

# Effectiveness of the Preservation Protocol within EPA Method 200.8 for Soluble and Particulate Lead Recovery in Drinking Water



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## **Notice**

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## **Abstract**

Lead (Pb) is a toxic trace metal that is regulated in drinking water. The U.S. Environmental Protection Agency (USEPA) issued the Lead and Copper Rule (LCR), which defines the action level (AL) for lead at the tap as 0.015 mg/L. Researchers and drinking water utilities typically employ EPA Method 200.8 to quantify lead and other trace metals in drinking water and wastewaters, using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). EPA method 200.8 instructs how to properly preserve and analyze a water sample after collection. Recently, researchers have raised concerns about the preservation protocol, and its effectiveness in recovering actual concentrations of particulate lead in water samples. Specific concerns with the acidification protocol include bottle types, and occurrence of lead particulates in water samples. To investigate these concerns, a two-phase study was performed. Phase One investigated the recovery of dissolved lead in water samples by using the standard preservation protocol of the method and varying the water source, bottle type, and preservation pH. Phase Two investigated the recovery of three lead particulates in water samples, by comparing the standard preservation protocol of the method to the more rigorous acid digestion of the method and to an alternative pre-filtration process. Results of Phase One indicated large losses of soluble lead onto glass bottles in unpreserved samples, while very little loss was observed in unpreserved samples collected in HDPE bottles. Proper eventual acid preservation rapidly recovered most of the “lost” lead, in water samples collected in both bottle types. The particulate findings of Phase Two indicated that the method’s acid digestion procedure was effective, but difficult to consistently implement with some lead particulates. These findings aid in determining the effectiveness of the EPA sample preservation protocol detailed in Method 200.8.

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## List of Abbreviations

AL	Action Level
Ca	Calcium
Cu	Copper
DI	Deionized Water
HCl	Hydrochloric Acid
HDPE	High Density Polyethylene
HNO <sub>3</sub>	Nitric Acid
ICP – MS	Inductively Coupled Plasma – Mass Spectrometry
IQ	Intelligence Quotient
LCR	Lead and Copper Rule
LSL	Lead Service Line
MCL	Maximum Contaminant Level
NaOH	Sodium Hydroxide
NTU	Nephelometric turbidity units
Pb	Lead
PbO <sub>2</sub>	Lead (IV) Oxide
SDWA	Safe Drinking Water Act
USEPA	United States Environmental Protection Agency
XRD	X-Ray Diffraction

## 1.0 Background

The United States Environmental Protection Agency (USEPA) is responsible for establishing regulations that ensure provision of safe drinking water throughout the country. Regulations under the Safe Drinking Water Act (SDWA) protect public health by establishing Maximum Contaminant Levels (MCLs) or other enforceable thresholds for contaminants including microorganisms, disinfection byproducts, inorganic/organic chemicals, and radionuclides (USEPA, 2012). Water quality monitoring by drinking water utilities is necessary to demonstrate regulatory compliance with these enforceable limits.

The Lead and Copper Rule (LCR) (USEPA, 1991) is unique compared to other regulations that target inorganic contaminants in drinking water. This is because compliance sampling for lead (and copper) occurs at household taps rather than at the entry point to the distribution system, acknowledging that premise plumbing materials can be primary sources of lead and copper contamination at the tap. Furthermore, the LCR established an action level (AL) rather than an MCL for lead (and copper) (USEPA, 1991). If more than 10% of the water samples (exact sample number depends on system size) exceed an AL of 0.015 mg/L for lead (1.3 mg/L for copper), then the drinking water utility is required to implement certain treatment techniques to control lead corrosion.

Sources of lead in tap water include old lead service lines (LSLs), old lead solders, and brass plumbing components (Triantafyllidou and Edwards, 2012; Sandvig et al., 2008; Schock, 1990). If present, LSLs can contribute up to 50–75% of the total lead measured at the tap (Sandvig et al., 2008). Total lead concentration at the tap consists of particulate lead and dissolved lead. Particulate lead is operationally defined as the lead fraction in a water sample that is retained by a 0.45  $\mu\text{m}$  water filter. The fraction of lead that passes through the filter is considered to be dissolved. Total lead (dissolved and particulate) released from plumbing materials into tap water can pose health risks when ingested. Although the LCR considers total lead concentration, knowing the form of lead is useful in identifying the cause of lead release and the type of lead exposure.

Lead is a neurotoxin, and lead exposure has long been associated with intellectual impairments in children (e.g., IQ deficits and behavioral changes) (Health Canada, 2013). Recently, such neurodegenerative effects in children and other health effects in adults (cardiovascular, renal, and reproductive) were summarized at much lower levels of lead exposure than previously reported (Health Canada, 2013). Clearly, assessment of potential human exposure to lead requires accurate quantification of the total lead concentration (dissolved and particulate) in tap water.

## 2.0 Introduction

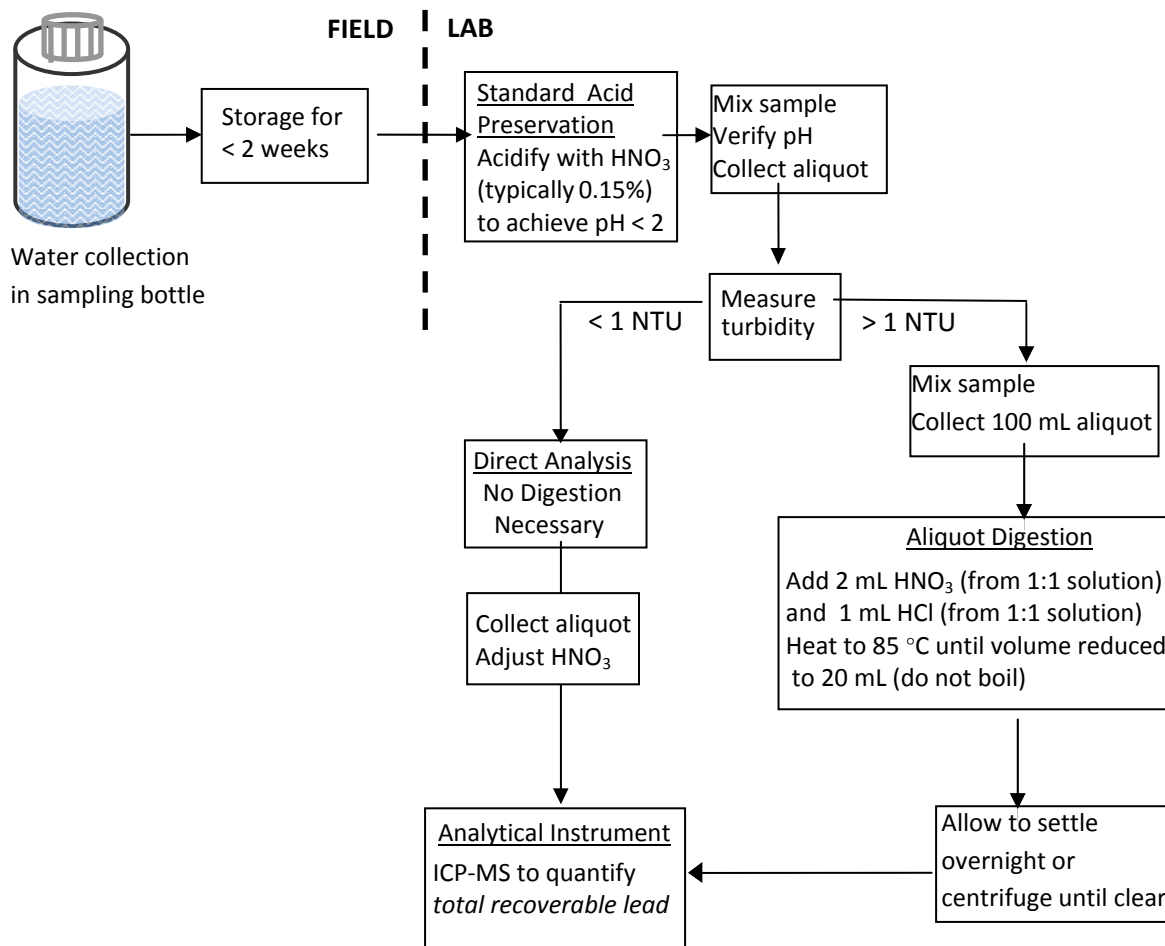
USEPA Method 200.8 is an accepted method for the determination of total lead and other trace elements in water (and wastes) by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (USEPA, 1994). Among other instructions, the method provides a protocol for acid preservation of water samples (Figure 1), because this step can affect lead quantification. Adding acid preservative to water samples aims to prevent metal precipitation and reduce metal adsorption onto the walls of sampling bottles (Sliwka-Kaszynska et al., 2003), thereby rendering all the metal soluble and thus quantifiable by ICP-MS.

For the determination of “total recoverable” lead, Method 200.8 requires that tap water samples are shipped to a lab for acid preservation and further processing (Figure 1). The method allows collection of samples without immediate acid preservation, to alleviate the safety concerns of handling acids in the field and during sample shipment to the lab. Preservation should therefore be performed in the lab as soon as practical, but may be delayed up to two weeks following sample collection. Research conducted by Miller et al. (1985) in support of this time frame, indicated that acidification of water samples could be performed up to two weeks after collection without gravely affecting lead recovery. In that work, mean lead recovery after two weeks of unpreserved sample storage and subsequent acidification was 90% for samples with 70 µg/L lead, and 94% for samples with 20 µg/L lead (Miller et al., 1985). Feldman et al. (1992) and Creed et al. (1995) similarly reported that if water samples were held for two weeks unpreserved, subsequent acidification to  $\text{pH} < 2$  re-solubilized the metals that had fallen out of solution.

Standard acid preservation under Method 200.8 involves acidifying the samples to  $\text{pH} < 2$ , and is typically achieved by addition of 0.15% v/v concentrated nitric acid ( $\text{HNO}_3$ ) in the lab. After a minimum 16-hour sample holding time from the moment of acid addition, the sample pH is measured. If the measured pH exceeds the required minimum, the pH is adjusted and the holding period time frame is repeated. If the measured pH meets the requirement of 2 or less, then an aliquot is collected to measure turbidity.

A decision tree for further sample processing is based on the turbidity measurement. If the turbidity is less than 1 nephelometric turbidity unit (NTU) then lead is assumed to have been

rendered soluble, and a sample aliquot can be directly analyzed by ICP-MS (Figure 1). If the turbidity is greater than 1 NTU, a sample aliquot must undergo a rigorous heated acid digestion step, with the addition of specified amounts of nitric acid and hydrochloric acid at 85 °C before analysis (Figure 1). This additional preservation step aims to ensure that any particulate lead present (as indicated by increased turbidity) dissolves so that it can be quantified by ICP-MS.



**Figure 1. EPA Method 200.8 (ICP-MS) specifies procedures to quantify total recoverable lead (and other trace metals) in drinking water samples. A slightly different digestion (not shown) is recommended if the sample contains >1% undissolved solids. Modified from Triantafyllidou et al. (2013).**

The standard acid preservation to pH < 2 has been shown to adequately quantify total lead, in water samples where lead contamination was fairly low and predominantly in dissolved form (Triantafyllidou et al., 2013; Deshommes et al., 2010), or in the form of very fine lead solder

powder which had been deliberately introduced to water samples (Lytle et al., 1993). In cases where water samples were highly contaminated with lead particles, the standard acid preservation was reported to miss some of the lead present, compared to more rigorous heated acid digestions (Triantafyllidou et al., 2013; Triantafyllidou and Edwards, 2007). In the presence of lead (IV) particles in water samples (which are far less soluble in water compared to Pb(II) particles), lead recovery was reported as low as 20% (Triantafyllidou and Edwards, 2007). Triantafyllidou and Edwards (2007) suggested increasing the concentration of nitric acid during sample preservation (2% HNO<sub>3</sub> instead of 0.15% HNO<sub>3</sub>), to achieve much lower pH in the water sample than the method-specified pH < 2, and thus to further increase lead solubility.

