

Effects of fluoridation and disinfection agent combinations on lead leaching from leaded-brass parts

Richard P. Maas^a, Steven C. Patch^{a,*}, Anna-Marie Christian^a, Myron J. Coplan^b

^aEnvironmental Quality Institute, The University of North Carolina-Asheville, One University Heights, Asheville, NC 28804, United States

^bIntelleguity, Natick, MA, United States

Received 1 March 2006; accepted 13 June 2007

Available online 30 June 2007

Abstract

This study concerns effects on water-borne lead from combinations of chlorine (CL) or chloramines (CA) with fluosilicic acid (FSA) or sodium fluoride (NaF). CL is known to corrode brass, releasing lead from plumbing devices. It is known that CA and CL in different ratios with ammonia (NH) mobilize copper from brass, which we have found also enhances elution of lead from leaded brass alloys. Phase I involved leaded-brass 1/4 in. elbows pre-conditioned in DI water and soaked in static solutions containing various combinations of CL, CA, FSA, NaF, and ammonium fluosilicate. In Phase II 20 leaded-brass alloy water meters were installed in pipe loops. After pre-conditioning the meters with 200 flushings with 1.0 ppm CL water, seven different solutions were pumped for a period of 6 weeks. Water samples were taken for lead analysis three times per week after a 16-h stagnation period. In the static testing with brass elbows, exposure to the waters with CA + 50% excess NH₃ + FSA, with CA and ammonium fluosilicate, and with CA + FSA resulted in the highest estimated lead concentrations. In the flow-through brass meter tests, waters with CL + FSA, with CL + NaF, and with CL alone produced the highest average lead concentration for the first 3-week period. Over the last 3 weeks the highest lead concentrations were produced by CL + NaF, followed by CL alone and CA + NH₃ + FSA. Over the first test week (after CL flushing concentrations were increased from 1.0 to 2.0 ppm) lead concentrations nearly doubled (from about 100 to nearly 200 ppb), but when FSA was also included, lead concentrations spiked to over 900 ppb. Lead concentrations from the CL-based waters appeared to be decreasing over the study period, while for the CA + NH₃ + FSA combination, lead concentrations seemed to be increasing with time.

© 2007 Elsevier Inc. All rights reserved.

Keywords: Water disinfection; Chlorine; Chloramines; Fluoridation; Lead leaching

1. Introduction

1.1. Motivation for this study

The continuing problem of ingested lead from lead-bearing water was highlighted at a US House of Representatives subcommittee hearing convened in March 2004 to investigate issues concerning “First Draw” water lead levels as high as 1000 ppb in Washington DC water circa 2001–2004. An expert witness (Edwards, 2004) testified that this was found in homes without lead service lines or lead soldered copper piping. The only possible lead source had to be leaded-brass plumbing and/or

brass faucets. The expert also suggested that a recent switch in disinfectant from chlorine to chloramine caused the problem. The study reported here, conducted by the Environmental Quality Institute of the University of North Carolina (EQI), focused on brass corrosion by combinations of disinfectant and fluoridating agents in two laboratory phases. In the first, small leaded-brass plumbing elbows (2% lead) were exposed under static conditions to DI water with chlorine and chloramines, either alone or in combination with municipal water fluoridating agents. Stagnant water lead data from that phase guided selection of combinations of disinfectant and fluoridating agent for a second phase in which brass water meters (8% lead) were exposed to seven water formulations under flow-through conditions. It was expected that Phase II results would be used to guide field tests under “real world” conditions in cooperating water plants, but the untimely demise of EQI Director Richard P. Maas prevented that follow-on step. Nevertheless, Phase I and Phase II results presented here provide at least heuristic insight

* Corresponding author at: Environmental Quality Institute, 209 Rhoades Hall, CPO# 2331, The University of North Carolina-Asheville, One University Heights, Asheville, NC 28804, United States. Tel.: +1 828 232 5194; fax: +1 828 251 6913.

E-mail address: patch@unca.edu (S.C. Patch).

into the “DC experience” and, more generally, shed new light on lead elution from brass by combinations of chlorine-based disinfectants and fluoridation chemicals.

1.2. Applicable terminology

Herein “CL” means a chlorine species used for potable water disinfection that may be injected as chlorine gas (Cl_2), or hypochlorite solutions carrying chloride ion, hypochlorous acid (HOCl), and/or hypochlorite ion (OCl^-) that may exist together in equilibrium. CL concentration may be expressed in parts per million (ppm) of “free chlorine” where 1 ppm is the stoichiometric equivalent of 29×10^{-6} mol of free chloride ion.

“NH” means ammonia added to CL treated water to produce mono-chloramine. NH may be injected as ammonia gas (NH_3), ammonium hydroxide solution, or as an ammonium salt solution. The desired proportion of CL/NH is 1:1 on a molar basis which is little less than 5:1 in ppm units.

“CA” means “chloramine” produced by adding NH to CL treated water; the desired mono-chloramine is actually part of a mixture with small amounts of di- and tri-chloramine. Actual amounts of NH and CL vary from time to time, yielding either undesired di- or tri-chloramine or excess NH. Chlorine in CA is also known as “combined chlorine,” a term also applied to products created when CL reacts with water contaminants (USEPA, 2004).

“SiF” applies to the silicon/fluorine complex (fluosilicate), a class of water fluoridating agents (aka fluorosilicates, silicofluoride, silicofluoric, hexafluorosilicate, and other names) from which fluoride ion (F^-) is released upon dissociation of $[\text{SiF}_6]^{2-}$ when diluted in water. The principal SiF agents are fluosilicic acid (H_2SiF_6), herein “FSA”, and its sodium salt (Na_2SiF_6). Concentrated (20–30%) FSA is injected as such into water plant water. Sodium fluosilicate (NaFSA) is added as a saturated solution. The term SiF covers $[\text{SiF}_6]^{2-}$ and its dissociation derivatives.

