that can arise from lead particles in drinking water and the under-appreciated hazard from specific taps.



Figure 3-15: Food cooked with tap water containing lead particles collected from home of lead-poisoned child (left), contains more lead than a lead paint chip in the size of a dime (right).

As a final point, it is well-understood by experts who understand lead corrosion, that utilities meeting the 90% tile lead action level of 15 ppb cannot ensure that lead levels are safe at 100% of taps. The CDC and those doing environmental assessments of lead poisoned children should always give consideration to the potential of lead exposure from drinking water, which would require changing existing published guidance (Edwards *et al.*, 2004). On the basis of experiences reported herein, North Carolina has a new policy requiring testing of drinking water in cases of elevated blood lead, and the authors recommend similar rules elsewhere. Relative to paint, exposure to lead from water in a home can be inexpensively mitigated with complete effectiveness using Brita type filters certified by the National Sanitation Foundation for lead removal.

CONCLUSIONS

- In cases where new particles of pure lead or Pb (IV) pass through an aerator screen, standard EPA methods can dramatically underestimate actual lead present in samples, because water at pH < 2.0 for 16 hours does not completely dissolve the lead.
- In the case of Pb (IV), the particles dissolve more readily in simulated gastric fluid than in the pH 2.0 EPA digestion, which means this lead is quite likely to be bioavailable. This is highly problematic in terms of protecting public health. Considering the likelihood that lead particles might be retained in the digestive track for a long period of time, the potential seriousness of this deficiency in sample handling should not be under-estimated.
- In the case of new solder particles the EPA method did not completely dissolve the lead. The simulated gastric fluid did not completely dissolve the lead either. But to the extent that small particles of lead were lodged in the intestine, they could serve as a long term source of lead.
- For new brass particulates, standard EPA procedures adequately dissolved the lead. However, the brass particulates differed from all other lead particles tested in that they were filings, i.e. smaller in size.
- In most real systems, routine EPA sampling procedures will dissolve the lead present in water samples.
- In some unusual cases in which particulate lead is present in samples, such as those described herein that were associated with childhood lead poisoning from solder particles, the EPA sampling method can miss a fraction of the lead present.
- Despite the noted limitations of the EPA sampling method, no potable water samples have yet been collected with high levels of particulate lead which tested below the 15 ppb EPA action limit. The action limit therefore has usefulness in detecting hazardous taps, but it cannot be construed to quantify the extent of the hazard.
- The contribution of water-borne particulate lead in food can pose a human health hazard that is underappreciated. Lead poisoning can occur in these circumstances even when the contaminated water is not directly consumed, but rather, is used to prepare food.
- In exceptional cases, such as those encountered in Greenville NC, Durham NC and Washington DC, water-borne lead can be a key source of elevated lead in children's blood. These cases are extremely difficult to monitor, since particulate lead occurrence in drinking water is variable and sporadic. For these exceptional cases, it is important to sample in a manner that truly captures the "worst case" in terms of human exposure.

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CHAPTER FOUR

ROLE OF CHLORIDE TO SULFATE MASS RATIO IN LEAD LEACHING FROM SOLDERED JOINTS AND BRASS

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ABSTRACT: Leaching of lead from 50:50 Pb:Sn solder joints and leaded brass can markedly increase with higher $\text{Cl}^-:\text{SO}_4^{-2}$ ratio of the water. At several utilities with relatively low levels of sulfate and chloride in their raw water supply, changing coagulant from alum (aluminum sulfate) to polyaluminum chloride (PACl) or ferric chloride triggered serious problems with lead contamination. Lead levels dropped after switching back to alum or to ferric sulfate coagulants. Extensive bench scale testing using water from one utility confirmed that the change in coagulant (and concurrent increase in $\text{Cl}^-:\text{SO}_4^{-2}$ ratio) increased lead leaching from brass and solder joints by factors of 1.2-2.7 and 2.3-40, respectively. For leaded solder, the mechanism of attack is galvanic corrosion via connection to copper, which sacrifices the lead anode and drives pH lower. A microelectrode detected pH 3.4 near the lead surface of a solder joint in water with high $\text{Cl}^-:\text{SO}_4^{-2}$ ratio (PACl-treated), pH 4.4 in the same water but with a lower $\text{Cl}^-:\text{SO}_4^{-2}$ ratio (alum-treated), versus pH 6.1 for solder without a connection to copper at both the low and high $\text{Cl}^-:\text{SO}_4^{-2}$ waters. Orthophosphate inhibitor could not control the lead problem arising from solder joints in waters with high $\text{Cl}^-:\text{SO}_4^{-2}$ ratio.

KEYWORDS: chloride, sulfate, coagulant, lead solder, brass, galvanic corrosion

INTRODUCTION

There is increasing evidence that lead and copper corrosion can be strongly influenced by seemingly innocuous changes in water treatment related to compliance with recent US EPA regulations. While it has long been understood that removal of natural organic matter (NOM) can sometimes increase the likelihood of copper pitting (Edwards *et al.*, 1994), it was also recently established that a switch from free chlorine to chloramine disinfection caused serious problems with lead leaching to water in Washington D.C. from lead pipe, solder and brass materials (Edwards & Dudi, 2004). Fallout from the latter experience prompted some minor revisions to the Lead and Copper Rule (LCR) and new research into corrosion of lead plumbing materials.

Conceptually, modern corrosion control attempts to reduce leaching from lead pipe, solder and brass materials by encouraging formation of low solubility lead hydroxyl-carbonate and phosphate films on the plumbing material surface (e.g. Schock *et al.*, 1996; Schock 1989). Practically it is understood that this is a dramatic over-

simplification of reality, since changes to water that make leaching better for one lead-bearing material can make leaching worse for others, and issues such as galvanic corrosion require specialized understanding suspected to be important in some instances (Lytle & Schock, 1996; Edwards & Triantafyllidou, 2006; Britton & Richards, 1981). Thankfully and in spite of proven gaps in current understanding (Edwards *et al.*, 1999), lead leaching in the majority of systems has responded favorably to stock cures such as raising pH, increasing alkalinity (i.e., dissolved inorganic carbon) or dosing of orthophosphate corrosion inhibitors.

Galvanic Corrosion of Solder/Brass and Copper Connections. There is some disagreement in the literature regarding the potential importance of connections between dissimilar metals including lead pipe-copper pipe and lead solder-copper pipe as a cause of problems with lead contamination. As background to the debate, Dudi (2004) asserted that in the absence of a connection to copper, corrosion of pure lead pipe is a relatively straightforward phenomenon. It proceeds with lead oxidation (anodic reaction) and reduction (cathodic reaction) occurring in relatively close proximity over the pipe surface (Figure 4-1, top). The OH⁻ produced via the cathodic reaction is at least partly neutralized by the acid produced via the anodic reaction, resulting in a slight increase or no change in pH of water contacting the lead pipe.

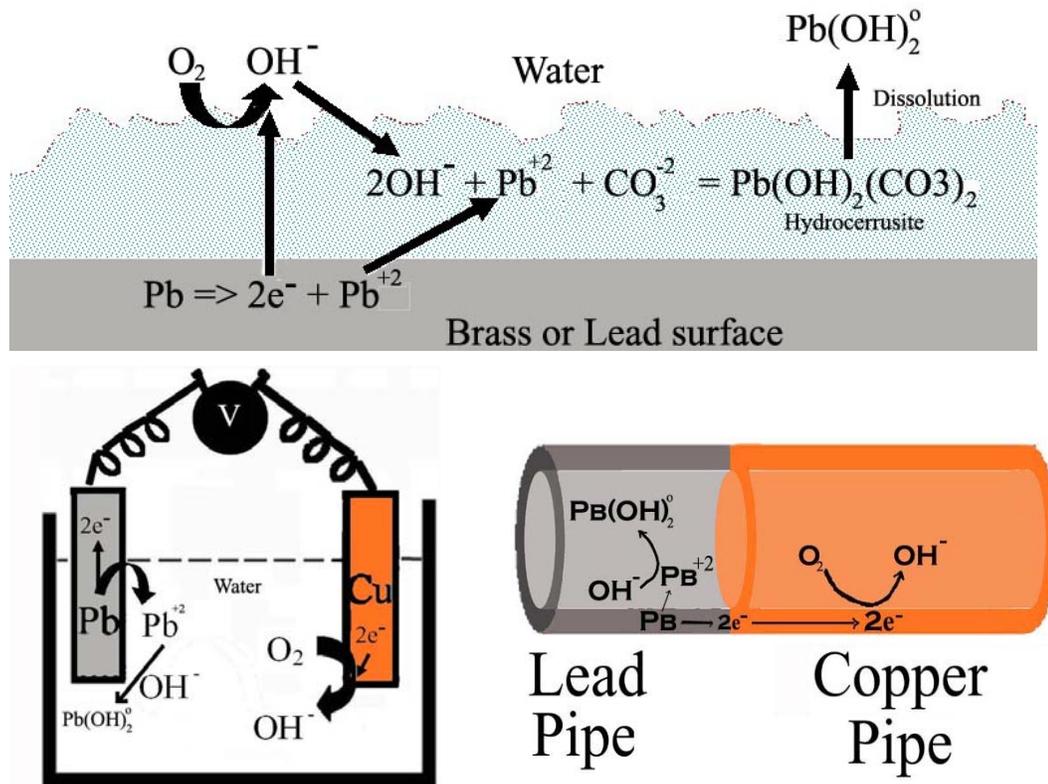


Figure 4-1: For corrosion of pure lead pipe, anodic reactions (lead corrosion) and cathodic reactions (e.g., dissolved oxygen reduction) occur in close proximity over the pipe surface (top), resulting in either no change or increase of water pH. Galvanic corrosion driven by coupled lead and copper separates anodic and cathodic reactions, accelerating the corrosion of the lead, dropping pH near the lead surface and increasing pH near the copper surface (bottom). After Dudi (2004)

When lead pipe is connected to copper the anodic and cathodic reactions are separated (Figure 4-1, bottom). The lead material becomes anodic and is sacrificed, whereas the cathodic reactions occur over the surface of the copper. In this situation lead leaching to water could be increased by higher corrosion rate and/or a lower pH at the surface of the lead material. Since lower pH tends to prevent passive film formation on lead surfaces, high galvanic currents could be somewhat self-perpetuating.

It is instructive to carefully examine the range of research that purposefully investigated concerns related to galvanic corrosion of lead materials relative to contamination of drinking water during stagnation in building plumbing. The studies of Reiber (1991, 2005) concluded that galvanic effects are short-lived and of relatively little consequence. These studies did not make direct measurements of lead leaching to drinking water, but relied on electrochemical measurements that are at best imperfect predictors of potential lead contamination. Moreover, both sets of experiments were conducted using Seattle tap water (or Seattle tap water occasionally amended with extra sulfate) which might not represent the range of galvanic effects encountered in drinking waters nationally. The Reiber work was also conducted under continuous turbulent flow (velocity of 0.25 m/sec in the 1991 study) which would tend to eliminate acidic pHs at lead surfaces that were hypothesized by Dudi (2005) to be a key factor in the problem.

Earlier research suggested that the consequences and longevity of galvanic corrosion are highly dependent on many of these factors. In an English study where various synthetic waters were examined, Oliphant (1983) noted the importance of chloride and sulfate levels. Chloride stimulated attack on lead when it was galvanically connected to copper, whereas it tended to protect leaded materials when they were not connected to copper. Sulfate on the other hand, was found to inhibit corrosion of lead-bearing materials both in isolation and in galvanic connections to copper. Scanning electron microscopy analysis (SEM) of corroded surfaces illustrated that sulfate had a profound effect on the physical form of the corrosion product layer on the lead solder which was connected to copper, changing it from needle-like crystals to flat platelets that were deemed more protective. Formation of the more protective layer required sufficient sulfate to overcome the negative impacts of chloride. As with the Reiber work, lead leaching was never measured directly in the Oliphant study, but conclusions were based on galvanic current measurements under continuous flow conditions.

