

Appendix B  
Bench Scale Treatability Study  
Omaha Lead Site



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**Draft Final**  
**Bench-Scale Treatability Study**

**Omaha Lead Site**  
**Omaha, Nebraska**

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## Table of Contents

<b>1.0</b>	<b>Introduction.....</b>	<b>1-1</b>
1.1	<i>Study Objectives .....</i>	<i>1-4</i>
1.2	<i>Rationale for Types of Soil to be Tested.....</i>	<i>1-5</i>
1.3	<i>Preparation of Soil Used for Treatability Study.....</i>	<i>1-6</i>
<b>2.0</b>	<b>Characterization Testing.....</b>	<b>2-1</b>
2.1	<i>Soil Characterization .....</i>	<i>2-1</i>
2.1.1	<i>Fundamental Chemical Characteristics.....</i>	<i>2-1</i>
2.1.2	<i>Particle-Size, Texture, and Soil Classification .....</i>	<i>2-2</i>
2.1.3	<i>Mineralogy-X-ray Diffraction .....</i>	<i>2-4</i>
2.1.4	<i>Speciation- EMPA.....</i>	<i>2-7</i>
2.2	<i>Bioaccessibility Testing.....</i>	<i>2-14</i>
<b>3.0</b>	<b>Laboratory Bench Testing.....</b>	<b>3-1</b>
3.1	<i>Total Phosphorus (P).....</i>	<i>3-2</i>
3.2	<i>Extractable P.....</i>	<i>3-5</i>
3.3	<i>SPLP- Leachable P .....</i>	<i>3-7</i>
3.4	<i>In Vitro Bioavailability.....</i>	<i>3-7</i>
3.5	<i>Post Treatment Speciation.....</i>	<i>3-10</i>
<b>4.0</b>	<b>Conclusions.....</b>	<b>4-1</b>
<b>5.0</b>	<b>References.....</b>	<b>5-1</b>
	<i>Illite .....</i>	<i>2</i>
	<i>Kaolinite.....</i>	<i>2</i>
	<i>Smectite.....</i>	<i>2</i>

## Appendices

- Appendix A Laboratory Testing Procedures
- Appendix B Metal Speciation Standard Operating Procedure
- Appendix C Relative Bioavailability Leaching procedure
- Appendix D Mineralogy by X-Ray Diffraction

## Figures

- Figure 2-1 Soil textural classes for the three OLS test soils
- Figure 2-2 Whole-rock XRD spectra for OLS test soils A
- Figure 2-3 Whole-rock XRD spectra for OLS test soils B

Figure 2-4	Whole-rock XRD spectra for OLS test soils C
Figure 2-5	Clay fraction XRD spectra for OLS test soils A
Figure 2-6	Clay fraction XRD spectra for OLS test soils B
Figure 2-7	Clay fraction XRD spectra for OLS test soils C
Figure 2-8	OLS Test Soil A Speciation Results
Figure 2-9	OLS Test Soil B Speciation Results
Figure 2-10	OLS Test Soil C Speciation Results
Figure 3-1	Post-Treatment, Total Phosphorus from Soil A
Figure 3-2	Post-Treatment, Total Phosphorus from Soil B
Figure 3-3	Post-Treatment, Total Phosphorus from Soil C
Figure 3-4	Post-Treatment, Extractable Phosphorus from Soil A
Figure 3-5	Post-Treatment, Extractable Phosphorus from Soil B
Figure 3-6	Post-Treatment, Extractable Phosphorus from Soil C
Figure 3-7	Post-Treatment, IVBA for Lead in Soil A
Figure 3-8	Post-Treatment, IVBA for Lead in Soil B
Figure 3-9	Post-Treatment, IVBA for Lead in Soil C
Figure 3-10	Post-Treatment, Lead Speciation in Soil A
Figure 3-11	Post-Treatment, Lead Speciation in Soil B
Figure 3-12	Post-Treatment, Lead Speciation in Soil C
Figure 3-13	EMPA At% of P-Pb in Post-Treatment, phosphate compounds.
Figure 3-14	EMPA At% of Pb-Cl in Post-Treatment, phosphate compounds.