Bottle type was shown to affect lead recovery in unpreserved water samples. Issaq and Zielinski (1974) found that 50% of the lead in unpreserved samples containing 400 µg/L lead was lost after 1 hour in glass bottles due to adsorption to the bottle walls, compared to a lower lead loss of 30% in polyethylene bottles after 1.5 hours. Acidification with nitric acid, however, was able to prevent losses due to adsorption onto container walls (Issaq and Zielinski, 1974). Salim and Cooksey (1979) noted that the water type could affect lead losses onto container walls, because presence of other ions in the water (e.g., zinc and calcium) would compete with lead for the available adsorption sites.

Overall, review of the literature indicated that the extent of lead contamination in water samples, the form of the lead (dissolved versus particulate), the preservation pH, the type of sampling container (e.g., glass or HDPE) and the type of water sample (i.e., the sample matrix) are important factors affecting acid preservation of water samples for lead quantification.

### **3.0 Project Objectives**

The main objective of this project was to investigate the effectiveness of the sample preservation protocol outlined in Method 200.8 in recovering lead from water samples. Lead recoveries were studied in various water samples spiked with lead, by evaluating lead sorption and desorption from sample bottles using ICP-MS. Specific concerns with the acidification protocol, bottle types, and occurrence of particulates in water, were investigated in two phases.

Phase One of the study focused on the recovery of dissolved lead within different water sources, bottle types, and preservation pHs. The lead recovery in glass and high-density polyethylene (HDPE) bottles was examined in DI water, ground water, surface water, and DI water containing 100 mg/L calcium. Similarly, lead recovery was compared between altered sample preservations at pH 2, 4, 5, 6, and 7. Phase Two examined the recovery of particulate lead from water samples, using direct and total recoverable analyses. Specifically, the recovery of lead phosphate, basic lead carbonate and lead (IV) oxide was evaluated.



## 4.0 Experimental (Materials and Methods)

The project was conducted in two phases. The first phase focused on the impact of water source, bottle type, and preservation pH on the recovery of lead in water samples spiked with dissolved lead. The second phase focused on what acid preservation and/or acid digestion conditions would achieve complete solubilization of particulate lead, prior to quantification by ICP-MS.

### 4.1 Materials and Reagents

Tests conducted during Phase One used 500 mL high density polyethylene (HDPE) bottles (Nalgene, Rochester, NY) and 500 mL glass media bottles (Wheaton, Millville, NJ) with polyethylene lined phenolic caps. Glass bottles were acid-washed in a 10% nitric acid ( $\text{HNO}_3$ ) solution before use, whereas HDPE sample bottles were used directly from the package. The acid wash solutions were prepared with reagent grade  $\text{HNO}_3$  (GFS Chemical, Columbus, OH). Tests conducted during Phase Two used 250 mL HDPE bottles directly from the package.

Acid concentrations, unless otherwise specifically stated, were dilutions from “concentrated” acids. Acids employed were double distilled, “Veritas” nitric acid ( $\text{HNO}_3$ , 15.9 N) and hydrochloric acid ( $\text{HCl}$ , 12 N) (GFS Chemical). The pH of water samples was adjusted with reagent grade sodium hydroxide ( $\text{NaOH}$ ) (GFS Chemical). Dissolved metal standards were prepared with ICP-MS lead standards (GFS Chemical). The DI water was obtained with a Thermo Scientific Barnstead B-Pure system, supplied with building reverse osmosis treated water.

Three different lead particulate compounds were investigated in Phase 2, including a) lead carbonate basic ( $[\text{PbCO}_3]_2 \cdot \text{Pb}[\text{OH}]_2$ ) (Alfa Aesar, Ward Hill, MA), b) lead oxide ( $\text{PbO}_2$ ) (Alfa Aesar, Ward Hill, MA) and c) lead orthophosphate ( $\text{Pb}_3[\text{PO}_4]_2$ ) (Johnson Matthey, Taylor, MI). Scanning electron micrographs revealed that the particles ranged from less than 1  $\mu\text{m}$  to approximately 10  $\mu\text{m}$  in size (Figure 2). The X-ray diffraction (XRD) analysis of the respective compounds determined that the primary mineralogical makeup of the standards was: a) hydrocerussite with traces of other Pb(II) carbonate hydroxide oxides, b) plattnerite with traces of other Pb(IV) oxides, and c) lead orthophosphate.

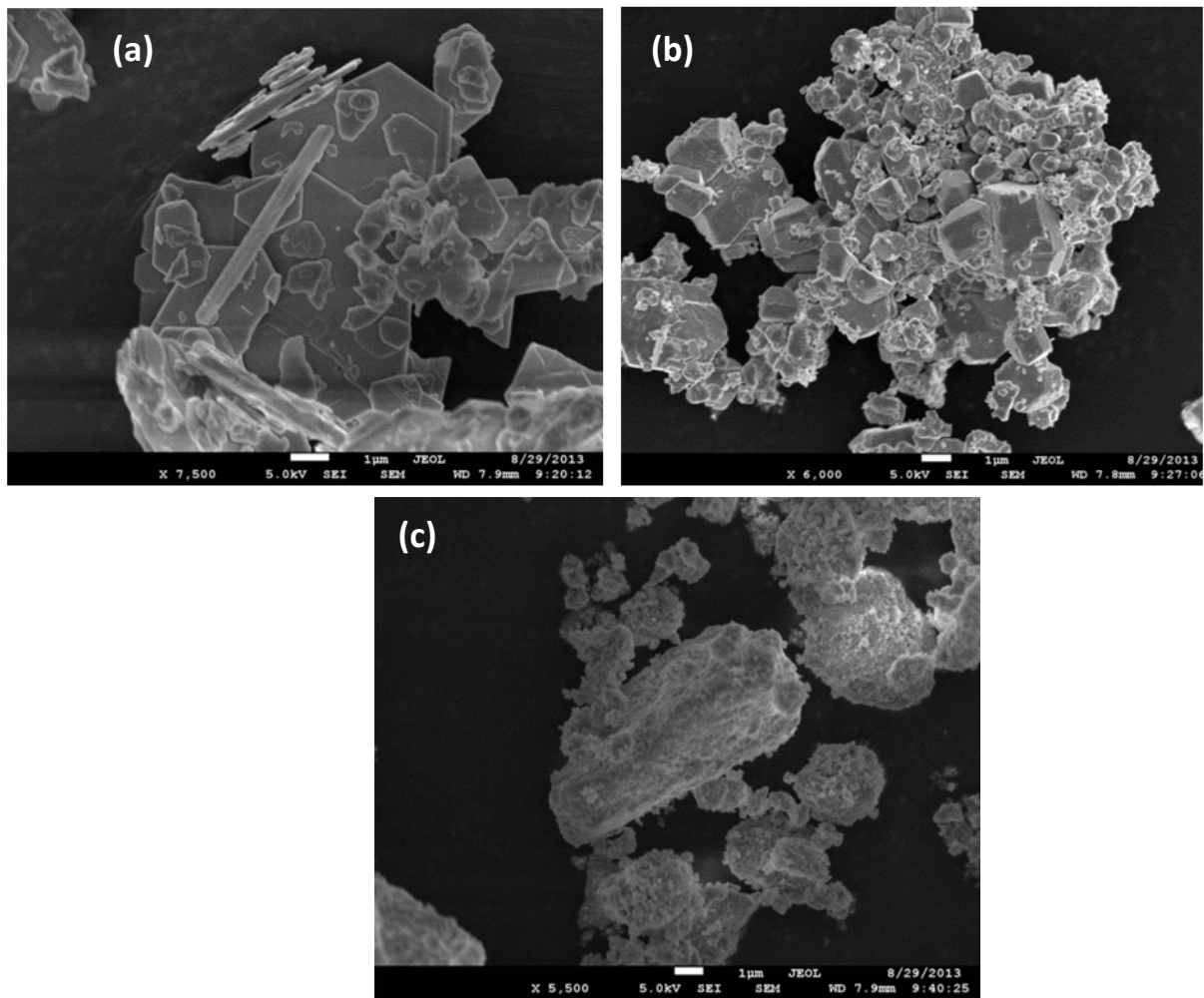


Figure 2. Scanning electron micrographs of lead particles added to water samples in Phase Two to investigate lead recovery: (a) basic lead carbonate, (b) lead oxide, (c) lead orthophosphate.

#### 4.2 Equipment and Instrumentation

Sample pH was measured using an Expandable Ion Analyzer pH meter (EA 940 Orion Research, Cambridge, MA) and a standard electrode. Three point calibrations were performed daily.

All heat digestions were performed using a *DigiPREP* Heat Block Jr. and Keypad (SPC Science, Champlain, NY). Heat digestions were performed at 85°C using 50 mL digestion tubes, a *DigiPREP* Heat Block Jr. and Keypad (SPC Science, Champlain, NY).

All direct and total recoverable analyses were performed using an Agilent (Santa Clara, CA), 7500cs Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) and a Thermo Elemental (Franklin, MA) ICP-MS model X7.

Particulate sample filtrations were performed with Fisherbrand™ 0.45 µm nylon luer lock syringe filters (Fisher Scientific, Pittsburgh, PA). Preliminary determinations revealed the filters did not impact dissolved metal concentrations when used on nitric acid preserved samples.

### **4.3 Phase One: Dissolved Lead Recovery**

#### **4.3.1 Preparation of Sample Bottles**

All tests in this phase were performed in 500 mL HDPE versus 500 mL glass bottles. The four water sources studied were DI water, DI water spiked with calcium, surface tap water and ground tap water (Table 1). The DI water spiked with calcium was prepared with 100 mg/L calcium ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) (Fisher Scientific, Waltham, MA). The surface water was collected from a faucet in the laboratory, distributed from the Miller Treatment Plant of the Greater Cincinnati Water Works (Cincinnati, OH). The ground water was collected from a faucet in a home, distributed from the Bolton Treatment Plant of the Greater Cincinnati Water Works (Cincinnati, OH). Each water outlet was flushed for ten minutes before water sample collection.