Chloride to Sulfate Mass Ratio (CSMR). Follow-up studies of Gregory (1985) using the Oliphant apparatus for 38 real waters in England reinforced the importance of the relative amount of chloride to sulfate in producing sustained, high galvanic voltages that sacrificed lead plumbing when connected to copper. Gregory developed a concept of chloride to sulfate mass ratio (termed CSMR henceforth in this work) to explain this dependency, with a formula and illustrative calculation for a water containing 10 mg/L Cl^- and 20 mg/L SO_4^{2-} as follows:

$$\text{Chloride to Sulfate Mass Ratio (CSMR)} = \frac{[\text{Cl}^-]}{[\text{SO}_4^{-2}]} = \frac{10 \text{ mg/L Cl}^-}{20 \text{ mg/L SO}_4^{-2}} = 0.5 \quad \text{Equation (1)}$$

In the above example the CSMR is equal to 0.5. Gregory verified Oliphant's previous finding that high chloride relative to sulfate, yielding CSMR's above 0.5, tended to increase galvanic corrosion of lead solder connected to copper pipe. Gregory also studied the effect of inhibitors and determined that zinc (alone or with orthophosphate) was most effective in reducing the voltage of galvanic connections, whereas orthophosphate was relatively ineffective in stopping this type of attack. But if waters were highly conducive to sustained galvanic voltages due to an elevated CSMR and other factors, the benefits of zinc were not always adequate in reducing corrosivity (Gregory and Gardiner, 1985). Once again, no measurements of actual lead leaching to water were made and the experiments were conducted under continuous flow (100 mL/min).

As part of a survey of hundreds of utility experiences during the initial rounds of the US EPA LCR, Dodrill & Edwards (1995) independently determined that as the relative concentration of chloride to sulfate increased in a water supply, a utility was more likely to have a higher 90th percentile lead concentration. In fact, for a sub-set of utilities studied in-depth, 100 percent of utilities (12 out of 12) with CSMR below 0.58 met the 15 ppb lead action limit, whereas only 36 percent of utilities (4 out of 11) with CSMR above 0.58 were in compliance. In attempting to provide a mechanistic explanation for this result, the earlier work of Oliphant and Gregory was reviewed and cited. Indeed, the critical level for adverse effects on lead leaching in the Dodrill study was remarkably similar to the level identified as causing galvanic corrosion of lead (0.58 versus 0.5 mg Cl/mg SO₄⁻²).

Other laboratory experiments provided data supporting the notion that lead/copper galvanic couples were impacted by higher Cl⁻:SO₄⁻². For example, Himdi *et al.* (1994) performed both galvanic current and lead release measurements, exposing pure lead connected to copper pipe in Boulder, Colorado tap water modified by sulfate addition. In two test waters, one with a low alkalinity of 45 mg/L as CaCO₃ and the other with 90 mg/L as CaCO₃, both at pH 7.8, the chloride to sulfate ratio was varied from 0.02 to 0.2. Even though these ratios are well below the critical threshold of 0.5-0.58 cited elsewhere, the higher CSMR increased galvanic current by about a factor of two.

Follow-up work by Dudi (2004) examined the effect of a 5X increase in chloride and 5X decrease in sulfate (overall 25-fold increase of CSMR) on lead release from brass hose bibs connected to copper pipe for a range of water conditions. After 3 weeks at the lower CSMR, the switch increased lead leaching in 11 of 12 waters tested, by an average factor of 2.4 but as high as 10 times under certain conditions. The increase in lead leaching occurred concurrently with an average 1.4 times increase in galvanic current. In that study, connecting a new copper pipe to old lead pipe resulted in hazardous levels of lead in the water (> 40,000 ppb) over a short term experiment of 3

days duration. Dudi noted that spatially separating the anodic (lead) and cathodic (copper) areas would result in lower pH for water near the lead pipe surface (Figure 4-1), and that the extent of the pH drop depended on the magnitude of the galvanic current.

Some other anecdotal evidence of links between higher CSMR and higher lead leaching at individual utilities has also been gathered. Bay City, MI and Columbus, OH both observed higher lead leaching after coagulant changes that increased the CSMR of the water supply. At both plants, the coagulant selection was temporally linked to an exceedence of the lead action level, which was promptly met again after lowering the CSMR by changing coagulant (Table 4-1). The Philadelphia Suburban Water Company (currently known as Aqua Pennsylvania), performed plant scale trials which also showed that elevated CSMR resulting from coagulation with polyaluminum chloride (PACl), increased lead leaching in test rigs from about 60 ppb to 80 ppb (Edwards *et al.*, 1999).

Table 4-1: Key water quality parameters, CSMR and LCR lead monitoring (wherever applicable) for selected case studies.

<i>LITERATURE CASE STUDIES</i>						
Name	Water pH	Alkalinity (mg/L CaCO ₃)	Corrosion Inhibitor	CSMR Range before/after	90% th ile lead before/after (ppb)	Reference
Bay City, MI*	9.1-9.3	30-40	-	1.0-2.0/ 0.4-0.6	>15/ <15	Kelkar <i>et al.</i> , 1998
Columbus City, OH	7.7-7.9	30-45	Zinc Orthophosphate	0.82-1.50/ 0.29-0.49	33/ 3	AWWA, 2005
Virginia Tech Study	8.5	38.6	One condition with ortho-P, all others w/ no inhibitor	0.79 vs 19.8 in experiments	N/A	Dudi, 2004
University of Colorado Study	7.8	45 and 90	No inhibitor	Varied from 0.02-0.2 in experiments	N/A	Himdi <i>et al.</i> , 1994

*Finished water quality parameters for Bay City reflect past conditions, at the time of high CSMR

While this literature review indicates substantial data on the potential importance of the chloride to sulfate mass ratio, well controlled experimental studies and mechanistic insights are limited. This has resulted in some understandable skepticism amongst the water industry regarding the potential importance of galvanic corrosion in lead contamination. To address this skepticism and some limitations of prior work, this study aimed to 1) conduct well-controlled experiments of several weeks duration to rigorously test the longevity of galvanic corrosion relative to lead contamination under stagnant conditions, 2) assess the relative effects of chloride and sulfate by directly measuring lead release into drinking water at different CSMRs, 3) evaluate the role of inhibitors in mitigating lead leaching via galvanic corrosion, 4) test the hypothesis of Dudi regarding very low pH at the surface of the lead anode as a potential mechanistic explanation of the galvanic acceleration in corrosion, and 5) conduct field investigations illustrating serious potential public health implications of galvanic corrosion at lead solder joints when elevated CSMR's are present.

PART 1: BENCH SCALE EXPERIMENTAL STUDY

Bench scale experiments were undertaken for eleven weeks in order to address research needs 1 through 4. PACl-treated water and alum-treated water (real waters originating from the same raw source) were compared head to head in terms of lead leaching from brass (5% lead content) and 50:50 lead:tin solder. These two leaded materials are present in home plumbing as well as in the publicly owned distribution system, where they are typically in direct electrical connection to copper pipe.

MATERIALS AND METHODS

New brass fixtures are considered major contributors to lead contamination of tap water (e.g. Kimbrough 2001; Lytle and Schock 1996; Mariñas *et al.* 1998). One of the most common types of brass used in faucets is C83600, an alloy with a lead content of 5% by weight. In this test small C83600 “as cast” brass coupons were fabricated from brass rods of 0.64 cm (0.25 in) diameter and 0.97 cm (0.38 in) height. The coupons were epoxied to the bottom of a 46 mL glass vial to study corrosion of brass by itself (Figure 4-2, left). This vial was filled halfway to the top with test water, in order to achieve a brass surface area to water volume ratio of 1.4×10^{-2} in²/mL. To simulate brass galvanically connected to copper, identical brass coupons were squeezed into a hole machined into a copper type M pipe coupon of ¼” nominal diameter and height of 2.0 in (Figure 4-2, right). All other aspects of exposure were the same for this sample. If anything, the brass galvanically connected to the copper had 14% more surface area exposed to the water, since no epoxy was used on the bottom surface.

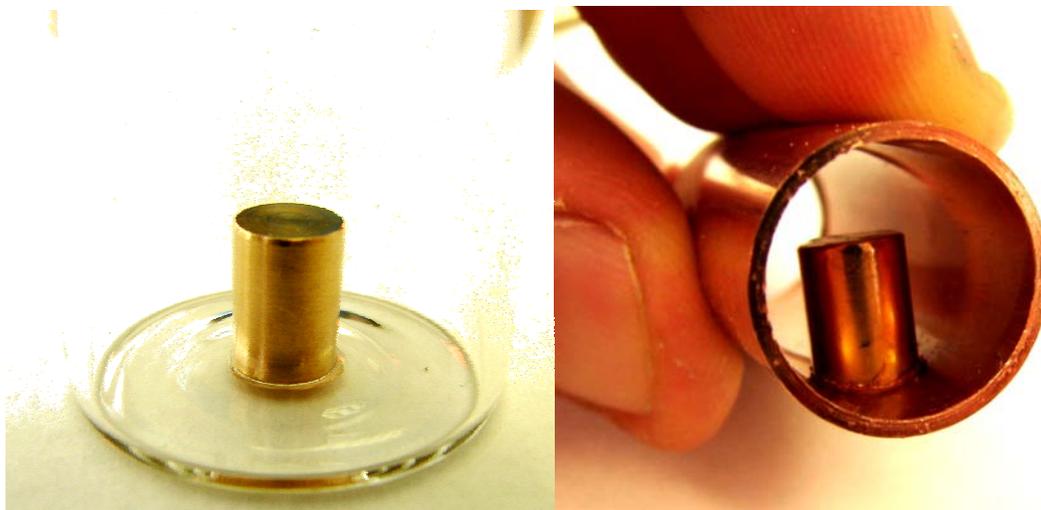


Figure 4-2: Experimental Setup for 5% leaded brass. Non-galvanic brass coupon epoxied to the bottom of glass vial (left), and brass coupon galvanically connected to type M copper tube (right).

Solder wire (50:50 lead:tin) pieces of 0.32 cm (0.125 in) diameter and 2.2 cm (0.854 in) height were epoxied to the bottom of a 46 mL vial (Figure 4-3, left), which was then filled halfway up with 25 mL of test water. To simulate the galvanic connection between copper pipe and solder at joints, an identical piece of solder wire was melted onto the inside surface of a copper tube (Figure 4-3, right). It is estimated that the solder connected to the copper pipe had about 40% more surface area exposed to the 25 mL of test water, versus solder by itself.

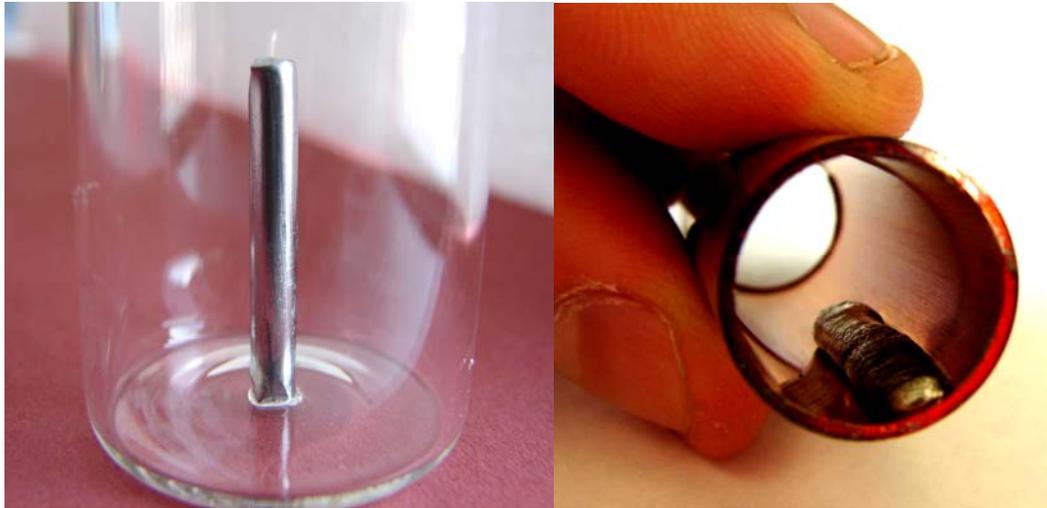


Figure 4-3: Experimental Setup for 50:50 lead:tin solder. Non-galvanic solder coupon epoxied to the bottom of glass vial (left), and solder coupon galvanically connected to type M copper tube (right).