### **Tables**

Table 2-1	Average Fundamental Chemical Characteristics of Test Soils
Table 2-2	Test Soil Particle-Size Analyses and Related Soil Properties
Table 2-3	OLS Test Soil A Speciation Results
Table 2-4	OLS Test Soil B Speciation Results
Table 2-5	OLS Test Soil C Speciation Results
Table 2-6	<i>In Vitro</i> Lead Bioaccessibility of OLS Test Soils
Table 2-7	<i>In Vitro</i> Arsenic Bioaccessibility of OLS Test Soils
Table 3-1	Post-Treatment Lead Speciation of Soil A
Table 3-2	Post-Treatment Lead Speciation of Soil B
Table 3-3	Post-Treatment Lead Speciation of Soil C
Table 4-1	Summary of Best Performing Amendment

## Acronymms

ABA	Absolute Bioavailability
ASTM	American Society for Testing Materials
bgs	Below Ground Surface
BVSPC	Black & Veatch Special Projects Corp.
Ca(OH) <sub>2</sub>	Calcium Hydroxide (Hydrated Lime)
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (aka Superfund)
EMPA	Electron Microprobe Analysis
EPA	United States Environmental Protection Agency
IEUBK	Integrated Exposure Uptake Biokinetic
IVBA	<i>In Vitro</i> Bioaccessibility
LEGS	Laboratory for Environmental and Geological Studies
mg/kg	milligram per kilogram = ppm
NPL	National Priorities List
OLS	Omaha Lead Site
Pb	Lead
ppm	parts per million = mg/kg
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RA	Remedial Action
RBA	Relative Bioavailability
RBALP	Relative Bioavailability Leaching Procedure
RD	Remedial Design
RI/FS	Remedial Investigation/ Feasability Study
ROD	Record of Decision
SOP	Standard Operating Procedure
SPLP	Synthetic Precipitation Leaching Procedure
SU	Standard Units
TSP	Triple Super Phosphate

## Glossary

ABA	Absolute Bioavailability – The amount of substance entering the blood via a particular biological pathway relative to the absolute amount that has been ingested.
AES	Architect-Engineer Services Contract between EPA Region 7 and Black & Veatch Special Projects Corp.
ASTM	American Society for Testing Materials – An organization that develops and publishes voluntary technical standards for a wide range of materials, products, systems, and services.
bgs	Below Ground Surface- An acronym that denotes a measurement or distance below the surface of the ground.
BVSPC	Black & Veatch Special Projects Corp. – The contractor under the EPA Architect-Engineer Services Contract who is serving as a consultant to EPA on the Omaha Lead Site.
Ca(OH) <sub>2</sub>	Calcium Hydroxide (Hydrated Lime) – Lime is used to raise the pH of the soil following application of the phosphate amendment to the soil.
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (aka Superfund) - The legislative authority that funds and carries out EPA solid waste emergency and long-term removal and remedial activities. These activities authorized by CERCLA include establishing the National Priorities List, investigating sites for inclusion on the list, determining their priority, and conducting and/or supervising cleanup and other remedial actions.
EMPA	Electron Microprobe Analysis – An analytical technique that is used to establish the composition of small areas on specimens by bombarding the specimen with a beam of accelerated electrons.
EPA	United States Environmental Protection Agency

FSP	Field Sampling Plan – The document that specifies the procedures that will be followed during the field sampling activities, including the number of samples collected and the sampling methodology.
<i>In-vitro</i>	Testing or action outside an organism (e.g. inside a test tube or culture dish.)
<i>In-vivo</i>	Testing or action inside an organism.
LEGS	Laboratory for Environmental and Geological Studies – The organization within the University of Colorado that performed the bench scale study and performed the chemical and physical testing of the soil during the treatability study.
mg/kg	milligram per kilogram = parts per million – A unit measure of the concentration of a substance, i.e., milligrams of lead per kilogram of soil.
MSDS	Material Safety Data Sheet - A compilation of information required under the OSHA Communication Standard on the identity of hazardous chemicals, health, and physical hazards, exposure limits, and precautions.
NPL	National Priorities List - EPA's list of the most serious uncontrolled or abandoned hazardous waste sites identified for possible long-term remedial action under Superfund. The Omaha Lead Site is on the NPL.
OLS	Omaha Lead Site – The Omaha NPL site. The OLS is comprised of individual residential properties that exceed the EPA action level for lead and are eligible for Superfund response.
Pb	Lead – The primary contaminant of concern at the Omaha Lead Site.
ppm	parts per million = mg/kg – Units commonly used to express contamination levels, as in establishing the maximum permissible amount of a contaminant in water, land, or air.