**Table 1. Background elemental analysis of surface water, ground water, and DI water spiked with calcium**

<b>Element</b>	<b>Surface water Concentration (mg/L)</b>	<b>Ground water Concentration (mg/L)</b>	<b>DI spiked with Ca Concentration (mg/L)</b>
<b>Lead</b>	0.0036	< 0.002	< 0.002
<b>Al</b>	0.0260	0.0127	0.0157
<b>As</b>	< 0.004	< 0.004	< 0.004
<b>Ba</b>	0.0288	0.0146	0.0027
<b>Be</b>	< 0.005	< 0.005	< 0.005
<b>Ca</b>	26.83	17.26	95.27
<b>Cd</b>	< 0.0003	< 0.0003	< 0.0003
<b>Cr</b>	< 0.001	< 0.001	0.0045
<b>Cu</b>	0.0046	0.0018	0.0017
<b>Fe</b>	0.0136	< 0.001	0.0026
<b>K</b>	1.822	3.304	0.3122
<b>Li</b>	< 0.005	< 0.005	< 0.005
<b>Mg</b>	8.089	21.18	< 0.005
<b>Mn</b>	< 0.001	< 0.001	< 0.001
<b>Na</b>	18.380	32.09	0.0341
<b>Ni</b>	< 0.001	< 0.001	< 0.001
<b>P</b>	0.1623	0.1175	< 0.005
<b>S</b>	18.92	19.69	< 0.003
<b>Sb</b>	< 0.003	< 0.003	< 0.003
<b>Si</b>	2.676	4.366	< 0.020
<b>Sn</b>	< 0.001	< 0.001	< 0.001
<b>Sr</b>	0.1645	0.1402	0.0160
<b>V</b>	< 0.001	< 0.001	< 0.001
<b>Zn</b>	0.0234	0.0005	0.00065

Water samples were spiked to 50 µg/L lead. Each trial included at least one preserved sample and duplicate unpreserved samples (Figure 3). Preserved samples were adjusted to a pH of less than two by adding HNO<sub>3</sub>. Unpreserved sample bottles were adjusted to a pH 7, with the exception of the investigation of different pH preservation levels, by adding 0.1 N NaOH until desired pH was reached.

The impact of preservation pH on lead recovery was studied by adjusting water samples to a pH of 4, 5, 6, and 7. After sample bottle preparation was completed, the sample bottles were stored and sampled according to the established protocol. After the designated storage time, the unpreserved samples were acidified using HNO<sub>3</sub> to obtain either a pH 2 or 4.

### 4.3.2 Sampling Method

Sampling of the unpreserved water (in HDPE versus glass containers) took place over a one-week or two-week time frame, with sample collection at 0, 24, 48, 96 hours and one and two weeks. This was done because according to Method 200.8, water samples can remain unpreserved for a period of up to two weeks. Duplicate 2 mL aliquots were taken from each sample bottle for analysis (Figure 3). Following acidification of the unpreserved samples, sampling continued for an additional one or two weeks, at 24, 48 hours, and one and two weeks. Each sample bottle was shaken for 10 seconds immediately before sampling. The pH of each sample bottle was monitored throughout each trial and recorded in a laboratory notebook.



**Figure 3. Duplicate 2 mL aliquots from each sample bottle (HDPE versus glass) were collected for lead analysis at specified time intervals in Phase One.**

### 4.3.3 Statistical evaluations

All statistical comparisons were performed with the two sided t-test and evaluated at the 95% confidence interval.

#### **4.4 Phase Two: Particulate Lead Recovery**

##### **4.4.1 Preparation of Sample Bottles**

All tests in Phase Two were performed in 250 mL HDPE bottles. No pre-cleaning of the bottles was performed. Particulate lead compounds were weighed on a 0.01 mg balance (Model M220D, Denver Instrument, Bohemia, NY). Aluminum foil weigh boats were employed to minimize errors frequently encountered with plastic weigh boats and static charge effects.

##### **4.4.2 Sampling Method**

Tests were performed in duplicate and individual aliquoting procedures were performed in triplicate. Results were then averaged. All dissolved lead determinations were performed on aliquots that had been filtered through 0.45 µm nylon luer lock syringe filters.

##### **4.4.3 Heat Digestion Protocol**

Heat digestions were performed at 85°C using 50 mL digestion tubes with elevated watch glasses. Samples were acidified with nitric and hydrochloric acid, allowed to reduce initial volumes to approximately 20 mL and then refluxed for a minimum of one hour. Samples were then reconstituted to original volume and allowed to equilibrate overnight prior to analysis by ICP-MS.

#### **4.5 Analytical Method**

The method employed was EPA Method 200.8 “Determination of Metals and Trace Elements in Water and Wastes by ICP-MS”. Lead determinations were based on a summation of Atomic Mass Units (AMU)  $^{208}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$ . Calibration was based on 4 standards (Spex, Metuchen, NJ) and periodically verified through second source standards (GFS Chemical, Columbus, OH). The method detection limit was 0.02 µg/L.

## 5.0 Results and Discussion

Lead recovery in soluble lead-containing samples collected in glass and HDPE bottles was investigated in deionized water first. This was done to determine the effectiveness of EPA Method 200.8 in the absence of potential chemical interactions present in other investigated water sources. Lead losses to the glass bottles were observed, but after applying the preservation protocol detailed in EPA method 200.8, the “lost” lead was recovered. Next, varying the preservation pH determined the relationship between lead loss and actual preservation pH. Further investigation was performed to determine the effectiveness of the preservation method, and the relationship between dissolved lead loss and preservation pH in other water sources, including deionized water spiked with calcium, and ground and surface-based drinking waters. These tests identified the lowest recovery of lead in unpreserved glass bottles. Additionally, particulate lead recovery was investigated within deionized samples collected in HDPE bottles. Results showed variability in lead recovery depending on particle type, which initiated further investigation of the preservation method in the presence of lead particles.

### 5.1 Phase One: Dissolved Lead Recovery

#### 5.1.1 Impact of Bottle Type on Lead Recovery in DI Water Before and After Acid Preservation

Lead losses in DI water to bottles were largely dependent on bottle type, when the water samples were not acidified (Figure 4). In the case of glass bottles, lead losses, presumably due to sorption to the bottle surface, were almost immediate and accounted for an approximate 20 µg/L drop in the measured lead concentration during the first sampling event (at 0 hours). The lead concentration decreased by another 10 µg/L within the next 24 hours, to approximately 20 µg/L, where it remained at equilibrium until the samples were acidified. Unpreserved lead concentration in one glass bottle dropped to as low as 17.1 µg/L, and the unpreserved glass duplicate dropped as low as 14.7 µg/L. Lead measurements in the duplicate glass bottles were in reasonable agreement. Average lead recovery in these duplicate unpreserved bottles before acidification was 19.5 µg/L, or 38.9% of the initial lead spike concentration.

The HDPE unpreserved duplicate bottles did not show such a significant drop in lead recoveries before acidification. The unpreserved HDPE bottles had an average lead concentration of 44.4

$\mu\text{g/L}$  and  $46.9 \mu\text{g/L}$  by the end of week 2, or 88.9% and 93.8% recovery of the lead spike concentration.

After being stored unpreserved for 336 hours (i.e., two weeks), the DI water samples were acidified according to EPA Method 200.8 (Figure 1). The two unpreserved samples stored in glass bottles yielded reproducible results after acidification. The average lead concentration of these samples increased from  $19.5 \mu\text{g/L}$  to  $47.3 \mu\text{g/L}$  following acidification, to an average recovery of 94.7% of the calculated lead spike concentration. The recovery of lead occurred within 24 hours of acidifying the unpreserved samples. Where sorption losses of lead were important under un-acidified conditions, lead recovery was rapid, within 24 hours of acidification.

Lead-containing DI water samples stored in HDPE and glass bottles had similar lead recoveries after acidification. The lead concentration in the duplicate HDPE preserved samples averaged  $47.4 \mu\text{g/L}$  and  $45.2 \mu\text{g/L}$  after 24 hours of acidification (Figure 4), which is a 94.8% and 90.3% recovery of the lead spike concentration, respectively. The lead concentration in the duplicate glass preserved DI water samples averaged  $48.1 \mu\text{g/L}$ , or 96.3% recovery of the lead spike concentration. Overall, acidifying DI water samples containing  $50 \mu\text{g/L}$  soluble lead according to EPA Method 200.8 was sufficient to prevent lead losses due to sorption, for both glass and HDPE bottles studied.



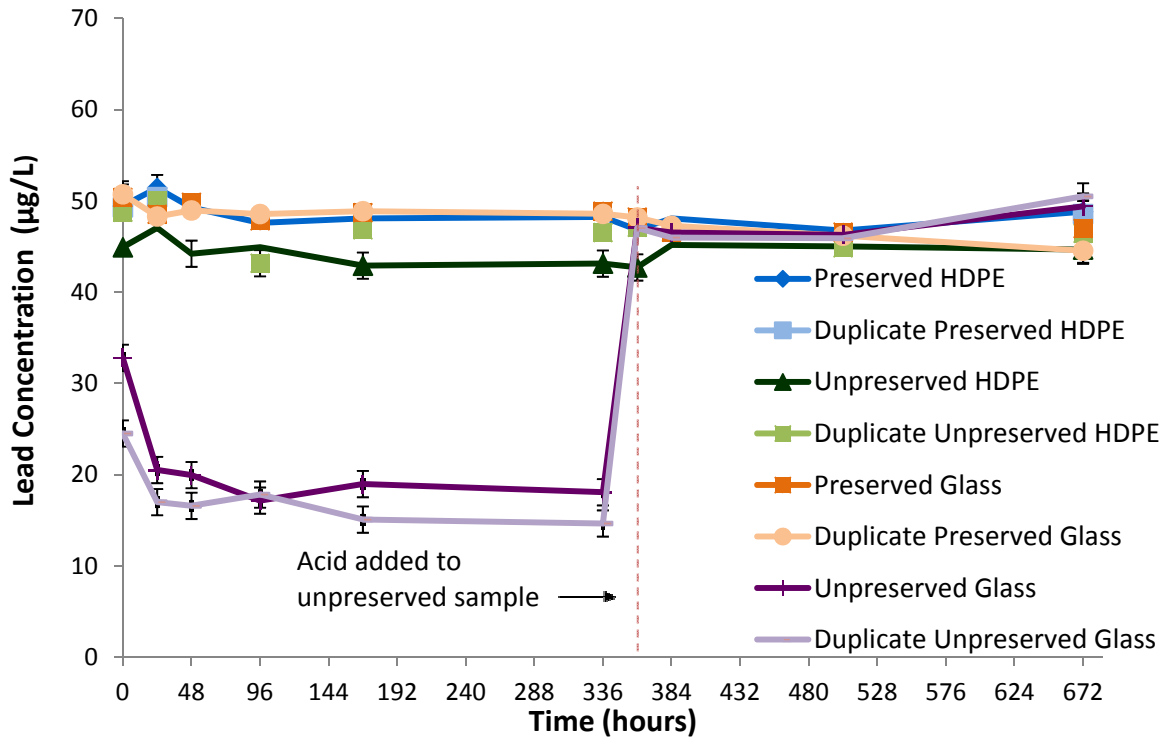


Figure 4. Lead concentration in DI water contained in glass and HDPE bottles.