Test water was obtained by weekly shipment of raw water from the Greenville Utilities Commission treatment plant (Greenville, NC). Collected water was separated and subjected to two simulated treatments that were otherwise identical except for the type of coagulant used. Treatment involved coagulation with PACl or alum, ozonation, filtration, fluoride addition, chloramination and final pH adjustment. The pH was adjusted to the same final value, producing two waters that were otherwise identical except that one had been treated with PACl whereas the other had been treated with alum (Figure 4-4). Since PACl adds chloride to the water it increases the ratio of chloride to sulfate, whereas alum adds sulfate, thereby decreasing the ratio.

All chemicals, with the exception of ozone which was produced on site, were provided by the Greenville treatment plant. Doses, timing of addition and duration of treatments were selected to simulate, to the extent possible at bench-scale, the full-scale treatment practice (Table 4-2). Tests of finished water UV_{254} at bench scale compared favorably to those at full-scale, providing some reassurance that the simulated treatment was successful. Slightly more UV_{254} was removed by alum

coagulation due to the lower coagulation pH inherent for that chemical relative to PACl.

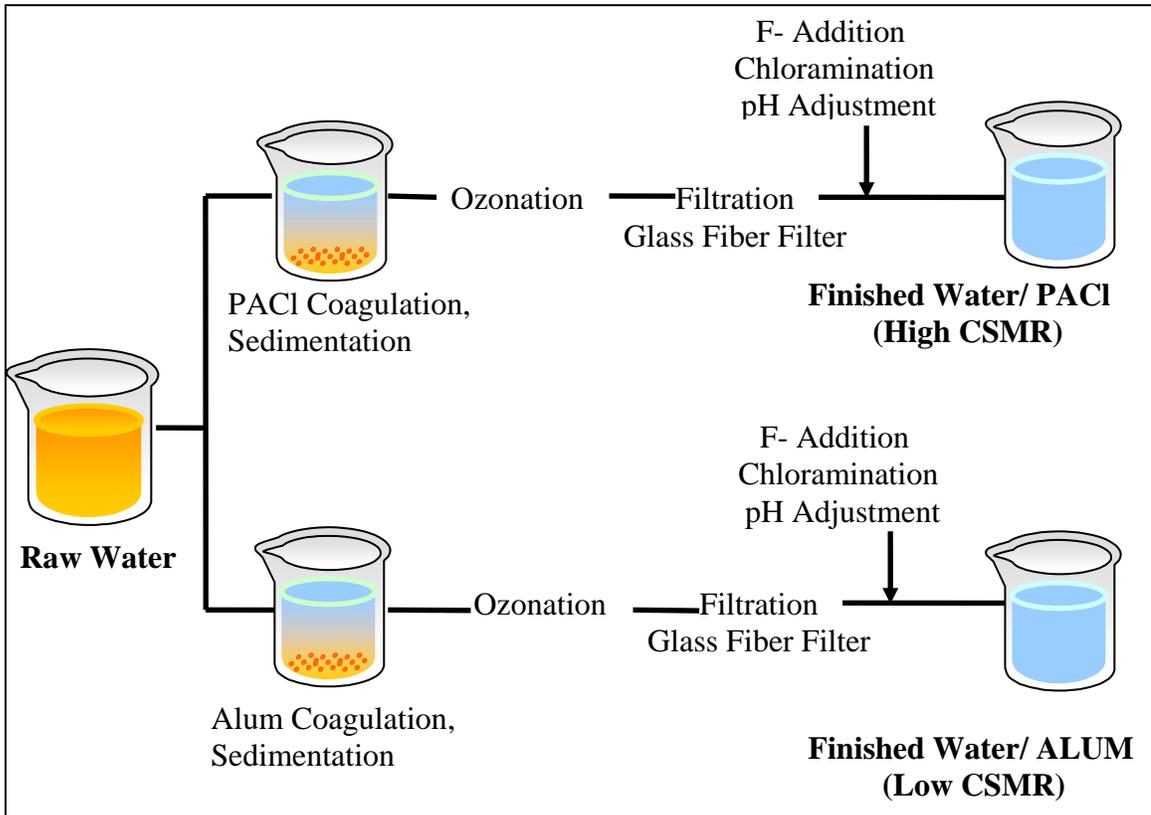


Figure 4-4: Simplified schematic of water treatment performed in the lab. Half of the raw water was treated with PACl as coagulant whereas the other half with alum, resulting in two finished waters with different chloride to sulfate mass ratios.

Table 4-2: Target levels for major water quality parameters and treatment chemicals.

PACl	14.3 mg/L
Alum	28 mg/L
H ₂ SiF	1.0 mg/L
Ozone (Primary Disinfectant)	1.5 mg/L
NH ₂ Cl (Secondary Disinfectant)	3.4-3.7 mg/L as Cl ₂
Ortho-P	1.0 mg/L as P
UV Reduction of finished water compared to raw water (at 254 nm)	90%
Final pH	7.6-7.8

Each water was then subjected to four different levels of corrosion control including: 1) No Inhibitor, 2) Orthophosphate dosed at 1.0 mg/L as P (current Greenville treatment), 3) Orthophosphate dosed at 1.0 mg/L as P and zinc dosed at 0.5 mg/L as Zn⁺², and 4) Zinc dosed at 0.5 mg/L as Zn⁺².

Exposure of the plumbing materials to water was via a “fill and dump” protocol three times per week (Monday/Wednesday/Friday). The water from each test condition was collected throughout the week and the composite was analyzed for metals. All glass vials were kept out of light throughout the testing period and each test was performed in triplicate. Metals analysis was performed via Induced Coupled Plasma Mass Spectrometry (ICP-MS). In addition to metals analysis, pH measurements were taken for water near the brass and copper surfaces using an MI-406 flat membrane pH microelectrode (Microelectrodes, Inc). Comparative bulk water pH measurements were taken at the same time.

RESULTS AND DISCUSSION

The experimental results are presented in five sections organized according to the research goals, after which field studies are reviewed and conclusions are drawn.

Role of Galvanic Connection and Exposure Time. Comparing lead release from samples with and without a connection to copper pipe provides direct insight to galvanic effects. For brass, the enhancement to lead leaching resulting from the galvanic connection was 52% in the water with high CSMR only during the first week of testing. Surprisingly, in all other conditions and times, the galvanic connection *reduced* lead leaching from the brass (Figure 4-5). Brass is close to copper in the electrochemical series and, in exceptional circumstances, brass can even be cathodic to copper, in which case the galvanic connection reduces lead leaching in theory and in practice (Dudi *et al.*, 2005, Triantafyllidou & Edwards, 2006). This might have been the case herein, since the galvanic connection between brass and copper reduced lead leaching by a factor of 4 times (= 4X) at high CSMR to 7 times (= 7X) at low CSMR, for average data from weeks 5-11 of the experiment (Figure 4-6). Alternatively, we speculate that the higher copper levels in the water from the presence of the copper pipe were somehow beneficial to lead leaching from the brass (Cu, Zn, Pb alloy). Lead release from brass dropped markedly (by up to 8X) after the first week of exposure (Figure 4-5).

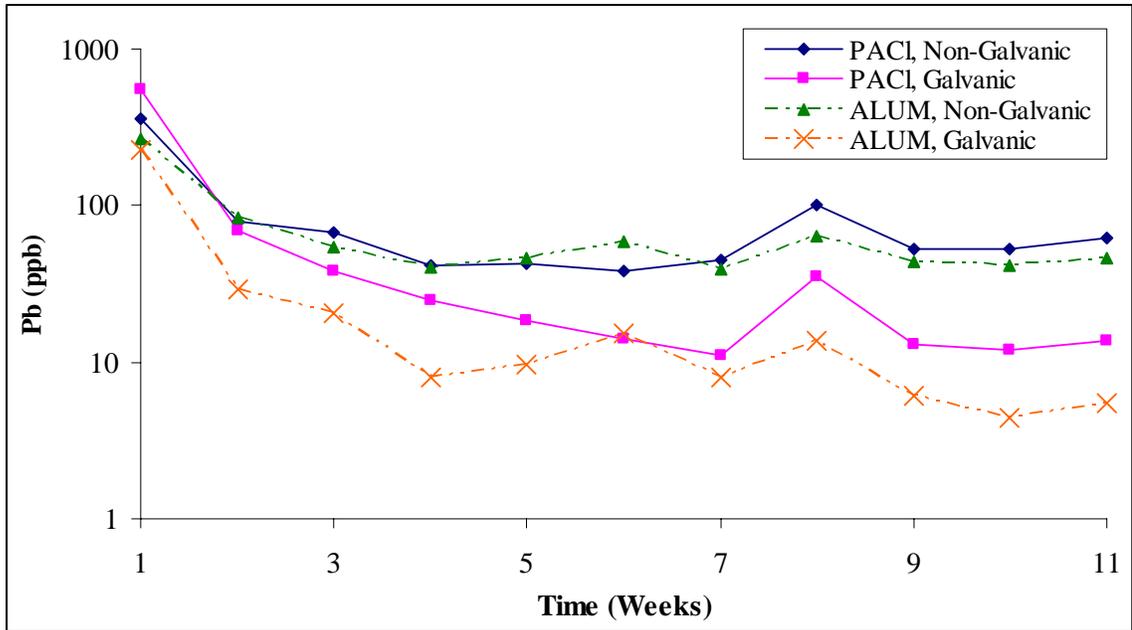


Figure 4-5: Lead release (log-scale) versus time for galvanic and non-galvanic brass samples, when no inhibitor was added to the water (control condition).

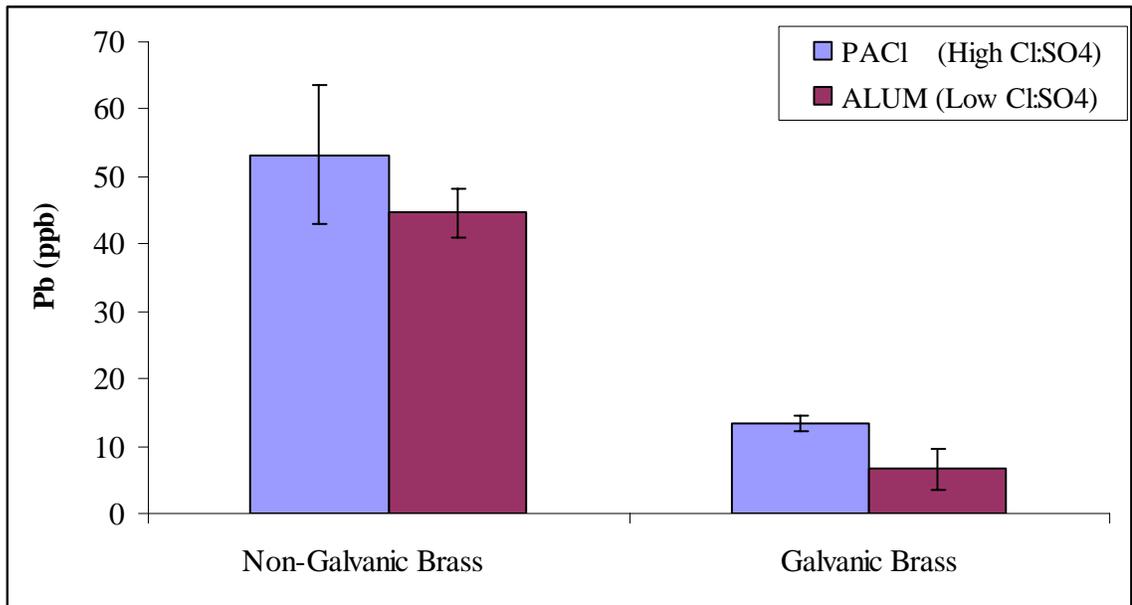


Figure 4-6: Effect of galvanic connection on lead release from brass, in PACl-treated water versus alum-treated water, when no inhibitor was added to the water (control condition). The values reported are averaged from weeks five through eleven of the experiment. The error bars represent 95% confidence intervals.