QA/QC	Quality Assurance - A system of procedures, checks, audits, and corrective actions to ensure that all EPA research design and performance, environmental monitoring and sampling, and other technical and reporting activities are of the highest achievable quality.
QAPP	Quality Assurance Project Plan – A plan prepared for the Omaha Lead Site that discusses the QA/QC procedures that will be implemented at the site.
RA	Remedial Action - The actual construction or implementation phase of a Superfund site cleanup that follows remedial design.
RBA	Relative Bioavailability - The ratio of the absorption of lead in soil to the absorption of a lead standard (lead acetate).
RBALP	Relative Bioavailability Leaching Procedure - A test that measures the fraction of a chemical solubilized from a soil sample under simulated gastrointestinal conditions. The in-vitro tests consist of an aqueous fluid, into which the contaminant is introduced. The solution then solubilizes the media under simulated gastric conditions. Once this procedure is complete, the solution is analyzed for lead and/or arsenic concentrations. The mass of the lead and/or arsenic found in the filtered extract is compared to the mass introduced into the test. The fraction liberated into the aqueous phase is defined as the bioavailable fraction of lead or arsenic in that media.
RD	Remedial Design - A phase of remedial action that follows the remedial investigation/feasibility study and includes development of engineering drawings and specifications for a site cleanup.
RI/FS	Remedial Investigation/ Feasibility Study - An in-depth study designed to gather data needed to determine the nature and extent of contamination at a Superfund site; establish site cleanup criteria; identify preliminary alternatives for remedial action; and support technical and cost analyses of alternatives. The remedial investigation is usually done with the feasibility study. Together they are usually referred to as the "RI/FS".

- ROD Record of Decision - A public document that selects and explains which cleanup alternative(s) will be implemented at National Priorities List sites.
- SOP Standard Operating Procedure – A written document that details the method for an operation, analysis, or action with thoroughly prescribed techniques and steps and that is officially approved as the method for performing certain routine or repetitive tasks.
- TSP Triple Super Phosphate - A fertilizer produced by the action of concentrated phosphoric acid on ground phosphate rock. TSP was one of the chemical amendments used in the treatability study.

## Executive Summary

The objective of this treatability study is to evaluate the influence of phosphate treatment on lead-contaminated Omaha Lead Site (OLS) soils. The information generated during this study will be used by EPA to evaluate and compare remedial alternatives in the final remedy selection process for the OLS. Studies conducted at other Superfund sites contaminated with similar forms of lead have concluded that the application of certain phosphate-based compounds (referred to as soil amendments) can result in the conversion of lead in soils to relatively insoluble minerals with reduced bioavailability. After treatment, lead remains present in the soil, but is transformed into a form that is less toxic.

It was estimated in the Final Remedial Investigation Report that approximately 8,135 OLS residential properties exhibit lead concentrations between 400 and 800 parts per million (ppm). If determined to be technically feasible, the amendment treatment of lead-contaminated soil at OLS residential properties exhibiting moderate lead levels (between 400 ppm and 800 ppm) could provide benefits over the excavation and replacement of soils at many OLS properties and provide protection of human health and the environment.

Prior to developing and implementing a field program, multiple amendment treatment scenarios were tested in the laboratory (bench scale) in an effort to limit the field program to the two or three most promising treatments. An extensive list of laboratory tests, including analytical chemistry and electron microprobe analyses, were performed on soil samples collected at various points in time during the study. The data from this group of laboratory tests, which are collectively referred to as “soil characterization testing,” and “bench-scale testing” will allow EPA to evaluate potential chemical and physical changes in test soils in response to amendment addition.

An *In Vitro* test method, relative bioavailability leaching procedure (RBALP), was utilized to evaluate changes in soil lead bioaccessibility in response to amendment treatment. The RBALP is referred to as bioaccessibility testing to distinguish it from *in vivo* bioavailability studies which involve animal feeding studies. The RBALP is used because *in vivo* testing is more costly to perform than the RBALP test and requires a longer period of time to perform the testing. In addition to the RBALP, the synthetic precipitation leaching procedure (SPLP) (EPA Method 1312) was used to evaluate the potential leachability of lead, arsenic and phosphate and lead speciation was conducted on the untreated and treated soils.

EPA has gained experience at other Superfund sites with similar types of contamination, and has performed side-by-side comparison testing of *In Vitro* bioaccessibility and *in vivo* bioavailability test methods. RBALP performed at pH 1.5

correlates well with *in vivo* relative bioavailability (RBA) in untreated soils as evidenced by the close agreement of the two methods on the same soils in a previous swine study for the OLS. RBALP performed at pH 2.5 significantly underestimates the RBA when compared to *in vivo* results at the OLS. No test methods have been validated to measure bioaccessibility in phosphate treated soil. Although RBALP has not been validated for phosphate treated soils at pH 1.5 or pH 2.5, the procedure may provide an indication of the potential effectiveness in reducing the RBA of lead-contaminated soils.