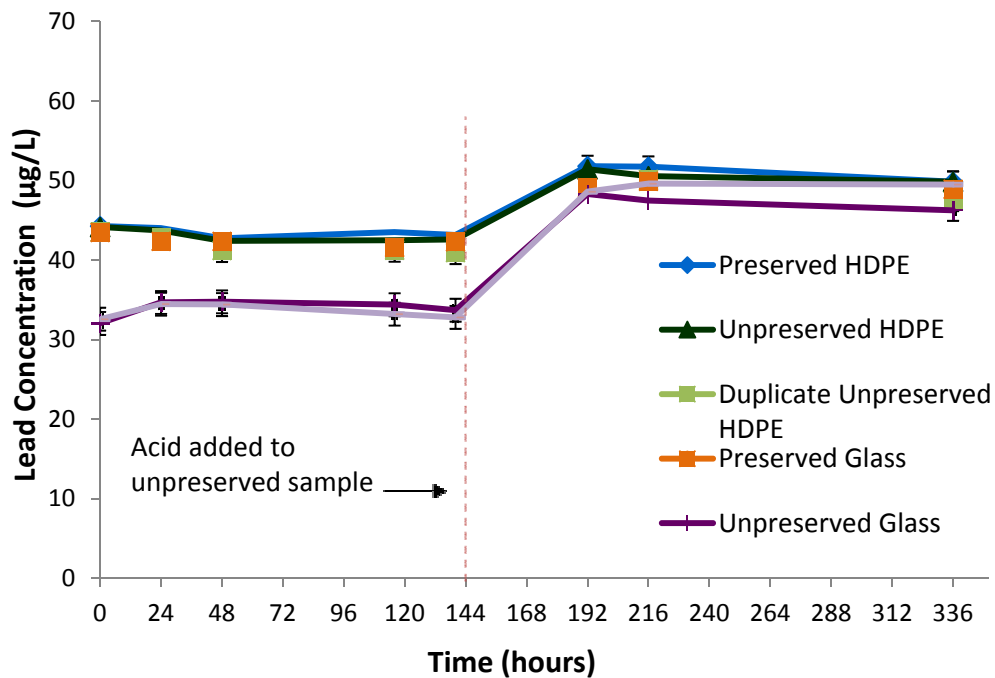


Figure 5. Lead concentration in DI water spiked with 100 mg/L calcium and contained in glass and HPDE bottles.

### *5.1.2 Impact of Bottle Type on Lead Preservation in DI Water with Calcium Before and After Acid Preservation*

Large losses of lead to unpreserved glass sample bottles were observed in the case of DI water (Figure 4). To test the sorption mechanism of lead loss and the importance of cation charge and concentration, calcium (100 mg/L) was added to the lead-containing DI water samples. Calcium was predicted to compete for cation sorption sites on the bottle surface. All HDPE and glass bottles showed no significant difference between duplicate bottles (Figure 5). The lead concentration in DI water containing calcium in unpreserved glass bottles averaged 33.5 µg/L, or 67.0% recovery of lead. The unpreserved HDPE samples had an average lead concentration of 42.5 µg/L, or 87.1% lead recovery before acidification. The presence of calcium clearly reduced lead losses to the glass bottle surfaces (Figures 4 and 5) confirming the importance of charge interactions and competing cations in the lead loss mechanism. After acidification to pH < 2 at 168 hours (i.e., 7 days), lead levels returned to the initial spike concentration (Figure 5).

### *5.1.3 Recovery of Lead in Drinking Water Samples Before and After Acidification*

The observation that the presence of calcium in DI water impacted lead losses to bottles suggests that the degree of lead loss in actual drinking water samples would also be impacted. The impact would likely be water quality specific, given the wide range and complexity of drinking water chemistries. To test the theory, lead recovery tests were performed in actual drinking waters at a pH of 7 to 8, having surface or ground water origin (see Table 1) in glass bottles.

There was no significant lead difference between duplicate bottles within each drinking water source. Greatest losses of lead to the glass bottles were associated with drinking water from the ground water source. Losses to the bottle all appeared to occur within the first 24 hours of unpreserved sample storage. Beyond 24 hours, lead levels remained unchanged. The lead recovery of unpreserved glass bottles containing ground water averaged 26.9 µg/L, or else 53.9% based on the initial calculated spike of lead concentration (Figure 6a and 7a).

Lead losses in drinking water of surface water origin were considerable (Figures 6b), but not as large as in drinking water produced from ground water (Figure 6a). And unlike groundwater trends, lead decreased or sorbed to the bottle exponentially up to 96 hours of standing before reaching equilibrium (Figure 6b). Measured lead concentrations averaged 36.7 µg/L, or 73.4%

recovery of the initial lead level. The unpreserved glass bottles of DI water containing calcium behaved similarly (Figure 7) and measured lead concentrations averaged 33.5 µg/L or a 67.0% recovery of the calculated initial lead level.

Lead concentrations in all unpreserved glass bottles showed an obvious difference when compared to the preserved glass bottles containing water from the same source. However, appropriate acidification was able to quickly recover lost lead (Figure 6a and 6b). The results illustrate that lead losses in unpreserved drinking water samples to glass bottles are complicated, and predicting losses is not straightforward.

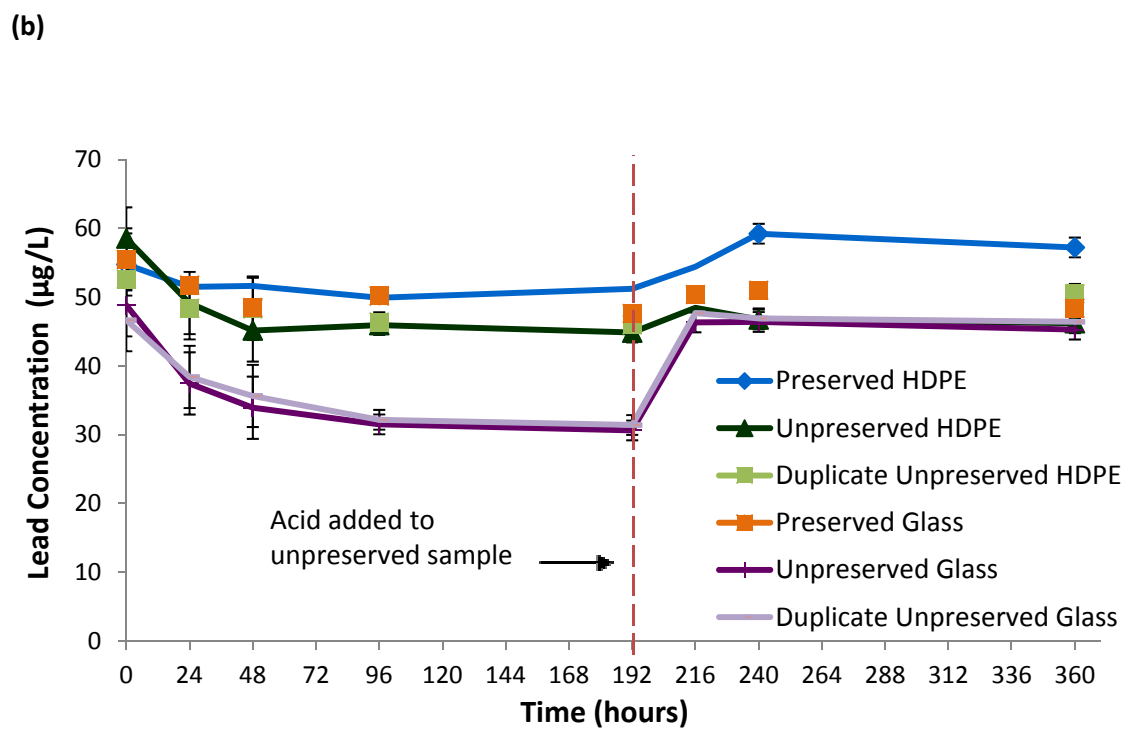
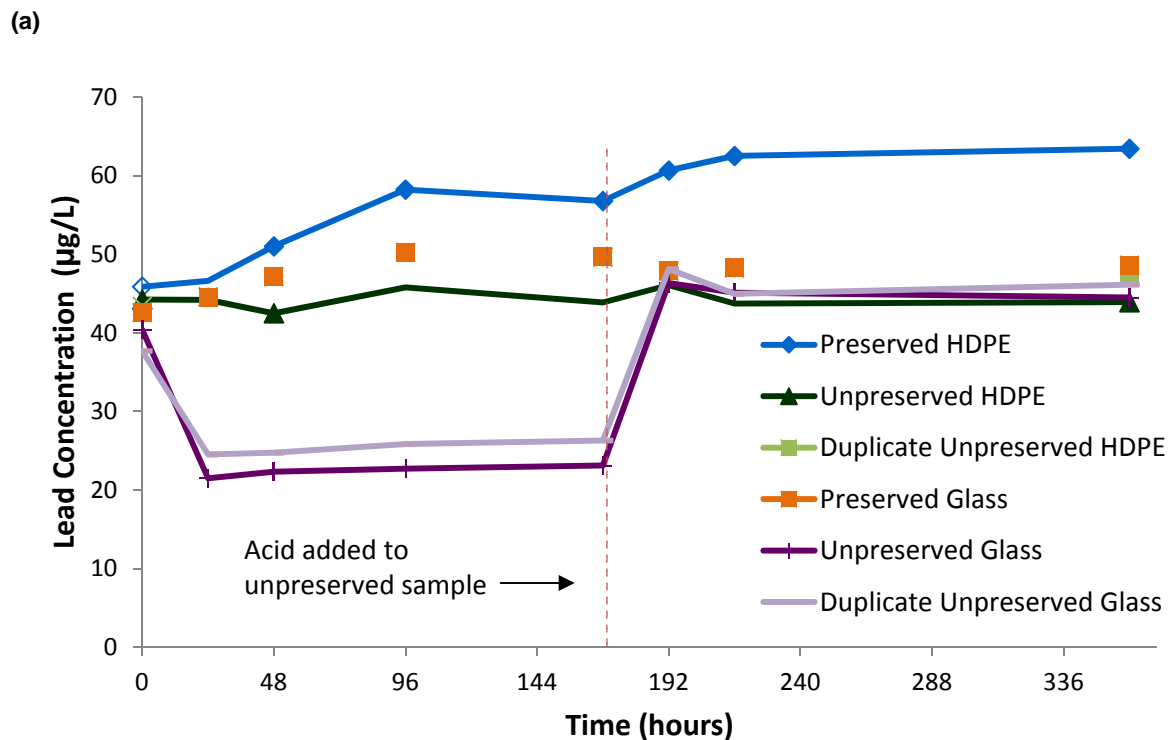


Figure 6. Lead concentration in drinking water from (a) ground water, and (b) surface water sources contained in glass and HDPE bottles.