2. Relevant background

2.1. Continuing problem of drinking water lead

Lead contaminated drinking water remains a significant public health issue in the United States, even though water-borne lead has steadily declined along with other lead sources such as lead-based paint, roadside soils, food, and other products. In 1991, the EPA estimated that drinking water was responsible for 14–20% of total lead uptake of all ages in the U.S. (USEPA, 1991). EPA’s Lead and Copper Rule (LCR) for potable water was expected to reduce drinking water lead levels by 50%. That did occur (Maas et al., 2005) after leaded-solders were banned under the Safe Drinking Water Act Amendments of 1986 (USEPA, 1986); water suppliers were required to reduce corrosivity of their finished waters (Maas et al., 1994; Ramaley, 1993; USEPA, 1991); with better control of alkalinity, pH, and additives (Cardew, 2003; Edwards et al., 1996; Lytle and Schock, 2000). On its own initiative, the California legislature set limits on lead content of leaded-brass plumbing devices and faucets (Patch

et al., 1998; State of California, 1995). Much research focused on preventing lead extraction from installed lead service lines by treating water with phosphatic agents (phosphoric acid, combinations of orthophosphoric acid and zinc orthophosphate, polyphosphates, or blends of orthophosphoric acid with polyphosphate) that produce inert barrier coatings inside lead pipes. Along with successes in this area there have also been conflicting results. Orthophosphate treatments can reduce soluble lead levels by 70%, but polyphosphate can actually increase lead and copper in drinking water (Edwards and McNeill, 2002), often manifested as particulates (McNeill and Edwards, 2004).

2.2. Complicating factors

2.2.1. Switch to chloramines for disinfection

Water lead problems have been exacerbated by EPA’s Stage I Disinfection By-products Rule (USEPA, 2002) requiring reduction of disinfection by-products (DBPs) such as trihalo-methanes (THM’s) and haloacetic acids (HAA’s) created by CL disinfection (ChemScan, 1997). A switch from CL to CA was recommended and adopted in some systems since it was less expensive than other disinfection methods and easy to add NH to already-chlorinated water. One explanation for the DC experience was that the switch from CL lowered the oxidizing potential of DC water, destroying the normally protective lead dioxide (PbO_2) scale inside lead pipes (Renner, 2004).

Although CA corrosivity has received a lot of attention, no studies have included fluoridating agents (Edwards and Dudi, 2004; Eisnor and Gagnon, 2004; Lin et al., 1997; Reiber, 1993; Sung et al., 2005). A microscopy study revealed how CA alone is a good solvent for lead (Switzer et al., 2006). Whatever these studies may have found under laboratory conditions, it should be noted that CA in the water plant is not added as a commercial product with consistent properties. It is formed by adding NH to CL treated water. Ideally, mono-chloramine is the principal product formed at pH 8 and the proper 1:1 NH/CL molar ratio. Maintaining exactly the ideal NH/CL proportion at all times is not very likely.

2.2.2. The role of fluoridating agents

Fluoridating agents can only complicate matters. Sodium fluoride (NaF), used to treat less than 10% of US fluoridated water, raises pH a little with negligible effect, but the same cannot be said for possible interference by the fluoride ion in the reaction of NH with CL. The effect of SiFs is another matter. The fluosilicate anion $[\text{SiF}_6]^{2-}$ of FSA and NaFSA provides the fluoride ion (F^-) in over 90% of fluoridated water. $[\text{SiF}_6]^{2-}$ releases F^- in a complicated, poorly understood, sequence of time-, temperature- and pH-dependent steps. Under water plant operating conditions, incompletely dissociated $[\text{SiF}_6]^{2-}$ residues may survive and react with other chemicals in the water. Under some conditions, NH and FSA, as such, react to produce silica and ammonium fluoride (Mollere, 1990). How that affects corrosion is not known, but whatever its reaction with NH may be, FSA does not leach lead simply because it is an acid.

The fluosilicate anion $[\text{SiF}_6]^{2-}$ and/or partially dissociated derivatives have a unique affinity for lead. Lead fluosilicate is

one of the most water soluble lead species known, a property recognized and exploited for many years (Stauter, 1976). FSA has been used as a solvent for lead and other heavy metals in extractive metallurgy (Cole et al., 1981; Kerby, 1979) and to remove surface lead from leaded-brass brass machined parts (Bonomi et al., 2001; Giusti, 2001, 2002). With or without CA, FSA would extract lead from brass. Besides, in the water plant situation it is reasonable to expect FSA to combine with NH as ammonium fluosilicate, an excellent solvent for copper alloys (Hara et al., 2002) and other metals (Silva et al., 1995).

It has been argued that FSA dissociates almost completely at the levels typically added to drinking water, and therefore cannot be more corrosive than sodium fluoride (NaF) (Urbansky and Schock, 2000). However, in a comprehensive follow-up review of the literature, Urbansky states that FSA may not dissociate completely in drinking water (Urbansky, 2002). Evidence for that is not new (Colton, 1958; Kolthoff and Stenger, 1947; Lenfesty et al., 1952; Munter et al., 1947; Thomsen, 1951). Titration of FSA to a pH 7 end-point only neutralizes the two hydronium ions produced by ordinary hydrolysis of H_2SiF_6 , leaving the fluosilicate anion $[\text{SiF}_6]^{2-}$ intact. In addition to that, $[\text{SiF}_6]^{2-}$ dissociation in cold water could take 20 min to reach 90% completion (Hudleston and Bassett, 1921; Rees and Hudleston, 1936) and may never get to that condition below pH 9 (AWWA, 1994).

Consequently, incompletely dissociated $[\text{SiF}_6]^{2-}$ residues may remain in water plant water that is not above pH 8 or some commonly occurring low temperature. Apart from problems with incompletely dissociated $[\text{SiF}_6]^{2-}$ residues, injection of concentrated of FSA simultaneously and in close proximity with NH almost guarantees unanticipated side reactions.

2.2.3. Distribution of lead in brass

The varied, occasionally conflicting, reports on elution of lead from brass may have a common explanation. Lead alloyed with copper is not molecularly distributed, as in a solid solution. Discrete lead nodules are embedded in a copper matrix. Agents that attack copper are likely to foster lead mobility, adding significantly to lead (probably particulate) in drinking water. CL, CA, or excess NH are all capable of doing that, either by copper stress cracking (Flom, 2002) or mobilization in an ammonia/copper complex (Clark, 2003), thereby exposing lead nodules in brass for easier transport into water.

This may help to explain the DC experience that homes with only brass as a possible source of lead, not only had high water lead, but were also experiencing serious pitting of copper pipe. In many cases, particulate lead may predominate over soluble lead eluted from brass, as well as other lead sources (McNeill and Edwards, 2004).