In the case of solder alone, lead leaching was increased by 6X (low CSMR) to 16X (high CSMR) due to the galvanic connection over the duration of the study (Figure 4-7, 4-8). The greatest enhancement to leaching from the connection to copper (66X) occurred during week one and for the high CSMR water, with 14,400 ppb lead

released in the galvanic connections versus 220 ppb in solder alone. Indeed, the water exposed to the solder galvanically connected to copper became very turbid, whereas turbidity was not visually observed for solder alone (Figure 4-9). By week two the galvanic enhancement was 27X for the high CSMR condition (low sulfate) and 4X for the low CSMR (high sulfate). This is consistent with the observation of others (Oliphant, 1983; Peters, 1985) that waters with high sulfate passivate galvanic attack for lead. It may also explain the rapid passivation observed by Reiber (1991, 2005). However, in the water with high CSMR the galvanic effect was much more sustained, since the lowest observed enhancement to lead leaching was 14X, during weeks five and nine of the experiment.

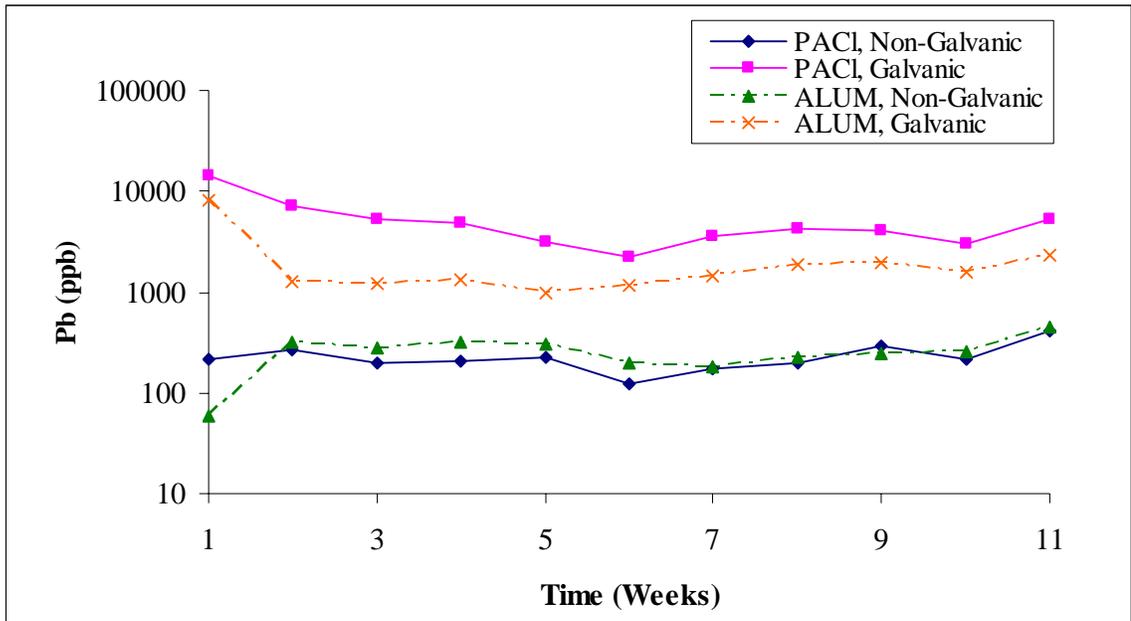


Figure 4-7: Lead release (log-scale) versus time for galvanic and non-galvanic solder samples, when no inhibitor was added to the water (control condition).

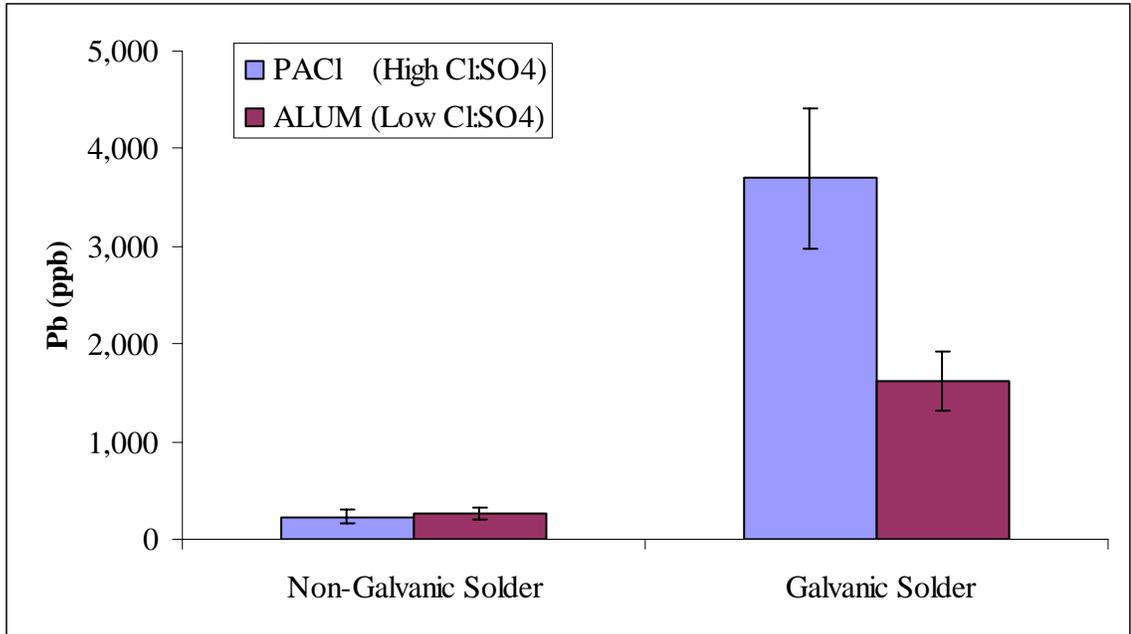


Figure 4-8: Effect of galvanic connection on lead release from solder, in PACI-treated water versus alum-treated water, when no inhibitor was added to the water (control condition). The values reported are averaged from weeks five through eleven of the experiment. The error bars represent 95% confidence intervals.



Figure 4-9: Turbid PACI-treated water after exposure to galvanic solder during week one of experiment (left), and clear PACI-treated water after exposure to solder alone (right), for the no inhibitor condition.

Effect of CSMR and inhibitors on lead leaching from solder galvanically connected to copper. The experimental condition that was most affected by the chloride to sulfate ratio was when orthophosphate was added to the water. For that condition, during week one of the experiment more than 19,000 ppb lead was released in the PACl-treated water, whereas 490 ppb were released in alum-treated water. By the ninth week, solder released just 4 ppb in the alum-treated water, whereas it released 482 ppb lead in the PACl-treated water (Figure 4-10).

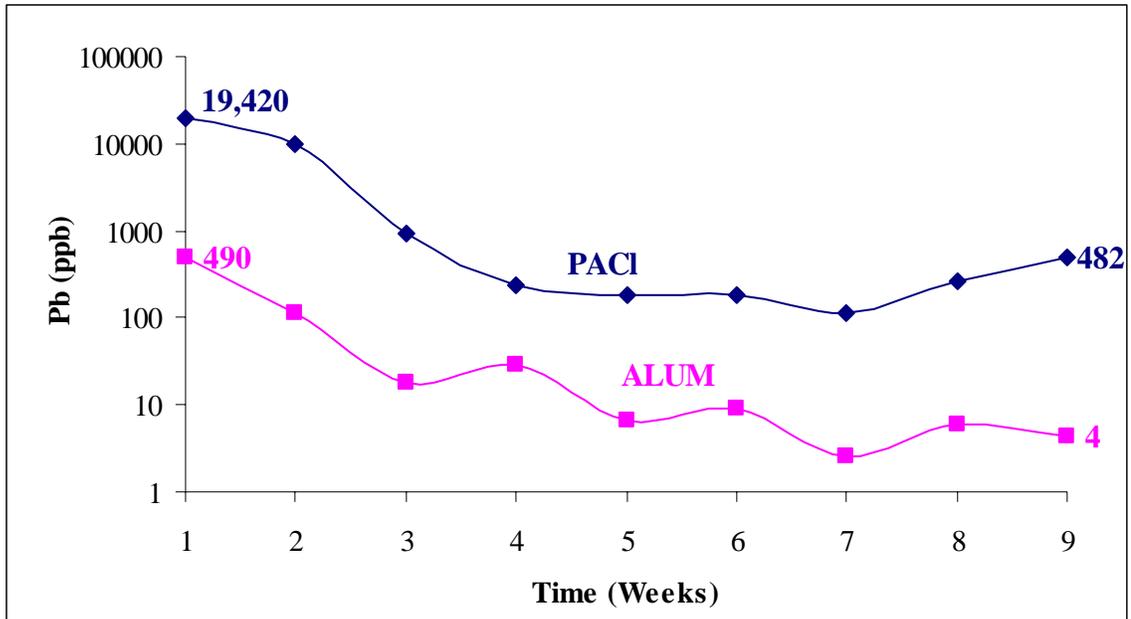


Figure 4-10: Lead release (log-scale) versus time for galvanic solder and for the orthophosphate condition, in PACl-treated water versus alum-treated water. Results presented are for the least aggressive sample out of the triplicate set, which was monochloraminated throughout the study.

In order to directly compare the relative effect of higher CSMR for each water tested, a lead leaching ratio $R_{(Pb)}$ was calculated:

$$R_{(Pb)} = \frac{\text{Pb Release in PACl - Treated Water (High CSMR)}}{\text{Pb Release in ALUM - treated Water (Low CSMR)}} \quad \text{Equation (2)}$$

From this perspective the PACl-treated water typically increased lead leaching by 1.5-3X relative to alum treated water. When the orthophosphate inhibitor was added to the water, a much more dramatic difference of 40X on average was noted for the duration of the study (Figure 4-11).

Generally speaking, the inhibitors were ineffective in countering the adverse effects of higher CSMR in PACl-treated water. The exception was the condition with zinc orthophosphate, for which alum-treated water had higher lead leaching in 5 out of 11 weeks of testing ($R_{(Pb)} < 1$ in Figure 4-11).