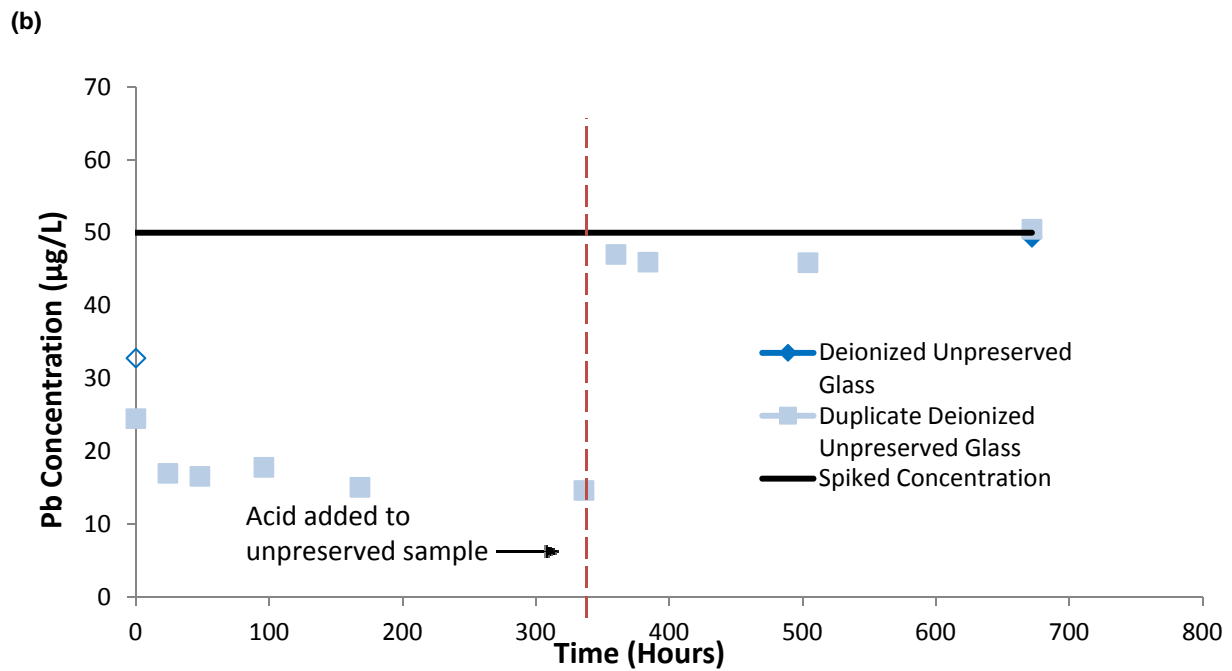
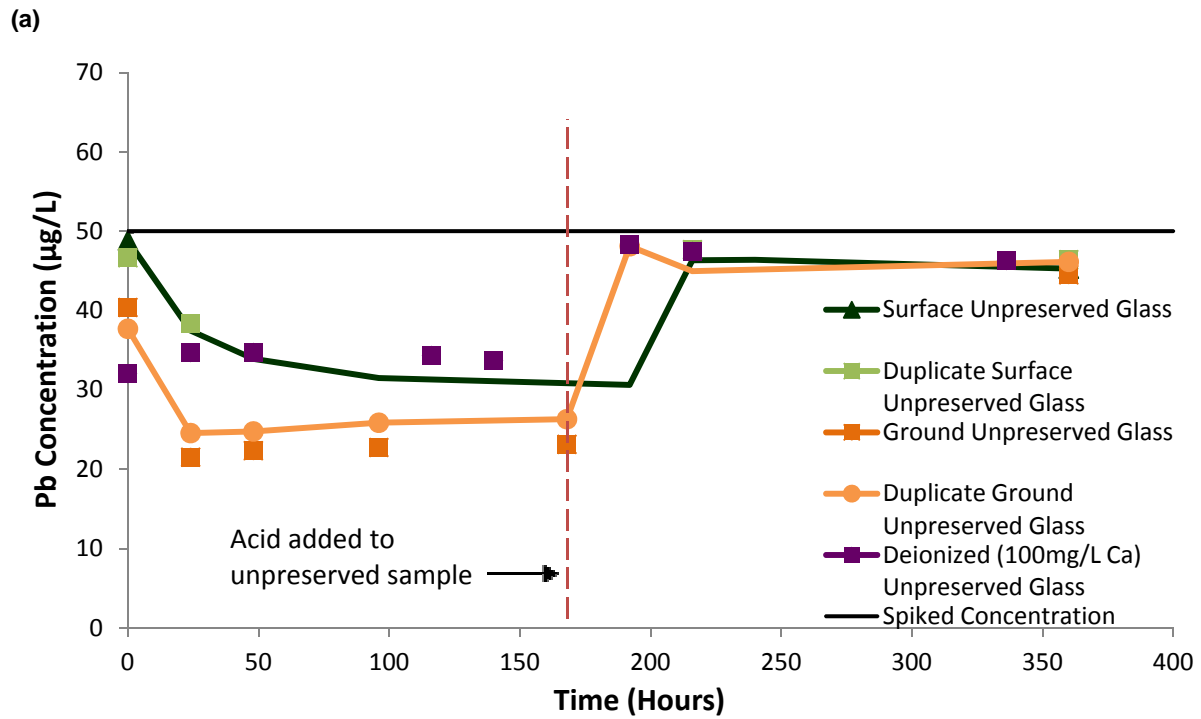
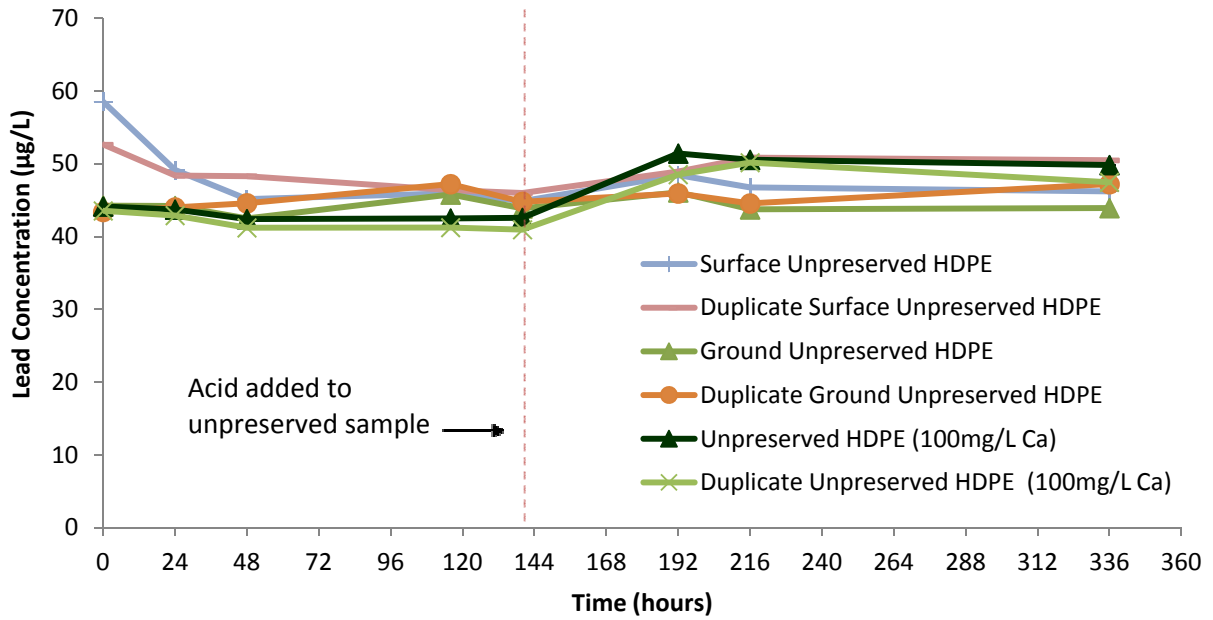


Figure 7. Lead concentration in various unpreserved water sources collected in duplicate glass bottles: (a) surface water unpreserved, and (b) ground water unpreserved.

Lead recovery in drinking water was much greater in unpreserved HDPE bottles (Figure 8a and 8b) compared to glass, which was consistent with DI waters. There was no significant difference between drinking water samples from the ground water source in unpreserved HDPE bottles. The average lead concentration prior to acidification was 44.5  $\mu\text{g/L}$  or a 88.9% lead recovery. The variability of the initial (time =0) determinations of the lead in the unpreserved surface samples in HDPE bottles prevented the ability to perform statistical analysis (t-test). Although statistical comparisons cannot be made with the unpreserved HDPE bottles, it was calculated that lead concentrations decreased to as low as 44.9  $\mu\text{g/L}$  and 46.0  $\mu\text{g/L}$  in these bottles which compares to the ground water results.

(a)



(b)

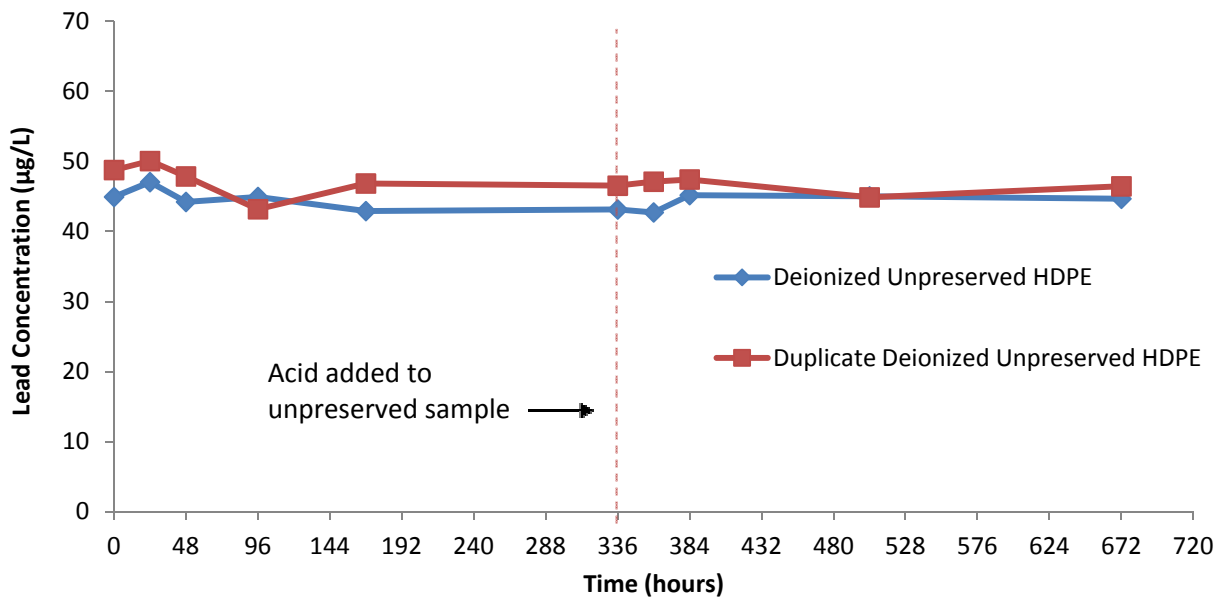


Figure 8. Lead concentration in various unpreserved water sources collected in duplicate HDPE bottles: (a) surface water unpreserved, ground water unpreserved, and deionized water with calcium unpreserved (100 mg/ L Ca); (b) deionized water unpreserved.

#### *5.1.4 Impact of Sample pH and Acid Preservation pH on Lead Recovery in DI Water*

The effect of the initial pH on lead losses was investigated in both bottle types. The impact of acidification pH at 384 hours (<2 according to EPA 200.8 versus a higher pH of 4) was also examined. Generally, as the initial sample pH increased from 4 to 7, lead recovery in unpreserved samples (before preservation) decreased and lead losses increased in the glass bottles (Figures 9a and 9b). All samples preserved to a pH less than 2 after delayed acidification, recovered greater than 90% of the original spiked concentration. The greatest lead recovery occurred in bottles immediately preserved to pH less than 2 (Figure 9b). Furthermore, there was a significant difference in lead recovery between immediately preserved sample bottles and sample bottles with a delayed preservation.

Glass and HDPE bottles preserved immediately to a pH less than 2 showed reproducible results as also seen in the DI trial (Figure 9b). Preserved HDPE and glass bottles showed no statistical difference to one another, when results were averaged for the time frame of the trial. The preserved HDPE bottle recovered an average of 50.8 µg/L lead, yielding a 102% recovery, while the preserved glass bottle recovered an average of 51.5 µg/L lead, yielding a 103% recovery (Figure 9b). These concentrations were slightly greater than the original 50 µg/L spiked concentration, suggesting noise within the instrument.