3. Materials/methods and statistical analyses

3.1. Phase I (static tests of 2% leaded-brass elbows)

Sixty 2% leaded-brass 1/2 in. barb 90° elbows were purchased locally. Three elbows were assayed for lead in a small piece sliced from one end. Measured lead concentrations

ranged from 1.70 to 1.82%. Elbows were labeled, thoroughly rinsed, and placed in a tray of deionized (DI) water for conditioning. The water was changed twice and agitated three times a day for 18 days. After conditioning, two sets of static bottle tests were conducted as follows: individual elbows were removed from the trays of DI water, rinsed with DI water and placed in their own labeled bottle. Exactly 100 mL of the appropriate test water was added to each bottle which was capped and set aside to sit undisturbed overnight. After 16-h stagnation exposure, each elbow was removed from its bottle of test water with plastic tongs, rinsed with DI water, and placed back into its tray of DI water. Test waters were analyzed for lead using the EPA 200.8 method for graphite furnace atomic absorption spectrophotometry.

In the first set of bottle tests, elbows were exposed to waters at pH 7 and pH 8, comprising 2 ppm each of: (1) CL only; (2) FSA only; (3) CA only; (4) CA + FSA. CL was adjusted by adding the appropriate amount of dilute sodium hypochlorite (NaOCl) solution. For the FSA waters, enough FSA was added to produce 2.0 ppm F^- which represents above average, but not unusual conditions within the highest permissible level (MCL) for drinking water fluoride. FSA was added as pre-diluted 26% FSA.

Although the CDC nominal “optimum” adjusted F^- concentration is 1.0 ppm, it is only a mid-range figure (CDC, 2001). The CDC recommends adjusting F^- according to mean annual local temperature. In colder areas (50–54 °F annual mean) such as Great Lakes States, the optimum is 1.1–1.7 ppm and in warmer areas (71–79 °F) it is 0.7–1.3 ppm. An allowance is also made for deviation from these boundaries by 0.1 ppm on the low side and 0.5 ppm on the high side (CDC, 1999). Hence, a water plant taking water in December through April from Lake Ontario or the Northern reaches of the Mississippi River could comply with CDC’s optimum F^- at 2.0 ppm. Also, the recommended optimum F^- for school water systems is 4.1–5.0 ppm for the middle temperature range (CDC, 1999). Therefore, the 2.0 ppm F^- concentrations in this study were in the range experienced by much of the U.S. public.

CA was prepared as a stock solution comprising ammonium hydroxide and sodium hypochlorite in stoichiometric equivalent concentrations. For test water exposure, appropriate amounts of stock solution were pH adjusted upward by adding sodium bicarbonate (NaHCO_3) or downward using hydrochloric acid (HCl). Elbows were randomly assigned to test waters so that each water composition had five elbows assigned to it.

The conditionings using pH 8 were dropped in the second set of bottle tests to allow testing of more types of water additives. The same procedures used in the first set of bottle tests were carried out in the second set at pH 7 and 2.0 ppm of each constituent: (1) DI water only; (2) CL only; (3) CA only; (4) CA + 50% excess NH; (5) CA + FSA; (6) CA + 50% excess NH + FSA; (7) CA solution into which 26% FSA was added to produce 2 ppm of fluoride without pre-dilution; (8) FSA + NH; (9) CA + ammonium fluosilicate.

CL, CA, FSA, and pH were adjusted the same way as the first bottle tests. NH was adjusted by adding ammonium hydroxide

in appropriate 1:1 molarity with CL alone as well as with 50% excess NH to represent water plant control deviations described above regarding excess ammonia. The 50% excess NH is consistent with 50% greater than nominal 1 ppm F^- optimum, therefore a reasonable condition to occur in a water plant with the risk of side reaction between SiF and NH. The difference between conditions 5 and 7 was based on that premise. In condition 5, FSA was diluted before adding it to the mixture, as was done for other treatments using FSA. In condition 7, it was added at 26% concentration and the resulting mixture diluted to 2 ppm F^- .

For reasons described earlier, mixing concentrated FSA with NH with ample time to react should approximate water plant conditions, producing a species with corrosion potential differing from that when pre-diluted dissociated FSA meets ammonia. It should be noted here that concentrated FSA and NH are frequently injected into water plant water in close proximity to each other (District of Columbia Water and Sewer Authority, 2002). The rationale for including conditions 8 and 9 was that NH is known to react with copper, forming the soluble copper/ammonia complex, thus possibly exposing additional lead surface in the brass.

3.2. Phase I statistical analyses

For both sets of bottle tests, ANOVA analyses conducted on the natural-log-transformed lead concentrations found no evidence of significant non-normality (Kolmogorov–Smirnov p -values = 0.124 and 0.100) or heterogeneity of variances (Levene p -values = 0.191 and 0.979). Tukey's least significant difference (LSD) procedure was used to perform a multiple comparison of log lead concentrations between each combination of water and pH. Confidence intervals for the median lead concentrations of all elbows that might be exposed to those conditions were calculated for each water-pH combination under the assumptions that the log lead concentrations were approximately normally distributed with common variance. Least square means and corresponding individual confidence intervals were calculated from the ANOVA analysis for these log lead concentrations for each combination, and then the inverse transform was conducted on the least square means of the logged data to obtain the estimated medians and 95% confidence intervals for the median lead concentrations.

3.3. Phase II (flow-through tests 8% leaded-brass meters)

Twenty leaded-brass Hersey Model 430 water meters were purchased locally in Asheville, NC. Three meters were selected randomly and assayed for lead on a small slice from the meter exterior with results ranging from 7.59 to 8.44% lead. Meters were randomly assigned to one of seven types of water and hooked up to a plumbing manifold consisting of three meters for each of six waters and two meters for one water. Connected plumbing included a Flojet Model 2100-953-115 plastic vacuum pump and a 100 L Nalgene laboratory carboy (see Fig. 1).

Each manifold system was conditioned by flushing 350 mL of a 1.0 ppm CL/DI water solution through all the meters about



Fig. 1. Picture of Phase II setup.

15 times each weekday for 2.5 weeks for a total of approximately 190 times. One additional week of conditioning was completed by flushing 350 mL of the CL/DI water through the meters another 63 times. For this final week, samples were taken on Wednesday, Thursday, and Friday mornings at approximately 8:30 a.m. The late afternoon before each sample was taken a 2-L flush was completed at 4:30 p.m. and the meters sat undisturbed overnight 16 h until the morning sample at 8:30 a.m. Conditioning provided stagnation water lead data for 1 ppm CL prior to switching to test waters. After conditioning, the following waters with 2.0 ppm of each constituent were studied: (1) CA + FSA; (2) CA + 100% excess NH + FSA; (3) CA + 100% excess NH; (4) CA + 100% excess NH + NaF; (5) CL + FSA; (6) CL + NaF; and (7) CL alone. The target pH for all waters was 7.5 with an acceptable range of 7.3–7.7. The 100% excess NH was used as a potential worst-case scenario simulating a situation that might reasonably occur from time to time in a water plant. The CL, CA, FSA, NH, and pH were adjusted using the same methodology as that of Phase I.