Bioaccessibility testing results, together with the soil characterization data generated during this treatability study, are intended to provide the information required to evaluate the effectiveness of phosphate treatment on OLS soils. Although the information obtained from the treatability study will be useful to evaluate future remedial action alternatives at the OLS, the information from the study is not conclusive because of the following limitations of the study.

- It is difficult to perform *in-vivo* testing on soils with lead concentrations between 400 ppm and 800 ppm, which are the soils that are most likely to be treated with the phosphate amendment at the OLS.
- The *in vitro* RBALP testing procedure used to estimate the relative bioaccessibility of lead in the soils has not been validated for use on phosphate amended soils.
- The bench scale treatability will only estimate the short term reduction in the RBA of lead in soils. There is no conclusive data indicating phosphate treatment results in long-term reduction in the RBA of lead in soils.

Duplicate matrices of soils were assembled containing controls and the phosphate amendments phosphoric acid (PA), phosphate rock (PR), and triple-super phosphate (TSP), both with and without amorphous iron. The matrices were run in triplicate using 2, 7, and 14 day reaction periods. The effectiveness of the amendments were evaluated based on the relative change *in vitro* bioaccessibility (IVBA) as measured using the RBALP *in vitro* procedure, with extraction fluids at pH 1.5 and 2.5.

Virtually all of the phosphate amendments showed some reduction in IVBA however, the 14-day, 1.5% PA (1.5 PA) (with iron) was the most reductive. All of the amendments behaved equally as well on the three soil-types, producing an increased presence of some phosphate form.

The measured effectiveness of the amendment techniques varied between the pH 1.5 and pH 2.5 *in vitro* results. The pH 1.5 data presented in Table 4-1, which has the strongest correlation with *in vivo* RBA, shows limited reduction in IVBA, ranging from 15 percent to 26 percent reduction for the three soil types tested. The RBALP at pH 2.5

showed more significant reduction in IVBA, ranging from 61 percent to 80 percent; however the RBALP at pH 2.5 did not show good correlation with *in vivo* results on the same test soils and has not been validated by *in vivo* studies.

One sample from each of the three soil types treated with 1.5 PA plus iron was speciated. The speciation indicated that the treatment procedure was forming a phosphate product. The speciation indicated the formation of a potentially more soluble primary or secondary orthophosphate rather than the more insoluble chloropyromorphite. These orthophosphates would be more bioaccessible than the lead phases in the untreated soils and support the limited decrease in IVBA observed in the treated soils. All of the phosphate amendments increased the solubility and potential release of phosphorus and arsenic.

## 1.0 Introduction

Black & Veatch Special Projects Corp. (BVSPC) has been tasked by EPA Region 7 to perform this treatability study for the Omaha Lead site (OLS) under Task Order 091 of EPA Contract No. EP-S7-05-06.

The OLS includes contaminated surface soils (generally between 0 to 6 inches below ground surface (bgs) present at residential properties, child-care facilities, and other residential-type properties in the city of Omaha, Nebraska, which were contaminated as a result of historic air emissions from lead smelting and refining operations. The OLS Focus Area encompasses approximately 27 square miles, centered on downtown Omaha, where two former lead processing facilities were located. The site includes only residential and residential-type properties and all non-residential properties are excluded from the OLS focus area, including commercial properties in the central business district.