Glass bottles initially preserved to pH 4 showed no significant difference between one another, even after acidifying one to a pH of less than 2 (pH 4 glass condition in Figure 9a versus 9b). Although each recovered greater than 90% of the initial spiked lead concentration, each showed a significant difference to the bottle that was immediately preserved to a pH less than 2. One HDPE bottle remained at a pH 4 throughout the entire trial. As seen in Figure 9a, lead recovery increased for this bottle after 384 hours, even though its pH of 4 remained constant throughout the trial. The initial average concentration was 46.2 µg/L lead, yielding a 92.4% recovery, and significantly increased to an average concentration of 47.9 µg/L lead, yielding a 95.8% recovery, after 384 hours. A possible speculation for this increase is slow dissolution of lead from the HDPE bottle, contamination problems during sample handling in the lab or sample mixing effects.



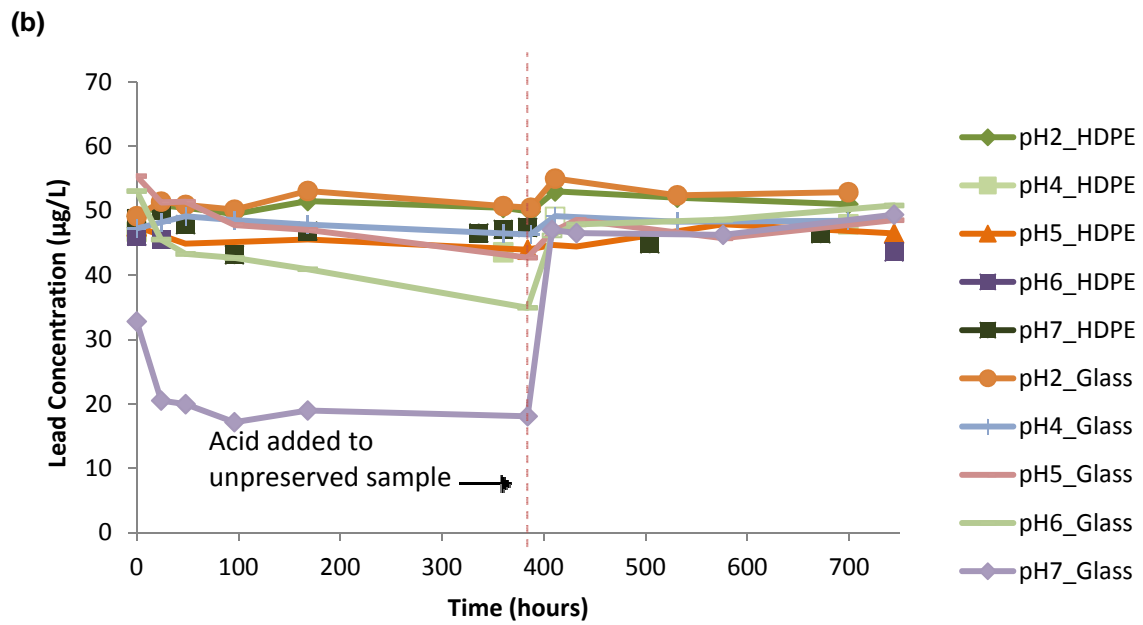
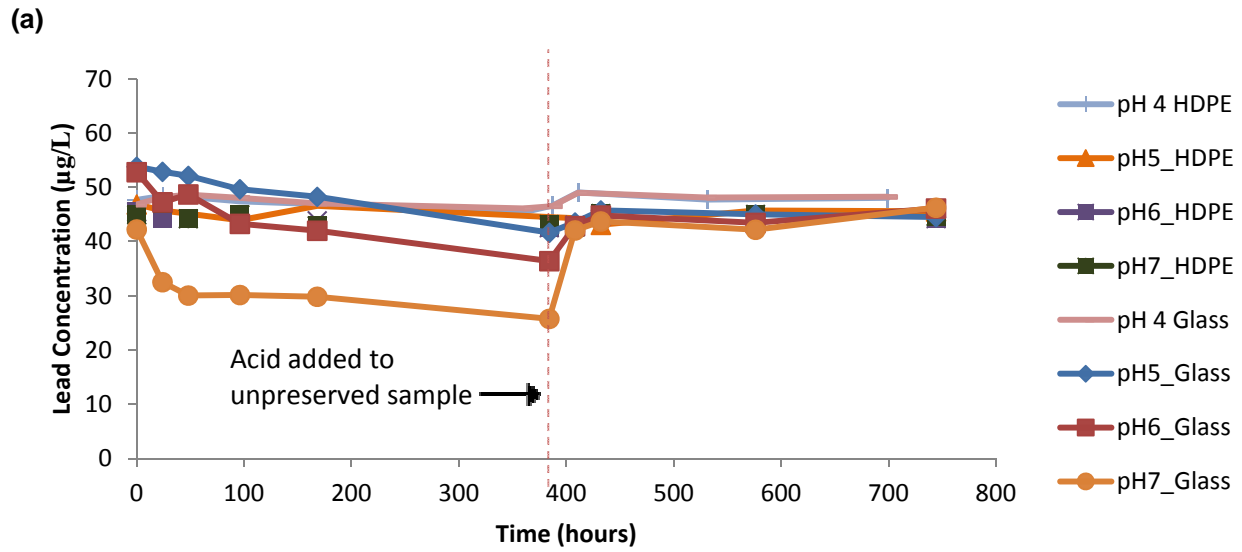


Figure 9. Lead concentration in HDPE and glass bottles based on initial preservation of (a) pH 4,5, 6, and 7 with a final preservation of pH 4 and (b) pH of 2, 4, 5, 6, and 7 with a final preservation of pH 2.

Although this bottle showed an increase in lead concentration while maintaining a pH of 4, the duplicate bottle that was eventually preserved to a pH less than 2 after 384 hours showed a decrease in lead concentration. The initial average concentration was 48.5 µg/L lead, yielding a 96.9% recovery, and after preservation lead significantly decreased to an average of 47.8 µg/L, yielding a 95.6% recovery (Figure 9a).

This variability was also observed at other preservation pHs. At pH 5, there was no significant difference between duplicate bottles of each bottle type. There was a significant difference between samples collected from HDPE bottles preserved at pH 5, when compared to samples collected from a HDPE bottle immediately preserved to a pH less than 2. This statistical difference was also seen in the duplicate glass bottle preserved at pH 5, but not in the original glass bottle. The original glass bottle showed no significant difference to the preserved glass bottle because the average included skewed results. The averaged concentration included concentrations as high as 53.8 µg/L lead to as low as 41.6 µg/L lead; therefore, the concentrations influenced the average to represent an average close to the preserved bottle.

After maintaining the initial pH to a fixed level (pH of 2, 4, 5, 6 or 7) for 384 hours (i.e., 16 days), sample bottles were preserved further to either a preservation pH 4 (Figure 9a) or a preservation pH less than 2 (Figure 9b). Although preservation was applied two days outside of the restricted two-week time frame of EPA Method 200.8, a preservation pH less than 2 had greater lead recovery compared to a preservation pH of 4, for the condition of initial pH 5 in both glass and HDPE bottles. The glass sample bottle preserved to a pH of 4 recovered 89.39% of the lead, whereas the duplicate bottle that was preserved to a pH of less than 2 recovered 94.78% of lead. As seen in Figure 9a, there was a slight decrease in lead recovery after preserving the HDPE pH 5 bottle to pH 4. At pH 5 the bottle recovered 90.9% lead and decreased to 89.4% lead recovery after further preservation to pH 4. Whereas after preserving the duplicate pH 5 bottle to a pH less than 2, an increase in lead recovery was observed from 91.1% to 91.8% lead. Although an increase was seen in glass and HDPE bottles preserved to a pH less than 2, there was still a significant difference in lead recovery when compared to the bottles immediately preserved to pH less than 2.

At an initial pH 6, the lowest lead recovery of 86.8% was observed in the glass duplicate bottle (Figure 9a). After further preserving these samples to a pH 4 or pH less than 2, there was no significant difference in lead recovery in HDPE bottles by applying either preservation. However, lead recovery was significantly different in glass bottles based on the preservation applied. When preserved to a pH less than 2, lead recovery was 96.8%, differing from the 88.6% lead recovery after applying a preservation pH 4. As seen with the preservation pH 5, a decrease in lead recovery was observed for pH 6 after applying the preservation pH 4. These lead recoveries were still significantly different from the recoveries of the immediately preserved bottle.

Finally, when comparing all initial preservation pHs, the lowest lead recovery was seen in glass bottles preserved to pH 7. Calculating from Figure 9b, the initial preservation pH of 7 yielded a 42.5 % lead recovery on average. The duplicate bottle (Figure 9a) yielded a 63.5% recovery on average. After further preservation within the glass bottles, lead recovery increased significantly. When preserved to pH 4, lead recovery increased to 87.1%. When preserved to pH less than 2, lead recovery increased to 94.6%. This increase was not observed in HDPE bottles; both showed an insignificant decrease in lead recovery after the same preservation was applied. Although these two HDPE bottles showed a decrease, they were significantly different from one another throughout the entire trial. Glass bottles only exhibited a significant difference in lead recovery after further preservations were applied. These differences indicated that there was variability among duplicate HDPE bottles when preserved to pH 7 and a significantly low lead recovery in glass bottles at this pH in deionized water.

### 5.1.5 Investigation of Possible Lead Contamination in HDPE Bottles

After observing an increase of lead concentrations greater than the 50 µg/L spiked concentration, an additional trial was performed to investigate lead recovery in “blank” HDPE bottles (i.e., no lead was added to the water sample). Fifteen HDPE bottles were filled with 500 mL DI water and preserved to a pH less than 2 using HNO<sub>3</sub>. Among these HDPE bottles, there was one occurrence where lead concentrations increased over time to 12.2 µg/L. As seen in Figure 10, any lead recovery above 100% within the HDPE bottles from the DI, surface and ground trials was very similar to the increase found in that one blank HDPE bottle. The increase in lead concentration within these bottles was therefore attributed to random lead contamination.

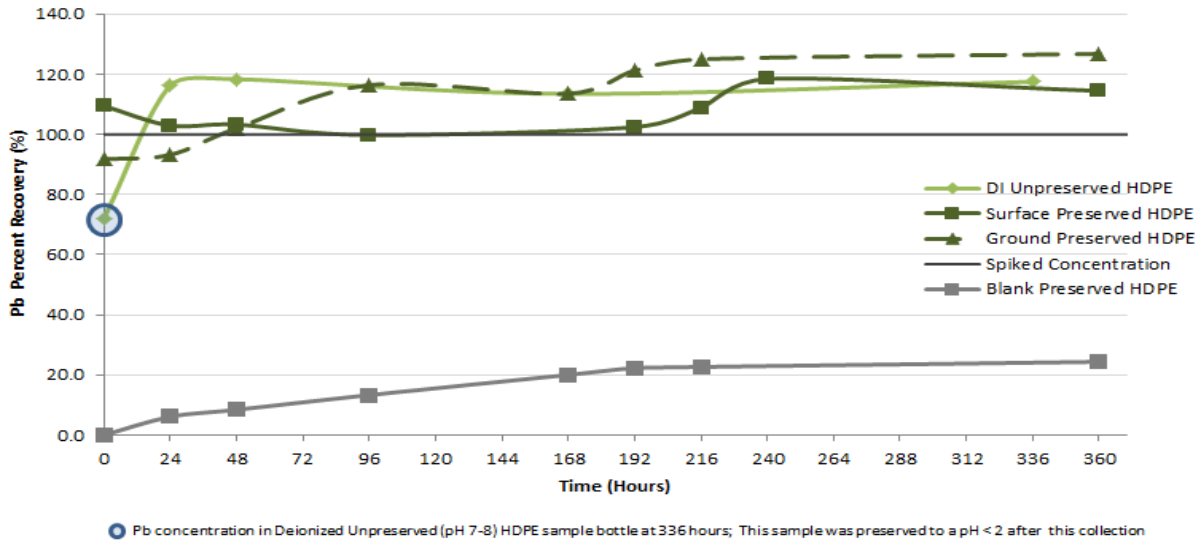


Figure 10. Lead recovery (%) in HDPE bottles preserved to pH < 2, and in one “blank” HDPE bottle preserved to pH < 2.