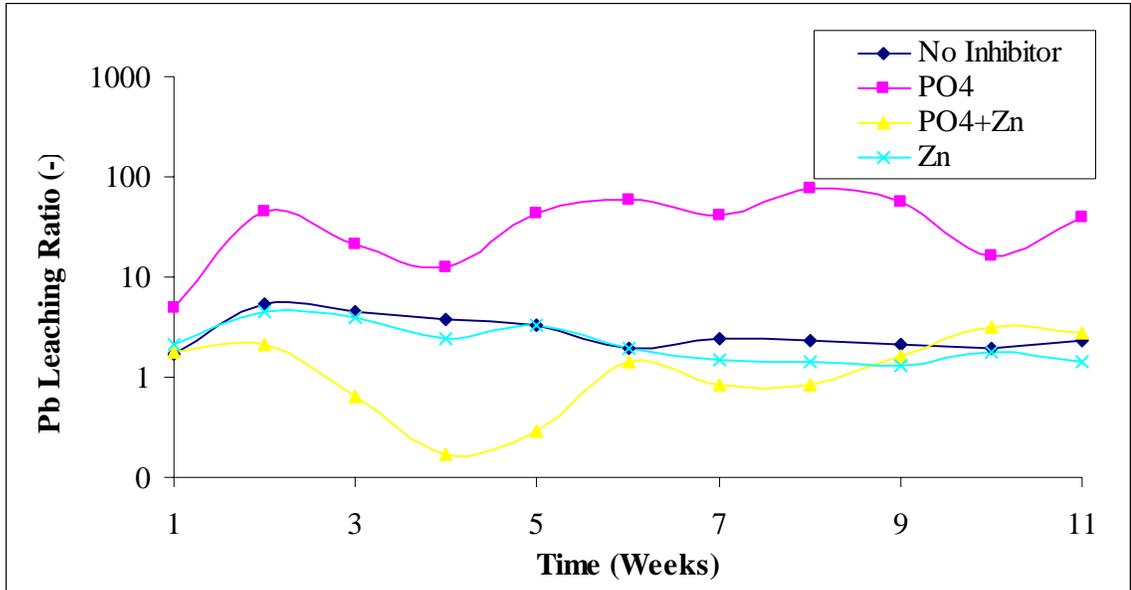


Figure 4-11: Lead leaching ratio versus experimental time, for galvanic solder.

Indeed, in weeks five through nine the higher CSMR did not increase lead leaching when zinc orthophosphate was used (Figure 4-12). Orthophosphate alone was most effective in reducing the concentration of lead leached among the inhibitors tested, regardless of CSMR (Figure 4-12). Zinc orthophosphate was the second most effective treatment in reducing lead leaching and zinc alone was the least effective treatment.

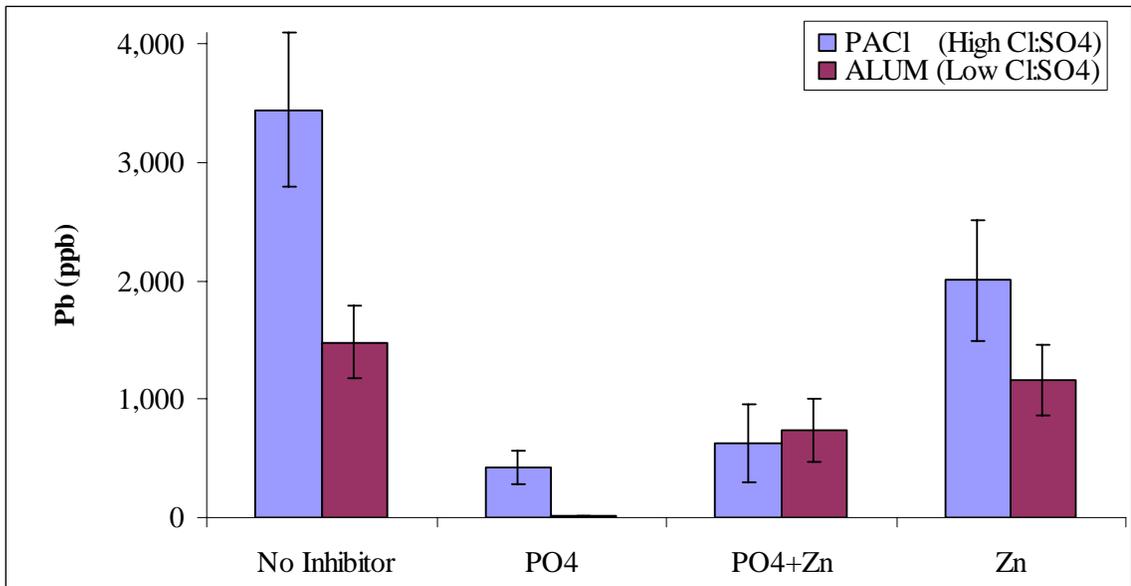


Figure 4-12. Lead release versus corrosion control treatment for galvanic solder, in PACl-treated water and alum-treated water, averaged from weeks five to nine of the experiment. The error bars denote 95% confidence intervals.

These findings are not consistent with expectations based on prior work (Oliphant, 1983; Gregory and Gardiner, 1985) which measured galvanic corrosion but did not measure lead leaching. These previous studies found orthophosphate ineffective and zinc effective in reducing galvanic current/voltage. This may reinforce the importance of directly measuring lead leaching to water. Future work should consider this potential discrepancy in greater detail.

Effect of CSMR and inhibitors on lead leaching from brass galvanically connected to copper. When comparing PACl and alum treatments for both the no inhibitor and orthophosphate cases, PACl-treated water was generally more aggressive towards lead release by about 50% in the long-term (Figure 4-13). When Zn^{+2} was the inhibitor the exact opposite effect was observed, in that the water treated with alum proved to be more corrosive as evidenced by an average of 50% more lead in the water versus PACl treatment. For the case of zinc orthophosphate there was no difference between PACl and alum treatments (Figure 4-13). Even though the above trends were observed for the case of galvanic brass between PACl and alum treatments, they were not significant at 95% confidence (Error bars plotted, Figure 4-13).

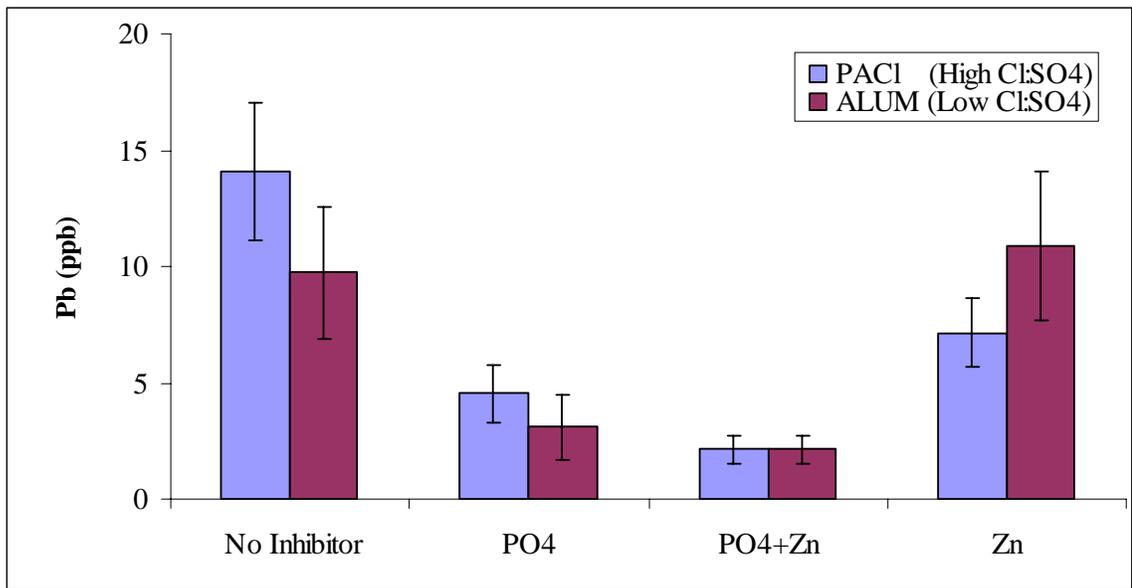


Figure 4-13: Lead release versus corrosion control treatment for galvanic brass, in PACl-treated water and alum-treated water, averaged from weeks five to nine of the experiment. The error bars denote 95% confidence intervals.

When comparing the different corrosion inhibitors and regardless of coagulation chemical, addition of zinc orthophosphate was the most effective corrosion control strategy for brass connected to copper, versus all others. Addition of orthophosphate alone was the second most effective condition, whereas addition of zinc alone was the least effective. The control condition without inhibitor was the most aggressive (Figure 4-13).

Mechanistic Insights via pH Microelectrode Measurements. Measurement of pH provided mechanistic insight to the observed trends. All pH measurements were taken after 48 hours of exposure to the test waters during week eleven. Measurements of pH were taken near the surface of brass and solder (within 1 mm from the surface), near the surface of the copper tube which served as the battery cathode in the galvanic samples, and in the bulk water for all conditions.

For brass, the galvanic connection dramatically reduced or had no effect on lead leaching for all the waters tested. Not surprisingly, measurements of brass and copper surface pH showed very little difference. Most differences were not significant at 95% confidence and the largest difference was only 0.3 pH units (Figure 4-14). In addition, for the one type of brass tested in this study, there was little difference between the pH on the surface of brass with and without a galvanic connection to copper (Figure 4-14). In general, measurements of pH at the surface of the brass detected lower pH than at the surface of copper, which tends to support the fact that the brass was slightly anodic to copper at this point of the experiment.

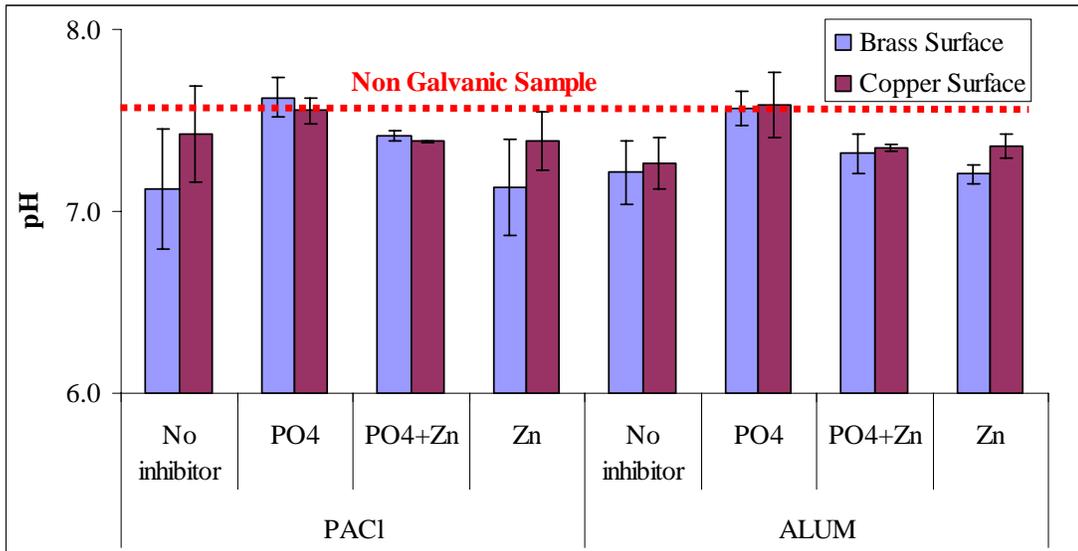


Figure 4-14: Local pH measurements for the 5% leaded brass samples, galvanically connected to copper pipe, after 48 hours of exposure. The error bars denote 95% confidence intervals. The red line represents the average pH for the non-galvanic brass sample.

In the case of solder dramatic differences were apparent consistent with the hypothesis of Dudi *et al.* (2005). In every case tested the pH near the surface of the solder anode was lower than near the surface of the copper cathode at > 95% confidence (Figure 4-15). From an initial bulk water pH of 7.6-7.8, the pH near the surface of the solder without copper present dropped to 6.1, whereas the pH near the surface of the solder in galvanic samples dropped to as low as 3.4 for PACI-treatment (zinc inhibitor), and as low as 4.4 for alum treatment (zinc orthophosphate inhibitor) (Figure 4-16). These lower pHs would markedly enhance lead leaching and decrease passivation of the solder connected to copper.