Three meters were tested for each water composition, except the CA + FSA combination which was tested with two meters. For 6 weeks the plumbing manifold systems were flushed four times each weekday. Each meter had 1 L of its respective test water flushed through it three times, and the final flush of each day was 2 L. Sampling occurred each week for the 6-week sampling period on Tuesday, Wednesday, and Thursday mornings following a 16-h stagnation period.

3.4. Phase II statistical analyses

To assure that no meter was used that might be particularly susceptible to corrosion, an ANOVA analysis was performed on the log-transformed lead concentrations for the samples taken during conditioning. Median values of stagnation water lead concentration were found for each set of meters and combination of day and water composition. As with the elbow data, the natural logarithm was taken for each lead concentration. Lead concentrations for each meter were averaged over

the first 3 and last 3 weeks of the study. These arithmetic means were log transformed to give a single value to each meter for each of the two periods.

ANOVA analyses were performed on these log-transformed means and individual 95% confidence intervals for the log-transformed means calculated. An inverse transform was applied to these values to estimate the typical mean stagnation water lead concentration produced by the given water over the given time periods. ANOVA data for each of the pre-treatment period, first 3 treatment weeks, and last 3 weeks provided no evidence of significant non-normality (Kolmogorov–Smirnov p -values = 0.079, >0.15, >0.15, respectively) or heterogeneity of variances (Levene p -values = 0.962, 0.475, 0.218, respectively).

4. Results

4.1. Phase I results (2% lead elbows)

For the first set of bottle tests pH, water treatment, and their interactive effect were all significantly related to log lead concentration (p -values = <0.001, <0.001, 0.006, respectively). Fig. 2 displays the 95% confidence intervals for medians of the first set of static bottle tests. As seen from the results of the Tukey’s LSD (Table 1) and individual confidence intervals (Fig. 2), lead concentrations are significantly higher at pH 7 for the CL and the CA waters, but not for the other two. The highest lead concentration was produced by CA + FSA under both pHs. CA at pH 7 produced the next highest lead concentration, but not significantly less than the highest. Absent

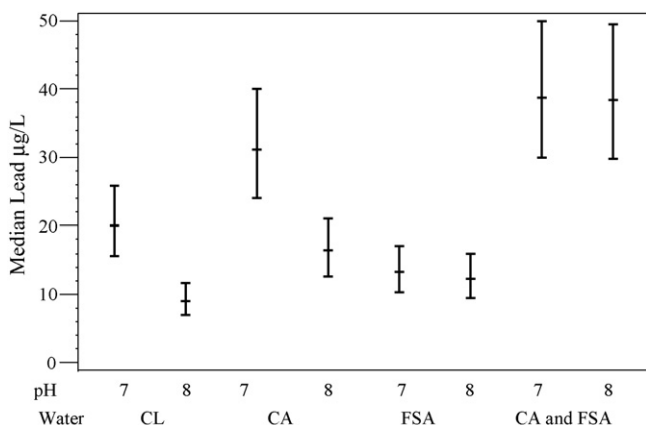


Fig. 2. Median 95% confidence intervals for bottle test 1 at pH 7 and pH 8.

Table 1
Estimated median lead concentrations for bottle test 1

	Water							
	Cl	FSA	FSA	CA	Cl	CA	CA + FSA	CA + FSA
PH	8	8	7	8	7	7	8	7
Estimated median	9.0	12.3	13.3	16.3	20.0	31.1	38.4	38.7

Combinations covered by the same line are not significantly different using Tukey’s LSD statistic with a significance level of $\alpha = 0.05$.

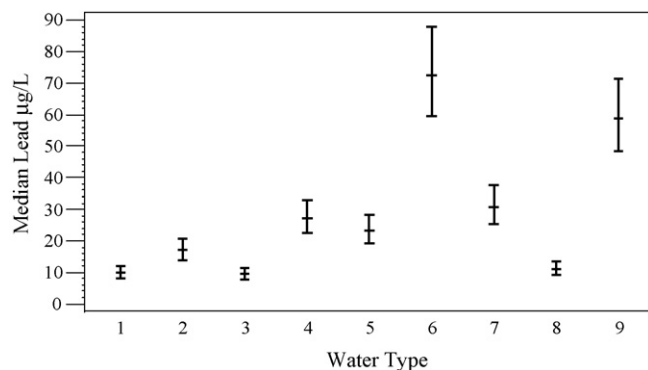


Fig. 3. Median 95% confidence intervals for bottle test 2. 1, Deionized Water; 2, CL Only; 3, CA Only; 4, CA and 50% excess NH; 5, CA and FSA 6, CA,50% excess NH, and FSA; 7, CA with 26% FSA Added; 8, FSA NH; 9, CA with concentrated ammonium fluosilicate.

a factorial design it was not possible to test formally for an interactive effect of CA + FSA. FSA alone gave results very similar to CL. Although CA + FSA produced the highest lead concentrations at both pHs, the combination was significantly higher than CA alone only at pH 8. Thus, bottle test 1 provides evidence, albeit not compelling, for a positive interactive effect of CA + FSA on leaded-brass corrosion.

For the second set of bottle tests, water composition was the only factor having a significant effect on log lead concentrations ($p = 0.000$). Estimated median and confidence intervals for the median lead concentration of each water is displayed in Fig. 3. From the individual confidence intervals (Fig. 3) and Tukey’s LSD results (Table 2) it can be seen that CA + 50% excess NH + FSA (#6) and CA + ammonium fluosilicate (#9) produced the two highest lead concentrations. CA + 50% excess NH; CA + FSA; CA + concentrated FSA produced intermediate concentrations. CL alone, CA alone, DI water alone, and the combination of NH + FSA produced the lowest concentrations. Unlike the first set of bottle tests at pH 7, CA alone produced significantly lower lead concentration than CL alone. CA + concentrated FSA produced a higher concentration than CA + pre-diluted FSA but the difference was not statistically significant.