## 5.2 Phase Two: Particulate Lead Recovery

### 5.2.1 Total Recoverable Metals using the standard preservation

The standard approach for determination of metal content on drinking water samples, with turbidity  $<1$  NTU, is to acidify the sample to  $\text{pH} < 2$  with 0.15%  $\text{HNO}_3$ , wait 16 hours (minimum) and then directly analyze the sample by ICP-MS according to EPA Method 200.8.

The effectiveness of this approach was evaluated against the three lead compounds, lead IV oxide, basic lead carbonate, and lead orthophosphate. Approximately 10 mg of each compound was added to 200 mL DI water, in duplicate, and then acidified to  $\text{pH} < 2$  with  $\text{HNO}_3$ . The solutions were sampled periodically over a one week holding period. The bottles were shaken prior to sampling. Aliquots were taken in triplicate, filtered through a  $0.45 \mu\text{m}$  nylon syringe filter and the nitric acid concentration was adjusted to 2% prior to ICP-MS analysis.

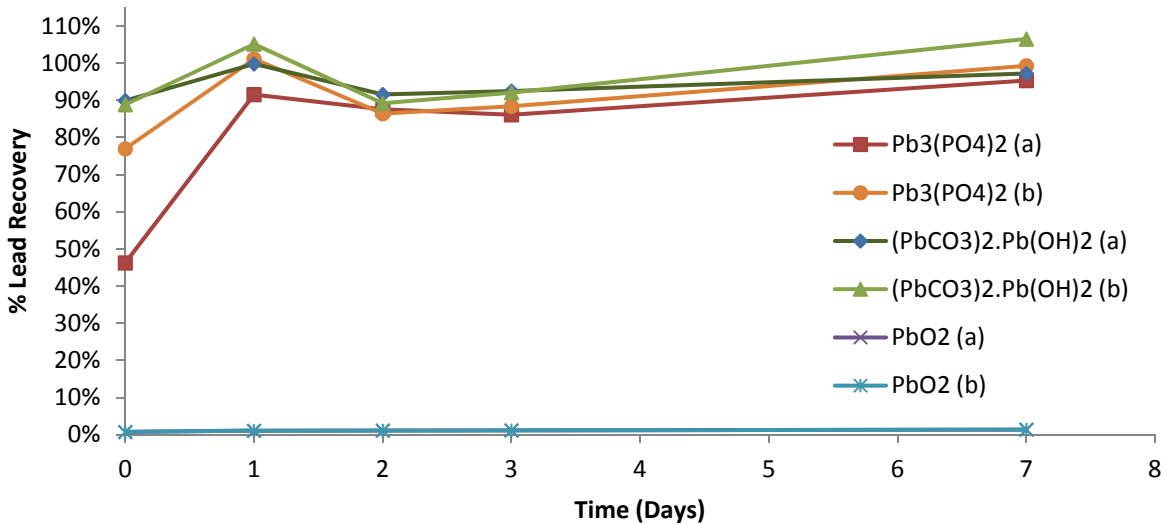


Figure 11. Dissolution of lead orthophosphate, basic lead carbonate and lead (IV) oxide, with standard preservation to  $\text{pH} < 2$  with nitric acid.

The lead carbonate and lead phosphate (lead (II) compounds) were solubilized within a one week period with the standard pH 2 (i.e., 0.15% nitric acid) preservation procedure (Figure 11). The lead (IV) oxide was only minimally dissolved (< 2%) over this time period (Figure 11). This is consistent with the higher-oxidized metal being relatively inert in the dilute nitric acid (0.024 N) at room temperatures.

### 5.2.2 *Determination of suspended and/or settled particulate*

Section 11.2.2 of USEPA Method 200.8 states that “For the determination of total recoverable analytes in aqueous samples of >1 NTU turbidity, transfer a 100 mL ( $\pm$ 1 mL) aliquot from a well-mixed, acid preserved sample to a 250-mL Griffin beaker. (When necessary, smaller sample aliquot volumes may be used)”. This approach is recommended for drinking water samples when undissolved particulate matter is suspected.

The three lead compounds were used to determine the efficacy of the wet digestion nitric acid/hydrochloric acid procedure detailed in the method for the dissolution of these solids (Figure 1). The lead compounds were weighed in triplicate, then directly transferred to the digestion vessels and processed according to the method with the addition of 2 mL HNO<sub>3</sub> (from 1:1 solution), 1 mL of HCl (from 1:1 solution) and 30 mL DI water. They were then covered with an elevated watch glass and placed on an 85°C hot plate for solution reflux for a minimum of one hour. Samples were then reconstituted and analyzed by ICP-MS.

**Table 2. Dissolution of basic lead carbonate, lead orthophosphate and lead (IV) oxide, with enhanced nitric acid and hydrochloric acid digestion**

Compound	Pb initial	Pb recovered	Recovery
	(mg)	(mg)	%
Lead Carbonate Basic (PbCO <sub>3</sub> ) <sub>2</sub> .Pb(OH) <sub>2</sub>	8.2	7.88	95.4%
	8.49	8.01	94.7%
	8.3	8.1	95.5%
Lead Orthophosphate Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	7.87	7.5	95.3%
	6.64	6.25	94.0%
	5.22	4.88	93.6%
Lead (IV) Oxide PbO <sub>2</sub>	10.1	9.74	92.5%
	8.95	8.72	97.9%
	9.12	8.98	93.0%

The digestion procedure was able to dissolve and quantify approximately 95% of the initial particulate compound (Table 2). Therefore, if a representative aliquot of the sample can be obtained, the digestion procedure can, in these cases, achieve dissolution of the target compounds.

### 5.2.3 Investigation of accuracy and precision of aliquoting multiphase samples

The method prescribes the collection of a “well-mixed” sample prior to the digestion procedure. Depending on the nature of the solids present, this collection may be difficult to achieve. This is particularly the case if the solids are not well dispersed and/or are significantly massive in nature, as to preclude homogeneous mechanical dispersion during sampling.

The ability to obtain a representative fraction of a sample containing particulate material (i.e. a “well mixed” homogeneous sample) was evaluated with the standard preservation resistant compound lead (IV) oxide. Sample agitation can be produced by physical shaking of the bottle prior to sampling or use of magnetic stir bar during sampling. Tests with a magnetic stir bar proved problematic when utilized for agitation of a lead (IV) oxide and DI water preserved with 0.15% HNO<sub>3</sub>. This was because PbO<sub>2</sub> was found to have been incorporated into the Teflon coating of the stir bar, with the inevitable impact on sample integrity. Further studies employed physical shaking of the bottle for sample dispersion.

20 mg of lead (IV) oxide (i.e., PbO<sub>2</sub>) was dispersed in 200 mL of DI water preserved with 0.15% HNO<sub>3</sub>, held for 24 hours and then sampled. The bottles were agitated and six aliquots were taken, three of which were filtered (0.45 µm nylon) and three remained unfiltered. All were then processed through the acid digestion procedure as detailed in Method 200.8.

**Table 3. Particulate PbO<sub>2</sub> recovery in acid preserved samples with nitric and hydrochloric acid digestion.**

Sample ID	Process	Pb (mg/L)	Recovery
digest 1	unfiltered	25.6	30.7%
digest 2	unfiltered	24.5	29.4%
digest 3	unfiltered	29.4	35.3%
digest 4	filtered	1.52	1.82%
digest 5	filtered	1.52	1.82%
digest 6	filtered	1.64	1.96%

The replicate sampling yielded reasonably consistent determinations for suspended particulate but the total recoveries were low (Table 3), consistent with the observation that settling occurred during the aliquoting procedure. The collection of a well mixed sample was determined to be not feasible under these conditions. This observation points to a larger concern; that a sample may contain only one particle, or a few, or a large number with a wide size and specific gravity range. Any of these situations would make the collection of a representative sample difficult. A new approach would be required.



#### 5.2.4 Evaluation of in-situ solubilization of multiphase samples

One approach would be to determine the effect of increasing the acid concentration of the preservation procedure in the original sample bottle, thereby affecting digestion in-situ. This would eliminate the difficulty encountered when attempting to analyze a subset of the original sample. The ICP-MS analytical procedure requires the sample matrix to be adjusted to 2% nitric acid prior to analysis, to ensure sample stability and eliminate memory effects in the sample introduction pathway. Therefore 2% nitric acid addition was chosen as a base concentration for this series of experiments. Hydrochloric acid was added to the sample in varying concentrations. Approximately 10 mg of lead (IV) oxide ( $\text{PbO}_2$ ) was dispersed in 200 mL DI water with 2% nitric acid. Hydrochloric acid was added at three concentrations of 0, 1 and 2%. Samples were prepared in duplicate. The solutions were sampled periodically over a one-week holding period. The bottles were shaken prior to sampling. Aliquots were taken in triplicate, and filtered through a 0.45  $\mu\text{m}$  nylon syringe filter to determine the dissolved lead component. The samples were then analyzed by ICP-MS.

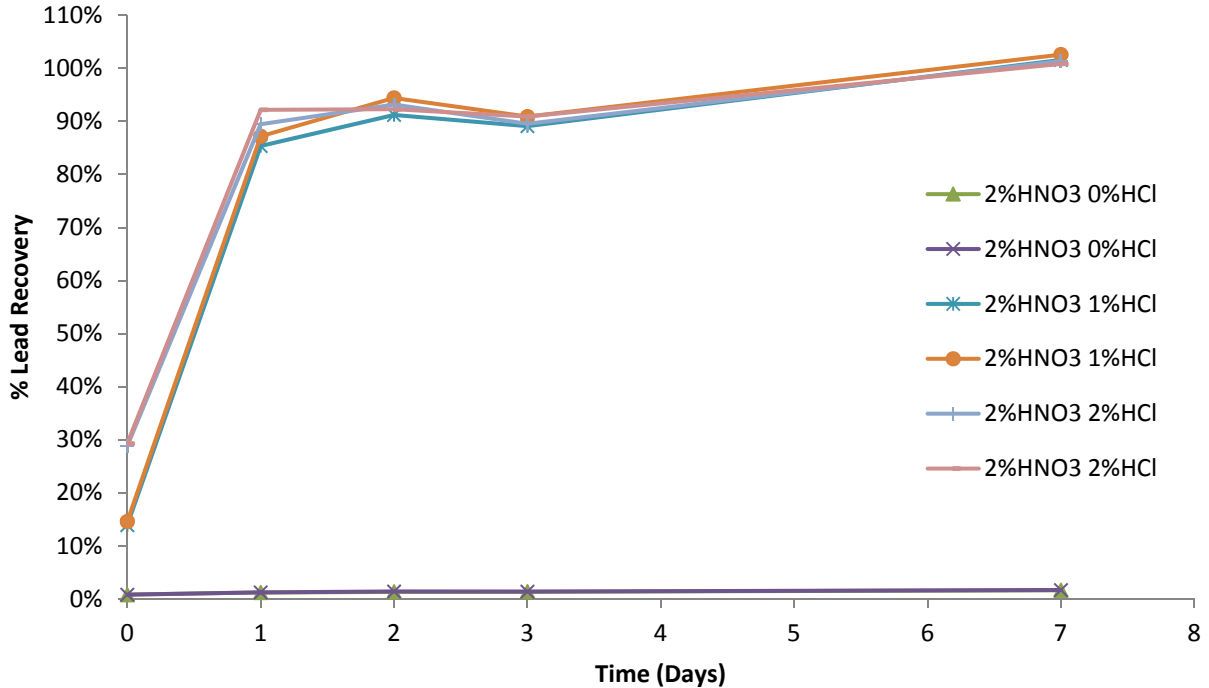


Figure 12. Particulate Pb(IV) oxide recovery with nitric and hydrochloric acid preservation.