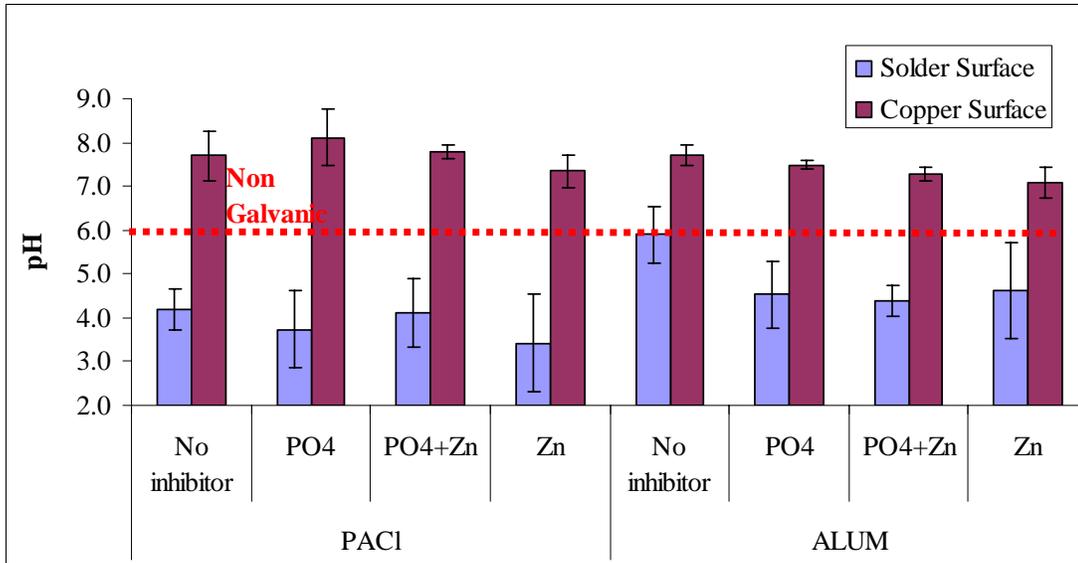


Figure 4-15: Local pH measurements for the solder samples galvanically connected to copper pipe, after 48 hours of exposure. The error bars denote 95% confidence intervals. The red line represents the pH of water close to the solder surface of the non-galvanic sample.

Aside from contribution of pH drop to lead leaching, other factors are obviously involved because the trend in pH (lowest for orthophosphate and highest for no inhibitor) (Figure 4-16) was inconsistent with the expected trend based on lead leaching. These factors probably include 1) type of solids formed at the anode and cathode, 2) differential formation of soluble lead Cl^- complexes at the anode, and 3) magnitude of the galvanic current between the anode and cathode. In any case, the preliminary pH measurements do reinforce the key role of pH reduction near the anode and warrant further investigation.

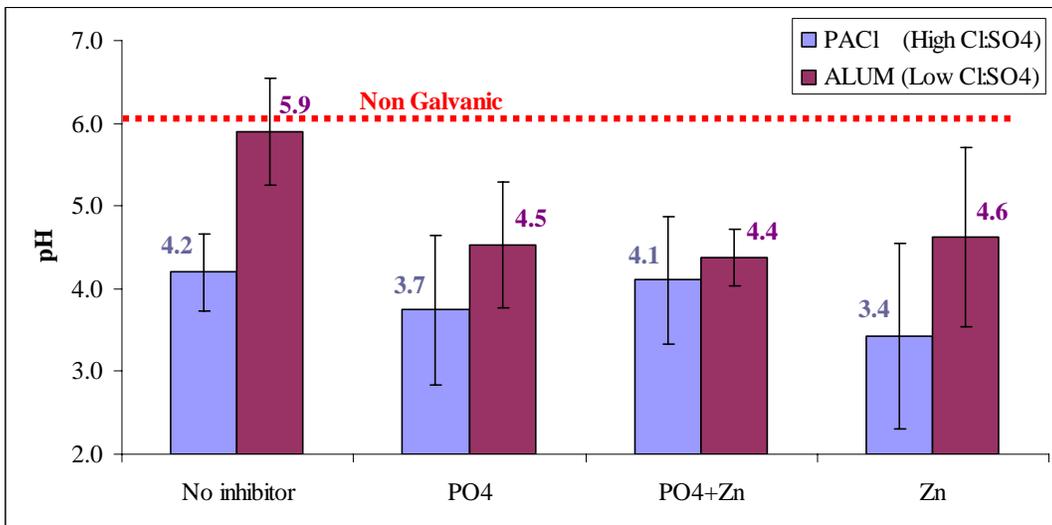


Figure 4-16: Local pH measurements on the surface of solder galvanically connected to copper. The measurements were taken after 48 hours of exposure to PACI- treated and alum-treated waters. The error bars denote 95% confidence intervals. The red line represents the pH of water close to the solder surface of the non-galvanic sample.

Preliminary Testing of Inhibitor Dose and Disinfectant Effects

After the above trends were clearly established, limited testing was conducted to determine whether disinfectant type and inhibitor dose had significant effects on lead release. These tests were short-term and were not performed in triplicate, but trends may be of interest to the water industry until more decisive data are collected.

Effect of Disinfectant Type on Lead Release. After week four of the experiment, the sample tending to leach the most lead from solder in each triplicate set of samples was identified. For that sample, free chlorine was henceforth dosed to this water rather than monochloramine at a concentration of 3.4-3.7 mg/L as Cl_2 . In a similar way, after week eight of the experiment, the sample leaching the second most lead from each triplicate set was identified, and was henceforth exposed to water with no disinfectant. In this manner the short-term effect of disinfectant type could be determined.

In all tests with leaded solder, chlorine inhibited lead release compared to monochloramine over a two week time period. This positive effect was transient and seemed to disappear by the end of the study. By the third week of chlorine dosing, the sample was again leaching the most lead out of the triplicate set. The switch from monochloramine to no disinfectant did not appear to alter trends in lead leaching for this condition (Figure 4-17).

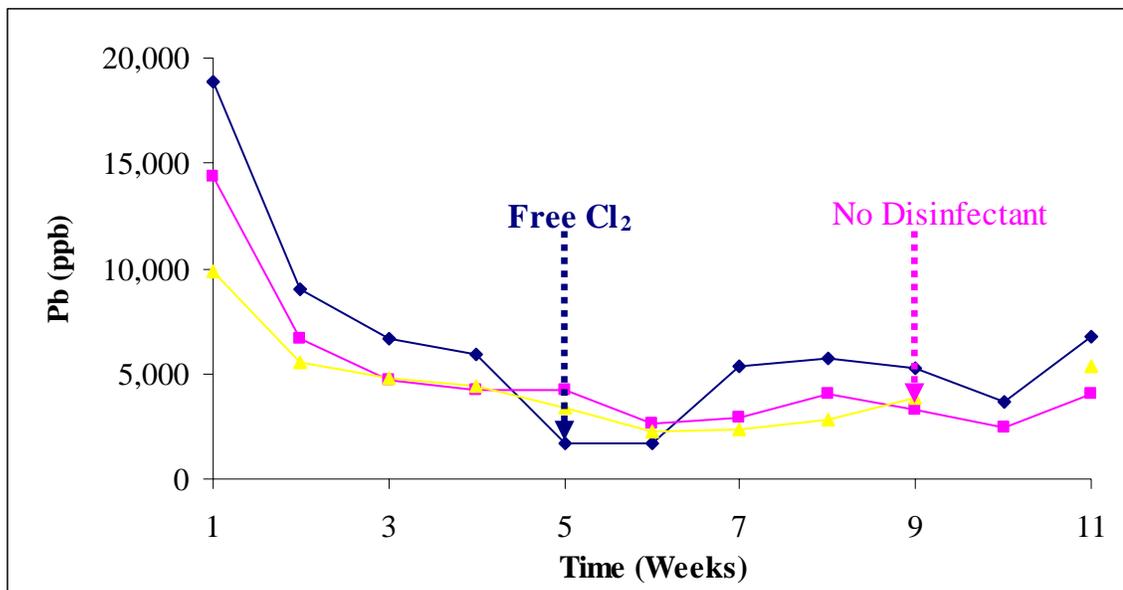


Figure 4-17: Lead release versus time for galvanic solder, in PACl-treated water and for the no inhibitor condition. Each line represents each of the triplicate samples tested, for which modifications were made on disinfectant type (yellow line: monochloramine throughout, blue line: free chlorine from week 5 and on, pink line: No disinfectant from week 9 and on).

The same interesting and short-term benefits of chlorine were noted in the low CSMR water treated by alum in this study (Figure 4-18).

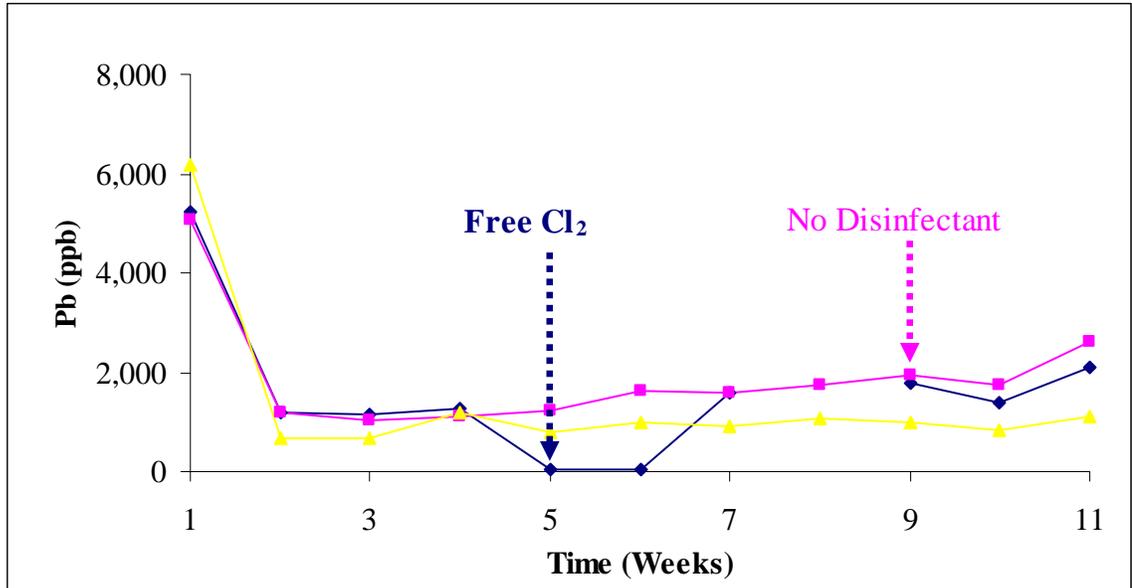


Figure 4-18: Lead release versus time for galvanic solder, in alum-treated water with zinc inhibitor. Each line represents each of the triplicate samples tested, for which modifications were made on disinfectant type (yellow line: monochloramine throughout, blue line: free chlorine from week 5 and on, pink line: No disinfectant from week 9 and on).

Effect of Orthophosphate Dose on Lead Release. At the time this laboratory study was conducted, treatment at the Greenville plant included addition of an orthophosphate corrosion inhibitor to the water. This condition was simulated in the lab by adding the exact same chemical at the same dose of 1.0 mg/L as P (or else 3.0 mg/L as PO_4^{3-}) in the water. In order to assess whether a reduced dosage would still reduce lead release, the orthophosphate dose was cut in half during the last two weeks of the experiment. The same change was implemented in the zinc orthophosphate condition, where zinc dosage remained the same but orthophosphate was dosed at 0.5 mg/L as P, for the last two weeks of testing. During the first week of reduction in the phosphate dosage (week 10), lead release from galvanic solder did not greatly change. During week 11 however, the lead levels doubled in water treated with PACl. During the same week, the lead levels went up 8X in the water treated with alum and orthophosphate, and by a factor of 4X for alum treatment and zinc orthophosphate addition (Figure 4-19). The implication is that lead levels increase when orthophosphate dose is reduced by 50% over the short-term.