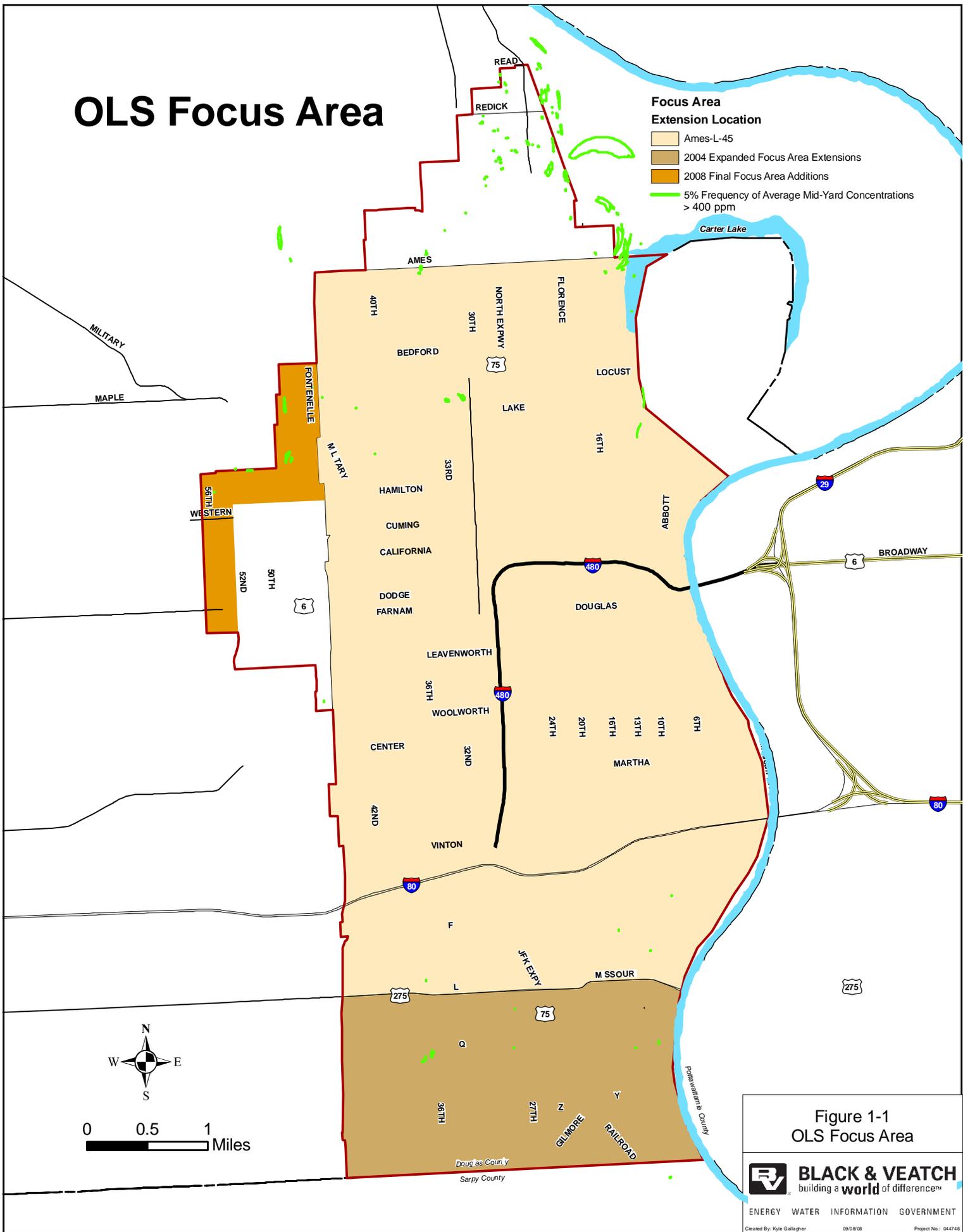
The United States Environmental Protection Agency (EPA) began sampling residential yards and properties used for licensed child-care services in March 1999. The original boundaries of the OLS Focus Area were established at the time the Site was listed on the EPA National Priorities List (NPL). During the Remedial Investigation in 2004 (RI, Ref. 2), the OLS Focus Area was expanded to include an area south of L Street to the Sarpy County line (Harrison Street), an area north of Ames Avenue to Redick Avenue, and an area to the west of 45<sup>th</sup> Street. The focus area now extends north to Read Street and west to 56<sup>th</sup> Street (See Figure 1-1).

Between March 1999 and December 2007, surface soil samples were collected from over 32,000 residential properties. The December 2004 Interim Record of Decision (ROD, Ref. 1) identified response actions to be taken while the final ROD was developed, including excavation and replacement of contaminated soils at the most highly contaminated residential properties with surface soil lead concentrations exceeding 800 ppm. In addition, childcare facilities and properties where children with elevated blood lead levels reside are eligible for remediation if one or more mid-yard soil sample exceeds 400 mg/kg. If a property is eligible for remediation, all soils that test greater than 400 mg/kg are removed, including drip-zone soils.

This treatability study will evaluate the effectiveness of phosphate treatment on the bioaccessibility of lead-contaminated OLS soils. Studies conducted at other Superfund sites contaminated with similar forms of lead have concluded that the application of certain phosphate-based compounds can result in the conversion of lead in surface soils to relatively insoluble minerals with reduced bioavailability (Refs. 3, 4, and 5.