Table 2
Estimated median lead concentrations for bottle test 2

Water code	Estimated median
3	9.4
1	9.9
8	11.1
2	17.0
5	23.3
4	27.2
7	30.8
9	58.8
6	72.3

Combinations covered by the same line are not significantly different using Tukey’s LSD statistic with a significance level of $\alpha = 0.05$.
1, deionized water; 2, CL only; 3, CA only; 4, CA and 50% excess NH; 5, CA and FSA; 6, CA + 50% excess NH + FSA; 7, CA with 26% FSA added; 8, FSA + NH; 9, CA + concentrated ammonium fluosilicate.

The interactive effects of CA and FSA on lead leaching cannot be directly examined from the set of waters in the second set of bottle tests. However, effects of excess NH, FSA and their interactive effect can be evaluated for the CA waters. The four conditions: (3) CA only; (4) CA + 50% excess NH; (5) CA + FSA; and (6) CA + 50% excess NH + FSA make up a two-way full factorial experimental design. ANOVA analysis on just those four conditions found that in the presence of CA, both 50% excess NH ($p = 0.000$) and FSA ($p = 0.000$) were positively related to log lead concentration, but their interactive effect ($p = 0.662$) was not significant. Thus, in the presence of CA, 50% excess NH and FSA had positive additive effects on log lead concentrations in the second bottle study.

Median lead concentration for CA + 50% excess NH + FSA was greater than for CA + ammonium fluosilicate, but not significantly so. Thus, it seems reasonable to believe that CA + 50% excess NH + FSA leaches lead through a mechanism similar to that for CA with ammonium fluosilicate as such.

4.2. Phase II results (8% leaded-brass meters)

ANOVA analysis of the log-transformed lead concentrations during exposure to conditioning water (1.0 ppm CL/DI water solution) found no significant differences in the median lead concentrations between the groups of meters selected for the seven different water treatments (p -value = 0.771). The estimated median lead concentration for meters exposed only to the conditioning regime was 84.0 $\mu\text{g/L}$.

On Day 13 after treatment began, a meter receiving CL + FSA was reported to have a stagnation water lead concentration of 2.9 ppb, while the other two meters had values of 49.5 and 62.4. The 2.9 outlier was not included in any analyses. The median ($n = 3$, except for CA + FSA where $n = 2$) lead concentrations for each day were obtained for each water chemistry. Fig. 4 displays the median lead concentrations for the CA-type waters over the 28 days of testing. Fig. 5 displays the median lead concentration for the CL-type waters over the 28 days.

The median range in lead concentrations for the three (or, in one case two) meters subjected to the same waters for the entire study period (not displayed on the figure) was 9.0 $\mu\text{g/L}$ over all days and waters. Some day-water sets had much higher meter-

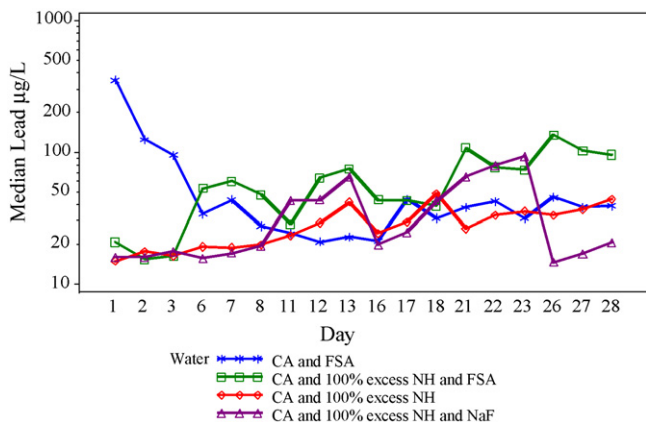


Fig. 4. Mean lead concentrations for the CA-based waters.

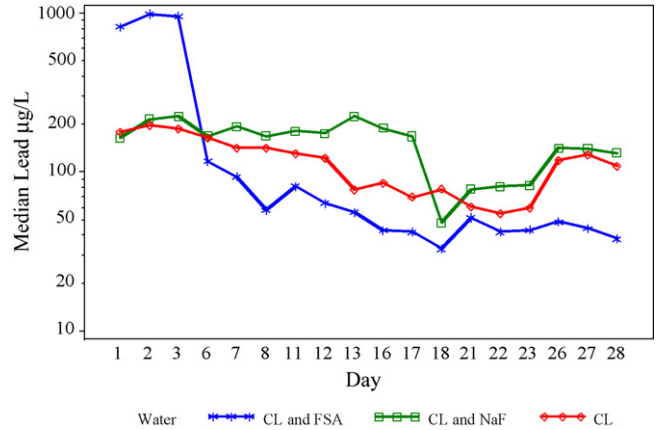


Fig. 5. Mean lead concentrations for CL waters by day.

to-meter ranges. For example, days 1–3 for CL + FSA water had ranges of 115.5, 217.3, and 136.4 $\mu\text{g/L}$, respectively, but these were measured for water lead data in the 1000 ppb regime. As expected for data that is approximately log-normally distributed, day-water combinations with larger medians tended to also have larger ranges.

Figs. 6 and 7 illustrate the variability of the stagnation water lead concentrations produced over the entire test period by meters receiving, respectively, CA + 100% extra NH and meters

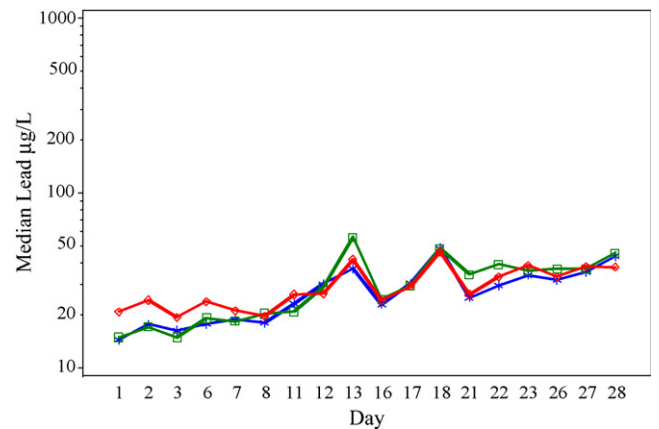


Fig. 6. Lead concentrations for meters using CA + 100% excess NH.