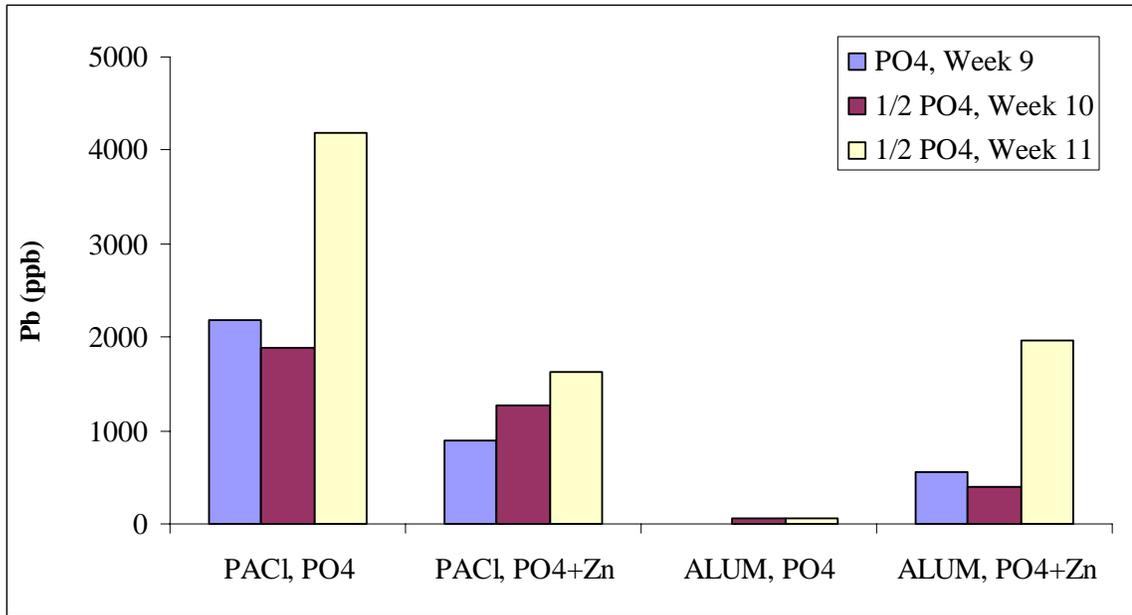


Figure 4-19: Effect of orthophosphate dose on lead release from galvanic solder.

PART 2: REAL WORLD IMPLICATIONS/CASE STUDIES

The knowledge gained from the literature synthesis and experiments presented herein were applied to instances where lead spiked in US drinking water. In all of these cases, changes in coagulant type during water treatment were made prior to the lead spikes, resulting in a higher CSMR.

Stafford, Virginia

The County of Stafford, VA has two water treatment plants that successfully used phosphate corrosion inhibitors (orthophosphate or ortho/poly blend) since 1984. All homes in the utilities' LCR monitoring program were built with lead solder. 90% 'ile lead was below the detection limit of 2 ppb in LCR monitoring in 1998 and 2000. Indeed, the highest first draw sample collected in 1998 was 4 ppb, and every sample collected in 2000 was below the detection limit for lead.

Treatment changes were made to comply with new disinfection by-product regulations. Specifically, in April 2003 one of the treatment plants switched from alum to ferric chloride coagulant to meet new disinfection by-product regulations, whereas the other plant continued to use alum. Both treatment plants changed from free chlorine to chloramine in February of 2004. In LCR monitoring conducted in summer of 2003, 38% of samples contained detectable lead (12 of 32), 16% of samples were over the 15 ppb action limit and 90% 'ile lead was 40 ppb. The highest first draw lead was 68 ppb. All of the samples with detectable lead came from the part of the distribution system that was served by water from the treatment plant which switched from alum to ferric chloride.

The utility increased their orthophosphate inhibitor dose and in summer 2004, 46% of samples had detectable lead and 90% 'ile lead was 54 ppb. The highest sample contained 441 ppb in the LCR monitoring pool. As before, all samples with detectable lead were from parts of the distribution system served with water with ferric chloride coagulant. Clearly, the seemingly innocuous change in coagulant type triggered a lead problem in part of the distribution system. All LCR monitoring at this utility instructed consumers to "DO NOT remove screens or aerators from tap before collecting sample," which might be important in detecting problems with particulate lead solder as noted previously in this thesis (Triantafyllidou, 2006).

The coagulant switch from alum (aluminum sulfate) to ferric chloride decreased the sulfate concentration of finished water from about 30 mg/L to 8 mg/L, whereas chloride increased from 10 to 38 mg/L. More specifically, the CSMR of the water supply was 0.29-0.38 in 2001-2002 with alum, and changed to 4.75 in 2003 using ferric chloride, an increase of 12.5X. In other words, when alum was used this ratio was well below the threshold of 0.58, which was reported by Dodrill *et al.* (1995) to be relatively non-aggressive to lead leaching, and it was far above the threshold after

the change. Analysis of the problem strongly suggested that the increase in CSMR had triggered the lead problem.

A recommendation was made to change coagulant from ferric chloride to ferric sulfate in order to reduce the ratio of chloride to sulfate in the water, while maintaining high level removal of disinfection by-product precursor material in this water (Edwards, 2004). After making this change in August of 2004, test samples collected in October of 2004 revealed non-detectable lead in all but two sites in the distribution system. One of the samples with detectable lead of 11 ppb came from a tap that had produced water with 441 and 718 ppb lead previously, when ferric chloride was used. When LCR testing was conducted in December of 2004, the 90%ile lead dropped to 11 ppb. More significantly, every home that was sampled before the coagulant change with first draw lead above 10 ppb had lower lead after the coagulant change (Figure 4-20). The minimum decrease was 70% in these homes and the average reduction was 87%. The 90%ile lead dropped back to 3 ppb by the first half of 2005.

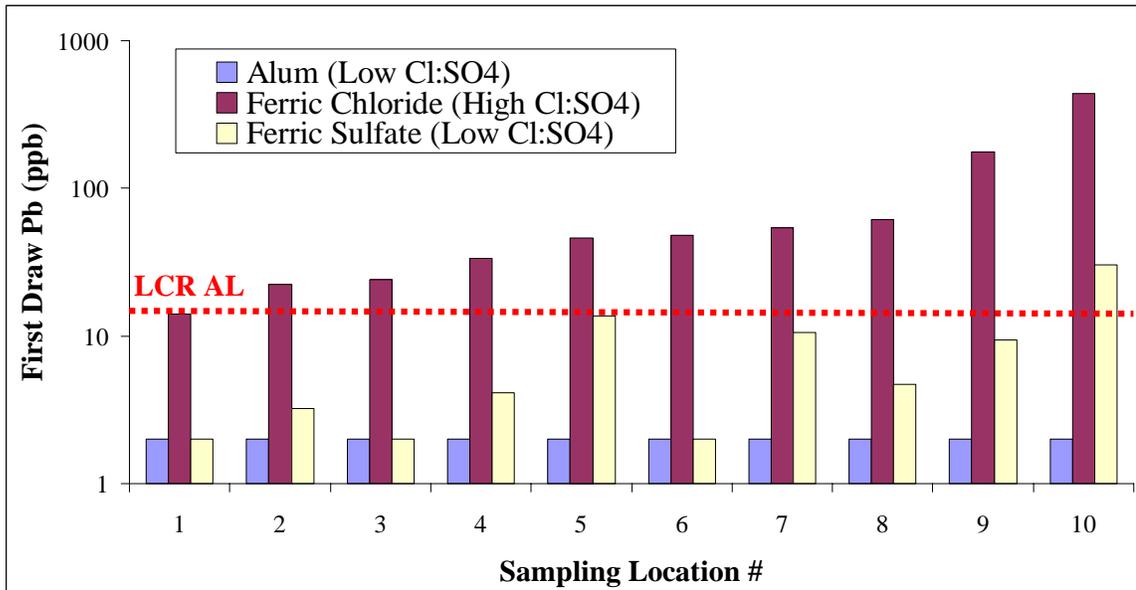


Figure 4-20: First draw lead sampling under the Lead and Copper Rule in Stafford County, VA for different coagulants employed. Lead measurements for alum-treated water and for all locations are actually below the 2 ppb detection limit that is reported on this graph.

Durham, North Carolina

The City of Durham, NC is supplied with potable water from two treatment plants. Based on EPA LCR monitoring Durham would be classified as a city without a lead corrosion problem, as evidenced by the 90%ile lead level of < 3 ppb in 2004. During an environmental assessment in the apartment of a lead poisoned child however, water was tested with 837 ppb lead in a 100 mL sample (Gronberg, 2006; Biesecker, 2006; Clabby, 2006) Worrisome levels of lead were detected throughout the

apartment complex and in other nearby buildings. Specifically, 13 of 51 apartments in the complex and 11 of 19 locations within a half-mile radius from that location had lead above the action level.

A site visit was conducted with a specialized sampling protocol in the apartment building and other nearby buildings. That work demonstrated that lead solder particles trapped in the aerator were a key source of lead, as was the case in the Greenville site investigation. Dependent on how samples were collected (e.g. flowrate, with/without the faucet aerator) potentially serious problems with lead could be missed (Edwards *et al.*, 2006). Water samples collected during the site visit also revealed a high chloride to sulfate ratio of 5.0.

In 2002, the coagulant chemical was changed from alum to ferric chloride at the Brown treatment plant. This change in treatment practice increased the chloride level of finished water from 9.8 mg/L in 2000 to 35.6 mg/L in 2005, while simultaneously decreasing the sulfate level from 22 mg/L in 2000 to 5 mg/L in 2005 (Table 4-3). The resulting CSMR ratio of finished water was therefore increased 16X (0.44 before the switch to as high as 7.1) and exceeded the threshold level identified by Dodrill *et al.* (1995) and Oliphant (1983) as necessary to trigger galvanic corrosion of solder. There was little doubt that the apartment complex in question was receiving water primarily from the plant using ferric chloride, based on measured levels of chloride and sulfate at the site, the utilities' conception of water flow through the distribution system, and the low reported ratio of chloride to sulfate at the other treatment plant of 0.42-0.46. Chloramines had also been introduced as secondary disinfectant in 2002.

Table 4-3: Chloride and sulfate levels for the two treatment plants serving Durham, NC during the years 2000 and 2005 (finished water averages). Both plants employed alum coagulation in 2000, whereas the Brown plant implemented polyaluminum chloride (PACl) coagulation in 2005.

	2000			2005		
	SO ₄ ²⁻ (mg/L)	Cl ⁻ (mg/L)	CSMR (-)	SO ₄ ²⁻ (mg/L)	Cl ⁻ (mg/L)	CSMR (-)
Brown Water Treatment Plant	22	9.8	0.44	5.0	35.6	7.1
Williams Water Treatment Plant	23	9.7	0.42	25	11.5	0.46

The site visit confirmed that all other aspects of water corrosivity, including pH and orthophosphate dose, were in an acceptable range. Although some earlier samples collected by the health department indicated pH below 7.0, these low pH values were not confirmed on the day we conducted the site visit. At least some nitrification was apparently occurring in the pipes as indicated by nitrite > 0.02 mg/L and positive BART test results for nitrifiers. While there is legitimate debate about the extent of the lead problem in the city and the impacts of sampling protocol in detecting it, to err

on the side of caution the Brown utility switched back to alum from ferric chloride in July 2006 (Clabby, 2006).