# OLS Focus Area

- Focus Area Extension Location**
- Ames-L-45
  - 2004 Expanded Focus Area Extensions
  - 2008 Final Focus Area Additions
  - 5% Frequency of Average Mid-Yard Concentrations > 400 ppm



0 0.5 1 Miles

Figure 1-1  
OLS Focus Area



Earlier studies involving phosphate-based compounds in this area (Refs. 25 and 26) indicated very low solubilities for many lead-phosphates ( $K_{sp}$  !27 to !66), particularly chloropyromorphite [ $Pb_5(PO_4)_3Cl$ ]. The transformation of soluble Pb mineralogical forms into chloropyromorphite continues to be the primary focus of many soil amendment studies. Sources of phosphorous used in the previous studies included phosphoric acid (PA) ( $H_3PO_4$ ), triple-super phosphate (TSP), phosphate rock (PR) (a phosphorous-rich natural sediment), and/or hydroxyapatite (HA). Studies have combined one or more of these phosphorous sources with or without the addition of lime, iron, and/or manganese in an attempt to enhance amendment qualities. Most phosphate amendments are formulated to contain between 0.5 and 1.0 percent phosphorous by weight. The sources for phosphorous used in this study include PA, TSP, or PR.

PA, also called orthophosphoric acid, is an odorless, clear, viscous liquid, having a typical pH 1.5. It is a highly corrosive acid, which is incompatible with powdered metals, strong bases, and iron containing compounds. Due to its incompatibility with iron compounds, PA is often used to remove iron-oxide (rust) stains from stainless steel. PA is found commercially in detergents, cleaners, insecticides, fertilizers and cattle feed additives. In the bench scale treatability study, 85% PA (Mallinckrodt Chemicals 2796-45), which has a heavy metal contamination of less than 10 ppm, was used.

TSP ( $Ca(H_2PO_4)_2$ ), also called monocalcium phosphate, is an off-white, granular solid. It is typically produced by reacting phosphate rock with sulfuric acid. This product was historically a very popular item used as a basic fertilizer, or mineral supplement in foods and feed; however, it has since been prohibited by most U.S. certifications. When combined with nitrate-based fertilizers it can create a highly volatile environment. Further, the phosphoric derivatives have a tendency to bind to iron, aluminum, calcium, magnesium, and sodium, essentially “tying-up” essential nutrients. Hi-Yield® *Triple Super Phosphate*, which has 45% available phosphate was used in the treatability study. Wet chemical analyses of this product indicated a lead concentration of 6 ppm.

PR, ( $Ca_{10}F_2(PO_4)_5$ ), also called Kap rock, or fluoroapatite, is a tan, black, gray, or white solid with an “earthy” odor. PR is the only naturally occurring resource of phosphate. PR rock beds are formed near oceans and are often contaminated with other minerals such as magnesium, fluoride and silica. It is mainly used in the production of fertilizers, feed, and industrial products. Whitney Farms™ *Granulated Rock Phosphate*, which contains 3% available phosphoric acid, was used in the treatability study. Wet chemical analyses of this product indicated a lead concentration of 50 ppm.

The previous studies using PA, TSP, or PR have produced mixed results and, to date, phosphate amendments have not been used to treat soils at any large, lead contaminated sites. One study, (Ref. 30) using a phosphate amendment and a post

treatment analyses period of five years was far less successful, with a reduction in IVBA (*in vitro*) of only 40%. In addition, (Ref. 30) showed a gradual increase in soil IVBA (3 to 65%) over the five year test period.

In addition, a number of potentially significant problems associated with phosphate amendments have been recognized, including both phyto- and earthworm toxicity (Refs. 27, 28, and 29). Both of these toxicities are primarily associated with very high applications of phosphorous and/or decreased soil pH. Additionally, treatment of soil with a phosphate amendment creates an additional risk of eutrophication of nearby waterways from surface water runoff.

Results from the soil characterization and bench-scale treatment studies described in this report may be used to design subsequent field studies for the treatability study. The scope and objectives of this portion of the treatability study correlate with the December 2004 Interim Record of Decision (ROD). The following paragraph is from the Interim ROD:

*The treatability study consists of an initial bench scale test to determine the effect that the treatment technology has on the bioavailability of lead in site soils under laboratory conditions. If initial findings are positive, the second phase of the study involves actual field testing and additional bioavailability studies.*

## **1.1 Study Objectives**

The overall objective of this treatability study is to provide data to help support a decision regarding the use of phosphate-based soil amendments at the OLS to treat lead-contaminated soils. As stated in the Interim ROD (EPA, 2004), “it is particularly important that the treatment process itself does not create a hazard to children or residents living at or near the affected properties. The end-products of the treatment process must also not pose an unacceptable short- or long-term risk to residents at or near treated properties. This treatability study must successfully demonstrate that unacceptable risks are not created at any time during the treatment process or thereafter.” Specific objectives for this portion of the study include the following:

- In response to amendment treatment, evaluate changes over time (2-14 days) in chemical and physical characteristics of the treated soils, including lead speciation and mineralogy.
- Evaluate the influence of phosphate treatment on the bioaccessibility of lead contamination in mid-yard and drip zone OLS soils.