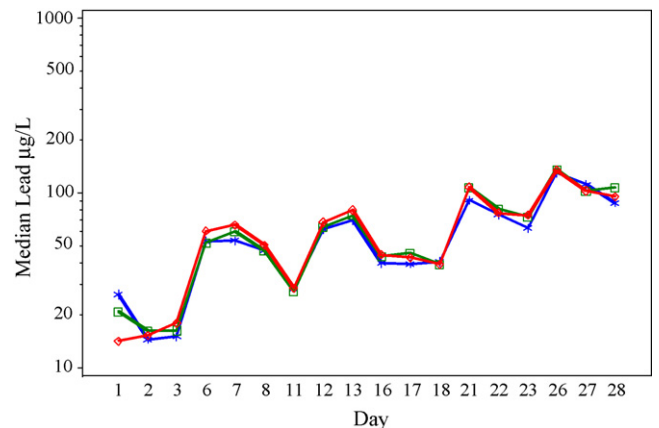


Fig. 7. Lead concentrations for meters using CA + 100% excess NH + FSA.

Table 3

Estimated median lead concentrations of meters by type of water averaged over day for the first 3 weeks of the study

Water	N meters	Estimated median (95% confidence interval)
CA and 100% extra NH	3	23.3 (21.0–25.9)
CA, 100% extra NH and NaF	3	28.1 (25.3–31.2)
CA, 100% extra NH and FSA	3	42.6 (38.4–47.3)
CA and FSA	2	83.1 (73.1–94.5)
CL	3	145.9 (131.4–162.0)
CL and NaF	3	185.3 (166.6–205.7)
CL and FSA	3	362.8 (326.7–402.9)

Water types that are covered by the same line are not significantly different from each other using Tukey's LSD with a significance level of $\alpha = 0.05$.

receiving CA + 100% extra NH + FSA. Clearly, for both treatment waters there is very little meter-to-meter variation in eluted lead on any one day. Such consistency is reasonable assurance that all the data reflect real effects, not merely random "chemical noise." Based on the premise that observed differences in stagnation water lead are not statistical aberrations, but due to explicable causes, day-to-day and week-to-week variability requires comment, which will be provided in the following section.

In the analyses shown in Figs. 4–7 a "week" is 5 days, since flushing occurred only on weekdays, and thus essentially no aging was considered to be occurring over weekends. Thus, Days 1–28 as shown in these figures represent 6 weeks of sampling on 3 successive days. Table 3 shows the median lead concentrations for all seven water chemistries averaged over the first 3 (5-day) weeks and Table 4 shows the corresponding results for the last 3 weeks of the study.

Fig. 4 and Tables 3 and 4 provide insights into corrosivity of CA-based test waters. The most corrosive of the CA-based test waters for the first 3 weeks was CA + FSA, while CA + excess NH + FSA was the most corrosive for the last 3 weeks and the only water showing a strong trend of increasing corrosivity over the whole experiment. Water with CA + excess NH and water with CA + excess NH + NaF were similar to one another in corrosivity which was significantly lower than the other waters. CA + excess NH + NaF displayed more variability over time than the other CA-based waters.

Fig. 4 and Tables 3 and 4 indicate that the water with CL + FSA was most corrosive for the first 3 weeks and CL + NaF

was most corrosive for the last 3 weeks and second most corrosive for the first three weeks. Water with CL only was third most corrosive for the first 3 weeks and second most corrosive for the last 3. Water with CL + FSA showed a decreasing trend over the course of the experiment, while the other two CL-based waters displayed irregular, slightly decreasing trends.

Comparing the CL-based waters to CA-based waters, CL-based waters were most corrosive over the first 3 weeks of the study and three of the four most corrosive over the last three. This is in contrast to the results of Phase I in which the CA-based waters tended to be associated with greater stagnation water concentrations. However, it should be borne in mind that Phase I elbows were only 2% lead while Phase II meters were 8% lead. The possible effect of this difference on water lead will be discussed below along with comments about why in Phase II the highest lead level was a spike to over 1000 ppb extracted by FSA + 2 ppm CL water after initial meter conditioning with 1 ppm CL water.

5. Discussion of findings

5.1. Consistency of test results

Meter-to-meter difference in stagnation water lead values was very low on any one day and for virtually all test waters. The few instances where above median meter-to-meter variation was found, the median lead values were also on the high side. In other words, meter-to-meter differences in water lead values were about the same percent of median water lead values for most days and water formulas.

Day-to-day lead values within any week were often consistent or with a trend up or down. Such trends might be explained by loss of volatiles from a given batch of water without make-up under laboratory conditions that would not occur in a water plant where composition is in constant make-up mode. For example, excess NH alone might gradually decline, with one effect on lead extraction and excess CL alone might decline with the same or another effect. Given the fact that CL and NH combine to form chloramine, neither NH nor CL would be lost, which would have its own effect.

On the other hand, notable shifts in lead extraction occurred when a fresh batch of treatment water was prepared, typically between weeks. The most extreme shift in the entire experiment occurred when meters were first exposed to CL + FSA after having been conditioned to 1% CL/DI water. Along with the 17 other meters, the lead released by this group of 3 during the conditioning process had reached around 100 ppb. The first day these meters were exposed to CL + FSA following meter conditioning, lead concentration leaped to 800 ppb and increased to over 1000 ppb by the third day.

The second week batch of FSA + CL water was made up with the same FSA composition as the first batch, but the CL charge was different, in that sodium hypochlorite solution had been adjusted to compensate for change in the CL stock solution over time. The first day of the second week, water lead was down to 100 ppb, the same level as that at the end of the conditioning period. Thereafter, lead levels dropped in the

Table 4

Estimated median lead concentrations of meters by type of water averaged over day for the last 3 weeks of the study

Water	N meters	Estimated median (95% confidence interval)
CA and 100% extra NH	3	34.8 (31.9–37.9)
CA and FSA	2	36.8 (33.1–40.9)
CA, 100% extra NH and NaF	3	43.2 (39.6–47.1)
CL and FSA	3	43.3 (39.7–47.2)
CA, 100% extra NH and FSA	3	79.2 (72.6–86.3)
CL	3	84.0 (77.0–91.6)
CL and NaF	3	115.2 (106.1–126.1)

Water types that are covered by the same line are not significantly different from each other using Tukey's LSD with a significance level of $\alpha = 0.05$.

next 2 weeks and settled into a consistent 50 ppb day-to-day and week-to-week.

A crucial fact about the make-ups of the first and second FSA + CL batches is that the first had a pH of 7.56 with 1 g sodium bicarbonate added while the second had a pH of 7.30 with 6 g of sodium bicarbonate added. It is doubtful that this pH difference accounts for first week lead starting on day 1 at 800 ppb, increasing to over 1000 by the third day. The fact that one sixth the amount of base in batch 1 than in batch 2 produced a higher pH in batch 1 than that of batch 2 suggests fluosilicate dissociation status was not the same for both batches.