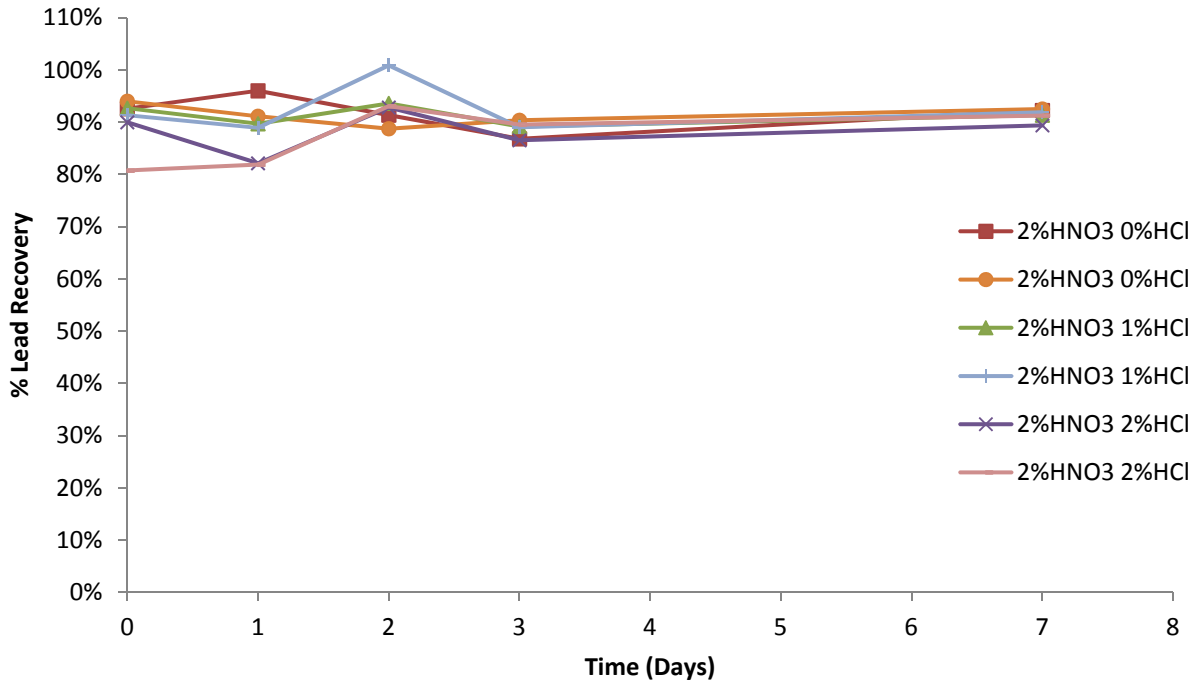


Figure 13. Particulate (PbCO<sub>3</sub>)<sub>2</sub>.Pb(OH)<sub>2</sub> recovery with nitric and hydrochloric acid preservation.

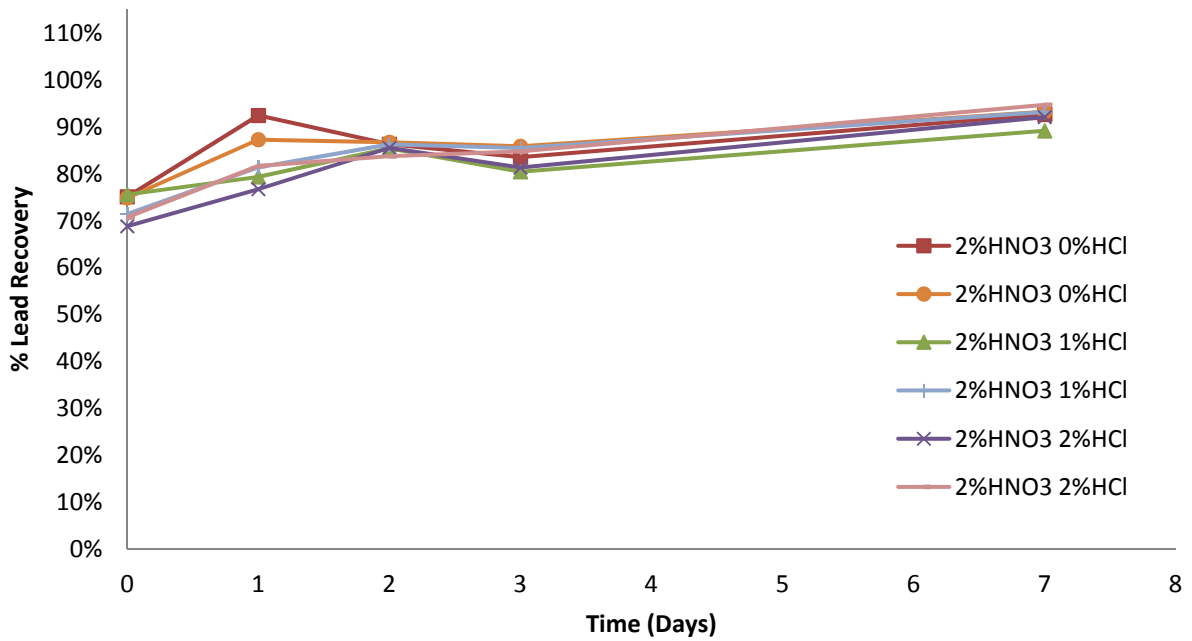
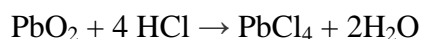


Figure 14. Particulate Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> recovery with nitric and hydrochloric acid preservation.

The results for the lead carbonate (Figure 13) and lead phosphate (Figure 14) were similar to the results with the 0.15% HNO<sub>3</sub> preservation experiments. Both exhibited recoveries in the 90 – 100% range after one week. These compounds are easily solubilized in low pH waters. The lead (IV) oxide was solubilized only in a hydrochloric acid matrix (Figure 12). The reduction of Pb (IV) to Pb (II) and the oxidation of chloride to chlorine in an acid matrix, are well documented thermodynamic principles<sup>1</sup>:



#### 5.2.5 *Evaluation of a pre-filtration procedure for the analysis of multiphase samples*

A pre-filtration approach, where the sample is filtered to allow processing of the particulate matter in a separate digestion procedure, would constitute a viable alternative to the problems associated with obtaining a “well mixed” representative aliquot for lead determinations. The procedure would require the sample to be filtered through a 0.45 μm filter, after which the filtered particulate and the filtrate portions would be digested according to the nitric/hydrochloric acid procedure in EPA Method 200.8.

Approximately 10 mg of lead (IV) oxide (PbO<sub>2</sub>) was dispersed in 200 mL DI with 0.15% nitric acid and was allowed to equilibrate for one week. The samples were then filtered through 0.45μm, 47mm HA filters (Millipore, Billerica, MA). The filter and filtration apparatus, stainless steel pressure vessels (Gelman Sciences, Ann Arbor, MI), were pre-cleaned with 250 mL, 0.15% nitric acid prior to each sample filtration. The filtered particles were then processed through the nitric/ hydrochloric acid digestion process along with a 30 mL aliquot of the filtrate solution. The

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<sup>1</sup> Descriptive Inorganic Chemistry, Third Edition - Geoff Rayner-Canham, Tina Overton, Macmillan, 2003

samples were then reconstituted with DI water and analyzed by ICP-MS. Digestion blanks and a dissolved lead standard were concurrently processed.

**Table 4. Particulate PbO<sub>2</sub> recovery through an alternative pre-filtration procedure.**

Sample ID	PbO <sub>2</sub>	Pb Initial	Filter	Filtrate	Pb Total	Pb Recovery
	(mg)	(mg)	(mg)	(mg)	(mg)	
1	13.08	11.33	10.155	0.177	10.332	91.2%
2	11.27	9.76	8.139	0.171	8.310	85.1%
3	10.25	8.88	7.812	0.123	7.935	89.4%
Pb Std	0	2.00	0.024	1.953	1.977	98.8%
Blank	0	0.00	0.022	0.016	0.038	
Blank	0	0.00	0.013	0.013	0.026	

The results indicate that the total Pb recoveries for the PbO<sub>2</sub> samples averaged 88.6% recovery (Table 4). The relatively low recoveries were attributed to losses within the filtration hardware. The particulate was observed to adhere to the sides of the metal jacket during filtration and was difficult to remove quantitatively. The dissolved lead standard recovery of 98.8% indicates the dissolved lead component of a sample is not significantly impacted by the filtration process. The background level of lead contamination in the blanks, 26–38 µg (Table 4), points to a larger concern with the approach in general. While this process could be ultimately enhanced to allow improved recoveries, the additional sample handling provides an opportunity for increased exposure to laboratory contamination.

## 6.0 Conclusions

### *Phase One*

Unpreserved glass bottles showed a significant decrease in lead concentration prior to acidification in all water sources. After acidification to a pH less than two, the lead recovery increased and showed no significant difference to the immediately preserved bottle in the DI, surface, ground and DI spiked with Ca trial. Within these glass bottles, DI water showed the greatest decrease, followed by ground water, surface water, then DI water spiked with Ca.

In the trials investigating the relationship between lead recovery and preservation pH in DI water samples, as pH increased, lead recovery decreased. As also seen within the other water source trials, the lowest lead recovery occurred in glass bottles preserved to pH 7 in this trial.

It was also determined that pH 4 was not an optimal preservation pH, because it did not always yield as high of a lead recovery as pH less than 2. In some cases, there was a significant difference between preservation to pH 4 and to a pH less than 2. This difference was seen in DI, surface and ground water samples collected in glass bottles. However, this difference was not seen in the bottles containing DI water spiked with 100 mg/L Ca. It is suspected that the high concentration of Ca present within the matrix influences lead recovery. Lead and calcium compete for the active sorption sites on the bottle's surface. It can be inferred from the results that calcium occupied the sorption sites, forcing lead to remain in solution at both preservation pHs.

Overall, all samples preserved to pH less than 2 recovered greater than 90% of the initial spiked dissolved lead concentration of 50 µg/L, independent of sample container type and delays in acidification.

### *Phase Two*

Recovery of lead particulates was more problematic than recovery of dissolved lead. A “well mixed” acid preserved sample was not always attainable, due to particulate inhomogeneity even if samples were vigorously agitated prior to aliquoting. A concentration of 2% HNO<sub>3</sub> and 1%

HCl provided complete solubilization of the three investigated lead compounds. This technique would require the addition of large amounts of reasonably expensive high purity acids (i.e., 20 mL nitric and 10 mL hydrochloric acid) to the 1L water samples mandated in the LCR. An alternative pre-filtration procedure offers advantages over the digestion procedure, specifically given the lower cost associated with the acid requirements. However, recovery of lead was not complete at 88.6% on average after the pre-filtration procedure.

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