- Provide data that could be used to evaluate issues related to potential remediation costs and public acceptance of the remedy.

Although the information obtained from the treatability study will be useful to evaluate future remedial action alternatives at the OLS, the information from the study is not conclusive because of the following limitations of the study.

- It is more difficult to perform *in-vivo* testing on soils with lead concentrations between 400 ppm and 800 ppm, which are the soils that are most likely to be treated with the phosphate amendment at the OLS.
- The *in vitro* testing procedure (Relative Bioavailability Leaching Procedure) used to estimate the relative bioavailability of lead in the soils has not been validated for use on phosphate amended soils.
- The bench scale treatability will only estimate the short term reduction in the relative bioavailability (RBA) of lead in soils. There is no conclusive data indicating phosphate treatment results in long-term reduction in the RBA of lead in soils.

## 1.2 Rationale for Types of Soil to be Tested

Three types of soils were subjected to amendment treatment in this study:

Test Soil	Soil Id.	Lab Id.	Average Lead Concentrations
A	93205	Soil A	Mid-yard soil between 400 & 800 ppm
B	93206	Soil B	Mid-yard soil greater than 1,000 ppm
C	93207	Soil C	Drip Zone soil greater than 1,000 ppm

The rationale for testing the 3 types of soil is as follows:

- Test Soil No. A has moderate lead concentrations between 400 and 800 ppm which is the potential treatment range discussed in the Interim ROD. For example, if an amendment treatment is found to be capable of lowering the bioavailability of lead by 50 percent, risks associated with elevated lead levels in soil may be reduced to acceptable levels. Bioaccessibility testing can be conducted on soils with lead concentrations below 1,000 ppm, but *in vivo* bioavailability testing is more suitable for soils with lead concentrations

greater than 1,000 mg/kg.

- Test Soil No. B is a mid-yard soil with an average lead concentration exceeding 1,000 ppm. If the soil characterization and bioaccessibility testing results indicate that amendment treatment appears to be effective, EPA could elect to perform an *in vivo* bioavailability study in order to corroborate the bioaccessibility results and to strengthen the correlation between the *in vitro* and *in vivo* results.
- Test Soil No. C is a drip zone soil with an average lead concentration greater than 1,000 ppm. By definition, the drip zone may be impacted by lead paint. EPA believes that it is of interest to evaluate the influence of phosphate treatment on drip zone soils because the information will be important when the remedial alternatives are evaluated in preparation for the Final ROD.

### 1.3 Preparation of Soil Used for Treatability Study

Soil used for the bench scale treatability study was prepared in accordance with the Treatability Study Work Plan (Ref. 20). Soil for the treatability study was collected from residential yards in OLS Focus Area. Candidate properties were identified based upon the lead concentrations in the yards. Soil screening at the properties involved collecting samples with a 2-inch diameter core barrel slide-hammer sampling device. Three soil types were prepared:

- Mid-yard soil with average lead levels between 400 and 800 parts per million (ppm);
- Mid-yard soil with average lead levels greater than 1,000 ppm; and
- Drip Zone soils with average lead concentrations greater than 1,000 ppm.

Soil was excavated from six of the candidate properties and transported to the OLS staging area and separated into three piles according to the lead concentration in the soil. The soil piles were thoroughly mixed and grab samples were collected from different locations in the piles of soil to confirm average lead levels in the soil. Soil from these piles was sent to the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado for testing in the bench scale treatability study. Average lead concentrations in the bulk soils from the three soil piles were 568 ppm, 1,247 ppm, and 1,418 ppm, respectively (Ref. 20, Appendix C).

The LEGS was responsible for sample preparation as discussed in the Treatability Study Work Plan. Soils were air-dried in a controlled environment prior to sieving. Soils

were then sieved with a #10 stainless steel sieve to provide bulk samples (particle size < 2 mm) for standard soil analyses and speciation testing. The bulk samples were sieved a second time using a #60 stainless steel sieve to provide fine samples (particle size < 250 $\mu$ ) for *in vitro* studies.

All non disposable equipment used for sample preparation was decontaminated before the tools and equipment were used or re-used. Stainless steel splitters or sieves were washed in RBS 35® detergent, triple rinsed in deionized (Type II) water, and air dried.