There also could have been serious error in batch preparation or analytical technique. But these explanations are at odds with the consistency of lead extraction measured during conditioning and very low meter-to-meter variation illustrated in **Figs. 6 and 7**. Neither human error in batch preparation, nor flaws in instrument performance can account for the high first day lead and upward trend that followed. A better explanation is that the combined action of CL and FSA in the first water batch started out very efficient and improved in the next 2 days. This would be consistent with release of particulate lead from the brass alloy in the first week leaving the remaining potentially mobilizable lead shielded from corrosive attack.

A similar, but less dramatic, effect was observed when FSA was added to CA with excess NH. After settling at the 100 ppb level during conditioning, the first day of exposure the test water produced a stagnation lead level of 350 ppb. Then, in this case, without any change in batch formula, after the first-day 350 ppb spike, the second day lead was 120 ppb, and the third day 100 ppb. Thereafter, for 5 successive weeks, with new batches each week, stagnation lead settled down to a very consistent 40–50 ppb.

On an obviously different scale, the same sensitivity of leaded-brass to corrosion by FSA + CL or FSA + CA can be expected in a water plant. It may not be observed when very tight controls are kept on treatment chemical compositions, but the results reported here are very much like what was found in the DC experience.

Considering the several different additives used in the plant, it is a forgone conclusion that deviations from an ideal dosage of any one additive are inevitable. The important data in this report should, therefore, be treated as providing reasonable confidence, not absolute proof of what would actually occur in a water plant.

6. Conclusions

In the “fluoridation debate” proponents frequently argue that the 1 or 2 ppm of fluoride in drinking water is so trivial that it cannot be a health danger. When one translates the ppm involved into molar concentrations, 2 ppm of fluoride is about twice the concentration of 2 ppm of chloride.

Ironically, the switch from CL to CA for disinfection that was made for health reasons, may have created a high water lead health problem. Published evidence has shown that chloramine used instead of chlorine for water disinfection enhances lead extraction from leaded-brass plumbing devices

and faucets. Prior to the present study, no one had looked at brass corrosion by combinations of either chlorine or chloramine with water fluoridating agents. Several factors applicable to such combinations can produce more corrosion than either of the disinfectants or fluoridating agents alone.

One such factor is that fluosilicic acid, the most widely used fluoridating agent, is a good solvent for lead. Another is that chlorine, ammonia, and chloramine are all hostile to copper in that they induce copper stress cracking and/or can dissolve it. A third factor is that ammonia added to chlorine to produce chloramine will also react with fluosilicic acid to produce ammonium fluosilicate, an established solvent for copper alloys.

Besides these chemical factors, the lead in brass is present as nodules, so that any attack on the copper matrix of brass would render particulate lead readily accessible for mobilization. Whatever the exact mechanism may be for the combined effect of CA and fluoridating agents on increased levels of water-borne lead, the fact is that SiFs (FSA and NaFSA), commonly used to fluoridate water, have been associated with elevated blood lead levels in children (Coplan et al., *in press*; Masters et al., 2000). In a related sense, it was recently found that the North Carolina water systems that use FSA and chloramine are associated with elevated blood lead levels in children (Allegood, 2005; Clabby, 2006; Miranda et al., 2006). EPA has claimed a year-long evaluation they conducted did not find a national problem comparable to that in DC, but EPA also acknowledged the need to update specific areas of the LCR and guidance materials (USEPA, 2006). That ought to include lead from brass (Dudi et al., 2005; Renner, 2006) (see Coplan et al., *in press*).

Acknowledgment

This paper is dedicated to Dr. Richard P. Maas 1952–2005.

References

- Allegood J. Water treatment process called potential risk. *Raleigh News and Observer*; May 18, 2005
- American Water Works Association, AWWA. Standard for Sodium Fluorosilicate; ANSI/AWWA B702-94 November 1994 and AWWA Standard for Fluorosilicic Acid; ANSI/AWWA B703-94; November 1994.
- Bonomi A, et al. Selective deleading process and bath for plumbing components made of a copper alloy. US Patent 6,284,053; September 4, 2001.
- Cardew PT. A method for assessing the effect of water quality changes on plumbosolvency using random daytime sampling. *Water Res* 2003;37(12): 2821–32.
- Center for Disease Control. Engineering and Administrative Recommendations for Water Fluoridation; 2001. <http://www.cdc.gov/MMWR/preview/mmwrhtml/00039178.htm#00001289.htm>.
- ChemScan. Water Chloramination Process Control. Avail from URL: <http://www.chemscan.com/applications/86.html> [revised November 1997].
- Clabby C. Durham lead fears widen; more tests turn up tainted water. *The News & Observer*; June 13, 2006.
- Clark J. Reactions of copper with ammonia; 2003. <http://www.chemguide.co.uk/inorganic/transition/copper.html>.
- Cole Jr ER, et al. Electrowinning of lead from H₂SiF₆ solution. US Patent 4,272,340; June 9, 1981.
- Colton E. Fluosilicic Acid. *J Chem Educ* 1958;35(10):562–3.