Greenville, North Carolina

The City of Greenville, NC receives its potable water from a conventional treatment plant. Sampling events under the US EPA LCR from 1992 to 2001 clearly show that the plant was easily meeting the lead action limit throughout this period (Figure 1). However, sampling in 2004 indicated a problem with lead leaching, which was reinforced by two cases of elevated blood lead attributed to lead from potable water in early 2004 (Landers, 2006; Allegood, 2005; ES & T, 2005; Norman *et al.*, 2005). Tap water from the affected child's faucet measured as high as 400 ppb lead, although lead was more commonly detected at 40-60 ppb. Greenville's main distribution system does not include lead pipes; thus, the key sources of lead in water are therefore leaded solder and leaded brass.

For the year 2004 about 22% of LCR samples contained lead above the action level. This percentage increased to 27% for the year 2005. The 90th percentile lead concentration was relatively constant at 28-30 ppb in 2004 and 2005.

Like many other utilities across the US, the Greenville water authority made a series of changes in their treatment process in order to comply with stringent federal regulations. Theoretically any of these changes, alone or in combination, could have caused the shift in water aggressiveness. The utility began using chloramines rather than free chlorine as secondary disinfectant in December 2002, in order to comply with US EPA regulations regarding DBP formation. At the same time and due to the introduction of chloramines, finished water pH was increased from about 7.2 to 7.7, in order to optimize monochloramine formation. Later on, in August 2003, the utility also switched from chlorine to ozone as primary disinfectant. Throughout these disinfection changes the plant implemented various corrosion control treatments (polyphosphate chemicals/ phosphate blend). Following exceedence of the LCR action level for lead in August 2004, the plant started dosing an orthophosphate corrosion inhibitor to mitigate the lead corrosion problems.

In addition, the plant changed its coagulant from alum (aluminum sulfate) to polyaluminum chloride (PACl) in January of 2001, in order to achieve better organic matter and turbidity removal. The switch from alum to PACl resulted in an increase of the CSMR of finished water leaving the treatment plant, as historical data clearly demonstrate (Figure 4-21). This ratio increased well above the threshold of 0.58 mentioned in the Dodrill study, after the coagulant switch. More specifically, the ratio of chloride to sulfate averaged 0.50 for the year 2000 (just before the switch), but increased by a factor of 9X and up to a value of 4.50 during the year 2003 (Figure 4-21).

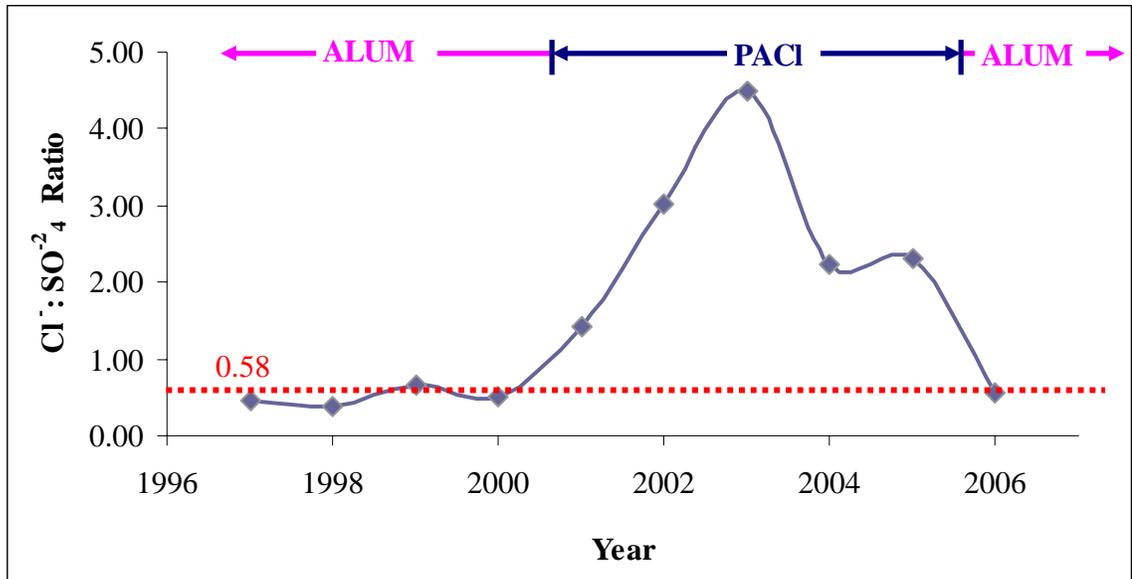


Figure 4-21: Historical plant data of chloride to sulfate ratio in Greenville, NC finished water. The numbers reported are the averages for any given year.

It should be noted that pilot tests were conducted on behalf of the utility in order to proactively examine whether the scheduled changes would increase water corrosivity. However, these bench-scale experiments examined the effect of different corrosion inhibitors and disinfectants on lead release, but did not investigate the potential effect of the coagulant since that change was deemed innocuous. The study also examined lead leaching from brass faucets, and did not examine lead leaching from solder, and with hindsight based on the experiments in this work solder was the main source of the problem.

After recommendations based on the results of the bench-scale experiments reported earlier in this paper, the utility switched the coagulation chemical back to alum in April 2006. This change reduced the CSMR to 0.55 (Figure 4-21). Limited sampling soon thereafter revealed a 38% reduction in lead levels at selected locations. In five out of seven locations, lead concentrations dropped after the switch to alum. This extent of lead reduction was verified during a much broader sampling event under the LCR, which tested water at 102 homes. The 90th percentile lead level dropped to 18 ppb within a few months after the switch back to alum (Figure 4-22). The measured 38% decrease in 90th percentile lead is roughly consistent with that observed in the limited distribution system testing.

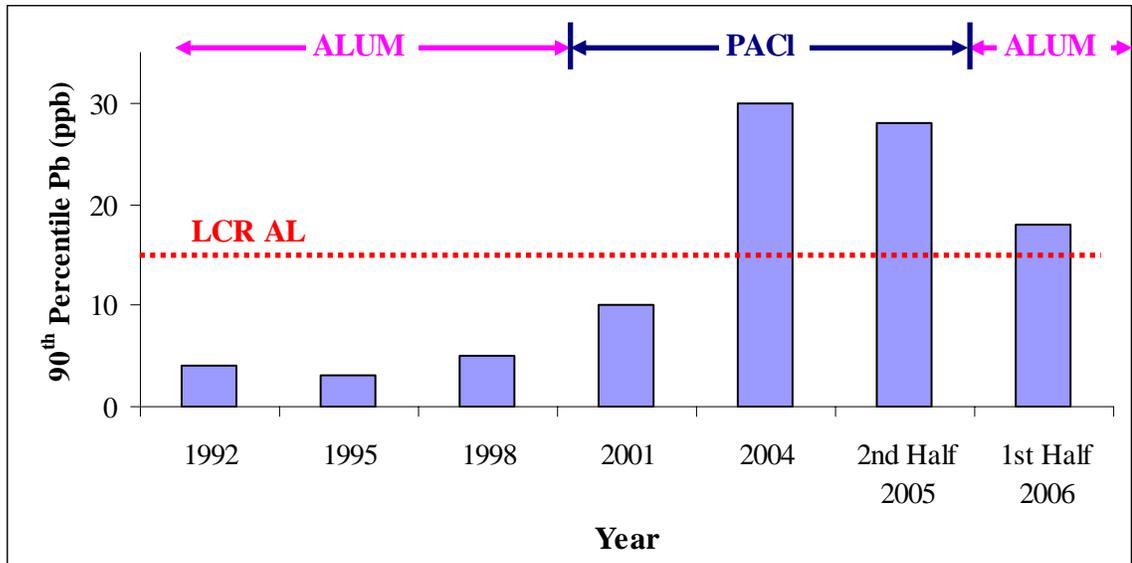


Figure 4-22: Compliance history with the LCR Action Level for lead, for Greenville, NC.

Synthesis of Case Study Findings. Galvanic corrosion of lead solder via a connection to copper can cause hazardous levels of lead in drinking water. In many instances the galvanic corrosion is of little consequence and passivates, but in other situations including -but perhaps not limited to- higher CSMR, enhancements to lead leaching cause violation of lead action limits and elevated blood lead. Even systems that are well passivated over a period of decades with orthophosphate can suddenly start to leach high levels of lead. A failure to consider this effect properly through well designed sampling programs and infrequent monitoring might allow high levels of lead to undetected for a long time period. Consistent with a hypothesis of Dudi *et al.*, (2004), problems may be most significant in source waters with relatively low levels of SO_4^{-2} and Cl^- , and in low alkalinity finished waters (Table 4-4).

Table 4-4: Summary of key water quality parameters, CSMR and LCR lead monitoring for the three US utilities examined in-depth in this study.

CASE STUDIES SUMMARY					
Name	Finished Water pH	Alkalinity (mg/L CaCO_3)	Corrosion Inhibitor	CSMR Range before/after	90 th ile lead before/after (ppb)
Stafford, VA	7.8	20	Orthophosphate	0.29-0.38/ 4.75	BDL*/ 40-54
Durham, NC	7.1-8.2	17-34	Orthophosphate	0.44/ 7.1	<3 after, but lead poisoning
Greenville, NC	7.5-8.0	12-35	Orthophosphate	0.50/ 1.42-4.50	<10/ 28-30

*BDL stands for below detection limit levels

CONCLUSIONS

Under well-controlled experiments that lasted for eleven weeks:

- Waters with high CSMR were consistently more aggressive in increasing lead leaching from solder galvanically connected to copper. Although orthophosphate reduced the extent of lead leaching, the adverse effects of higher CSMR were dramatic (e.g., 40X higher lead) even when phosphates were present. Zinc orthophosphate did counter the adverse effects of higher CSMR, whereas zinc alone had little effect.
- Waters with higher CSMR caused increased corrosion from brass. Dosing of phosphate did not mitigate the adverse effects of higher CSMR on lead leaching, whereas zinc orthophosphate or zinc did.
- Regardless of CSMR, orthophosphate was the most effective treatment in the case of galvanic solder, and zinc orthophosphate in the case of galvanic brass.
- The galvanic connection of solder to copper markedly increased lead release to the water under all conditions tested for a period of almost three months in the lab. The pH close to the solder surface dropped significantly from the neutral range to as low as 3.4 and 4.4 for the high and low CSMR waters, respectively. This reiterates the importance of the pH drop at the anode in sustaining galvanic corrosion and increasing lead leaching, even though other factors may be involved as well.
- The galvanic connection of brass to copper markedly decreased lead leaching over the long term for the one type of brass tested. The extent of the pH drop at the surface of brass (connected to copper) was relatively low.
- Free chlorine decreased lead release from solder galvanically connected to lead, but only for a short period of time in this study.
- Lead leaching from solder galvanically connected to copper worsens when phosphate dose is reduced from 1 mg/L as P to 0.5 mg/L as P.
- Field data demonstrates that changes in coagulants containing sulfate to those containing chloride can increase CSMR, which in turn, can create a lead hazard in water. The problems can arise even in systems in which solder has been passivated over a period of decades with orthophosphate inhibitor. Preliminary data and theory suggest that lead leaching is most sensitive to coagulant type when treating waters with relatively low Cl^- and SO_4^{2-} , since potential changes in CSMR are most significant in these situations. Lower alkalinity might also be an important factor, since low buffering capacity will increase the magnitude of the pH drop at the lead anode.

The effects of the chloride to sulfate mass ratio on lead release into drinking water are currently underappreciated and understudied. The work presented herein is a first step in filling some of the research gaps associated with the CSMR. Further research needs include providing an in-depth assessment of galvanic corrosion mechanisms that can create lead hazards. The issue of copper connected to lead pipe is also of interest.

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