- Coplan MJ, Patch SC, Masters RD, Bachman MS. Confirmation and explanation for elevated blood lead in children exposed to silicofluoride treated drinking water. *Neurotoxicology*; in press.
- District of Columbia Water and Sewer Authority. Year 2002 water quality report. http://www.dcwasa.com/news/publications/waterquality_report2002.pdf.
- Dudi A, Schock M, Murray N, Edwards M. Lead leaching from inline brass devices: a critical evaluation of the existing standard. *J Am Water Works Assoc* 2005;97(8):66–78.
- Edwards M. Written version of testimony presented orally on March 4, 2004 to US House committee investigating facts pertaining to the reporting of high water lead in Washington, DC, on-line at <http://www.dwatch.com/wasa/040305h.htm>.
- Edwards M, Dudi A. Role of chlorine and chloramines in corrosion of lead-bearing plumbing materials. *J Am Water Works Assoc* 2004;96(10):69–83.
- Edwards M, McNeill LS. Effect of phosphate inhibitors on lead release from pipes. *J Am Water Works Assoc* 2002;94(1):79–92.
- Edwards M, Schock MR, Meyer TE. Alkalinity, pH, and copper corrosion by-product release. *J Am Water Works Assoc* 1996;88(3):81–95.
- Eisnor JD, Gagnon GA. Impact of secondary disinfection on corrosion in a model water distribution system. *J Water Supply Res Technol* 2004;53(7):444–52.
- Flom Y. Stress corrosion cracking in copper alloys. NASA Report No. 046, 2002. http://code541.gsfc.nasa.gov/documents/materials_tips_PDFs/TIP%20046R.pdf.
- Giusti A. Low lead release plumbing components made of copper based alloys containing lead, and a method for obtaining the same. US Patent 6,270,590; August 7, 2001.
- Giusti A. Low lead release plumbing components made of copper based alloys containing lead, and a method for obtaining the same. US Patent 6,461,534; October 8, 2002.
- Hara T, Miyazawa K, Miyamoto M. Properties of copper interconnection layers deposited by electroplating using a copper hexafluorosilicate electrolytic solution. *Electrochem Solid-State Lett* 2002;5(1):C1–3.
- Hudleston LJ, Bassett H. Equilibria of hydrofluosilicic acid. *J Chem Soc (Lond)* 1921;119:403–16.
- Kerby RC. Bipolar refining of lead. US Patent 4,177,117; December 4, 1979.
- Kolthoff IM, Stenger VA. Volumetric analysis. Vol. II. Titration methods: acid–base, precipitation and complex-formation reactions. New York: Interscience Publishers; 1947.
- Lenfesty FA, et al. Equilibrium in the system silicon tetrafluoride–water. *Ind Eng Chem* 1952;44(6):1448–50.
- Lin NH, Torrents A, Davis AP, Zeinali M, Taylor FA. Lead corrosion control from lead, copper–lead solder, and brass coupons in drinking water employing free and combined chlorine. *J Environ Sci Health A* 1997;32(4):865–84.
- Lytte DA, Schock MR. Impact of stagnation time on metal dissolution from plumbing materials in drinking water. *J Water Supply Res Technol-AQUA* 2000;49(5):243–57.
- Maas RP, Patch SC, Winfield R, Pope J, Morgan D. Field-based corrosion control and monitoring strategies for meeting the lead and copper rule action levels. In: Proceedings of the AWWA Annual Conference. Am Water Works Assoc., New York, June 19–24; 1994.
- Maas RP, Patch SC, Morgan DM, Pandolfo TJ. Reducing lead exposure from drinking water: recent history and current status. *Public Health Rep* 2005;120(3):316–21.
- Masters RD, et al. Association of silicofluoride treated water with elevated blood lead. *Neuro Toxicology* 2000;21:1091–100.
- McNeill LS, Edwards M. Importance of Pb and Cu particulate species for corrosion control. *J Environ Eng* 2004;130(2):136–44.
- Miranda ML, Kim D, Hull AP, Paul CJ, Galeano MAO. Changes in blood lead levels associated with use of chloramines in water treatment systems. *Environ. Health Perspect.* <http://dx.doi.org/>; online November 7, 2006.
- Mollere PD. Production of silica and fluorine coproducts from fluosilicic acid. US Patent 4,915,705; April 10, 1990.
- Munter PA, et al. Hydrofluoric acid–water and hydrofluoric–hydrofluosilicic acid–water. *Ind Eng Chem* 1947;39(3):427–31.
- Patch SC, Maas RP, Pope JP. Lead leaching from faucet fixtures under residential conditions. *J Environ Health* 1998;61:18–21.
- Ramaley BL. Monitoring and control experience under the lead and copper rule. *J Am Water Works Assoc* 1993;85:64–9.
- Rees AG, Hudleston LJ. The decomposition of the fluosilicate ion in aqueous and in aqueous salt solutions. *J Chem Soc (Lond)* 1936;1334–7 [Project 508].
- Reiber S. Chloramine effects on distribution system materials. *Am Water Works Assoc Res Found* 1993.
- Renner R. Leading to lead. *Sci Am* 2004;291(1):22–4.
- Renner R. Mis-Lead. *Environ Sci Technol Online News: Science News* May 31, 2006. http://pubs.acs.org/subscribe/journals/esthag-w/2006/may/science/rr_mislead.html.
- Silva JM, Ribeiro MF, Ramôa Ribeiro F, Gnep NS, Guisnet M, Benazzi E. Dealumination of the outer surface of MFI zeolites by ammonium hexafluorosilicate. *React Kinet Catal Lett* 1995;54(1):209–15 In: <http://www.springerlink.com/content/n927577511007037/>.
- State of California. Consent Judgment and Settlement Agreements, *People v. American Standard*, San Francisco, CA. August 1, 1995: No. 948017.
- Stauter JC. Production of Metallic Lead. US Patent 3,972,790; August 3, 1976.
- Sung W, Huang X, Wei IW. Treatment and distribution system effects on chloramine decay, pH, nitrification, and disinfection by-products: case study. *J Water Res Plan Manage* 2005;131(3):201–7.
- Switzer JA, Rajasekharan VV, Boonsalee S, Kulp EA, Bohannon EW. Evidence that monochloramine disinfectant could lead to elevated Pb Levels in drinking water. *Environ Sci Technol* 2006;40:3384–7.
- Thomsen SM. Acidimetric titrations in the fluosilicic acid system. *Anal Chem* 1951;23(7):973–5.
- United States Environmental Protection Agency. Safe Drinking Water Act Amendments of 1986; December 6, 1986: Publ. No. 99-339.
- United States Environmental Protection Agency. Drinking water regulations: maximum contaminant level goals and national drinking water regulations for lead and copper. *Fed Regist* 1991; 53:110.
- United States Environmental Protection Agency. Disinfection Byproduct Information. Avail from URL: <http://www.epa.gov/enviro/html/icr/dbp.html>; updated June 18, 2002.
- United States Environmental Protection Agency, National Review of LCR Implementation and Drinking Water Lead Reduction Plan 2006. http://www.epa.gov/safewater/lcrmr/lead_review.html.
- United States Environmental Protection Agency. Drinking Water Criteria Document for Chloramines. <http://www.epa.gov/ncea/pdfs/water/chloramine/dwchloramine.pdf>.
- Urbansky ET. The fate of fluosilicate drinking water additives. *Chem Rev* 2002;102(8):2837–54.
- Urbansky ET, Schock MR. Can fluoridation affect lead (II) in potable water? . . . Hexafluorosilicate and fluoride equilibria in aqueous solution *Int J Environ Studies* 2000;57(5):597–637 In: <http://fluoride.oralhealth.org/papers/pdf/urbansky.pdf>.