Following sample preparation, LEGS sent split samples to the EPA Region 7 laboratory for Quality assurance (QA) metals analyses.

## 2.0 Characterization Testing

### 2.1 Soil Characterization

The purpose of soil characterization testing is to assess amendment-soil interactions and quantify changes in physical and chemical characteristics of test soils over time. The tests performed on untreated soils will provide “control” information against which subsequent characterization testing results will be compared in order to understand changes in response to amendment addition.

Soil characterization testing and analyses was performed by the University of Colorado LEGS. Characterization testing included the following parameters: metals, soil pH, acidity, particle size distribution, soil classification, phosphorus, nitrogen, total organic carbon, cation exchange capacity, and lead mineral speciation using an electron microprobe. Speciation testing is intended to provide the following information: lead mineral phase, matrix association, particle size (longest dimension), frequency of occurrence, and relative metal mass using electron microprobe (EMPA) techniques. A principal objective of EMPA analyses is to evaluate changes in lead mineral speciation through the duration of the study.

#### 2.1.1 Fundamental Chemical Characteristics

The chemical characteristics of the three test soils are provided in Table 2-1. Each parameter was run in duplicate (n=2) unless otherwise noted following the methods listed in Appendix A (Table 1A). All raw data and QA/QC are provided in accompanying electronic spreadsheets. A more extensive suite of metals was analyzed for each test soil on splits sent to EPA Region VII lab.

Table 2-1  
Average Fundamental Chemical Characteristics of Test Soils

Soil ID	Lab ID	Total Pb*	pH	Acidity	Total P	Extractable P	SPLP P	CEC	TOC	N
		mg/kg		Meq/100 g	mg/kg	mg/kg	mg/kg	cmol/kg	%	%
93205	Soil A	752	7.2	65.4	1233	12.7	0.92	20.4	3.748	0.247
93206	Soil B	1100	7.4	70.2	1447	13.4	0.69	21.0	5.072	0.260
93207	Soil C	2230	7.7	80.1	1005	6.4	0.32	20.4	2.532	0.154

\*Average lead concentration using analytical methods 3050 and 6010B. Concentrations vary from previously cited lead concentrations in bulk samples (BVSPC XRF results) because only a portion of the bulk sample was analyzed and different methods were used for analysis of soils.

### 2.1.2 Particle-Size, Texture, and Soil Classification

Soil texture refers to the relative proportion of sand, silt and clay size particles in a sample of soil. Clay size particles are the smallest being less than .002 mm in size. Silt is a medium size particle falling between .002 and .05 mm in size. The largest particle is sand with diameters between 0.05 for fine sand to 2.0 mm for very coarse sand. Soil scientists group soil textures into soil texture classes. A soil texture triangle is used to classify the texture class. Soil texture effects many other properties like structure, chemistry, and most notably, soil porosity, and permeability. Texture influences plant growth by its direct effect on soil aeration, water infiltration, and cation exchange capacity (CEC). Infiltration and permeability are rapid in sandy soils, very slow in clay soils, and intermediate in loam soils.

The three soils from the treatability study have been tested to determine their particle-size distribution, texture, and soil classification following the methods referenced in Appendix A (Table 1A). In addition, a number of related soil properties are provided. These results can be found in Table 2-2 and Figure 2-1. A single large (~125 g) sample was used for these analyses. All measurements and calculations can be found in electronic spreadsheets (Appendix D).

Table 2-2  
Test Soil Particle-Size Analyses and Related Soil Properties

Parameter	Soil A (93205)	Soil B (93206)	Soil C (93207)
<b>% Sand (.05-2.0mm)</b>	47.7%	47.4%	23.5%
<b>% Silt (.002-.05 mm)</b>	51.7%	44.9%	72.6%
<b>% Clay (&lt;.002 mm)</b>	0.6%	7.7%	3.9%
<b>Classification</b>	Silty Loam	Loam	Silty Loam
<i>Wilting Point (cm<sup>3</sup> H<sub>2</sub>O/cm<sup>3</sup> Soil)</i>	0.074	0.087	0.090
<i>Field Capacity (cm<sup>3</sup> H<sub>2</sub>O/cm<sup>3</sup> Soil)</i>	0.24	0.23	0.29
<i>Available Water (in. H<sub>2</sub>O/ft. Soil)</i>	2.0	1.73	2.45
<i>Bulk Density (mg/m<sup>3</sup>)</i>	1.15	1.20	1.15
<i>Porosity</i>	56%	55%	56%

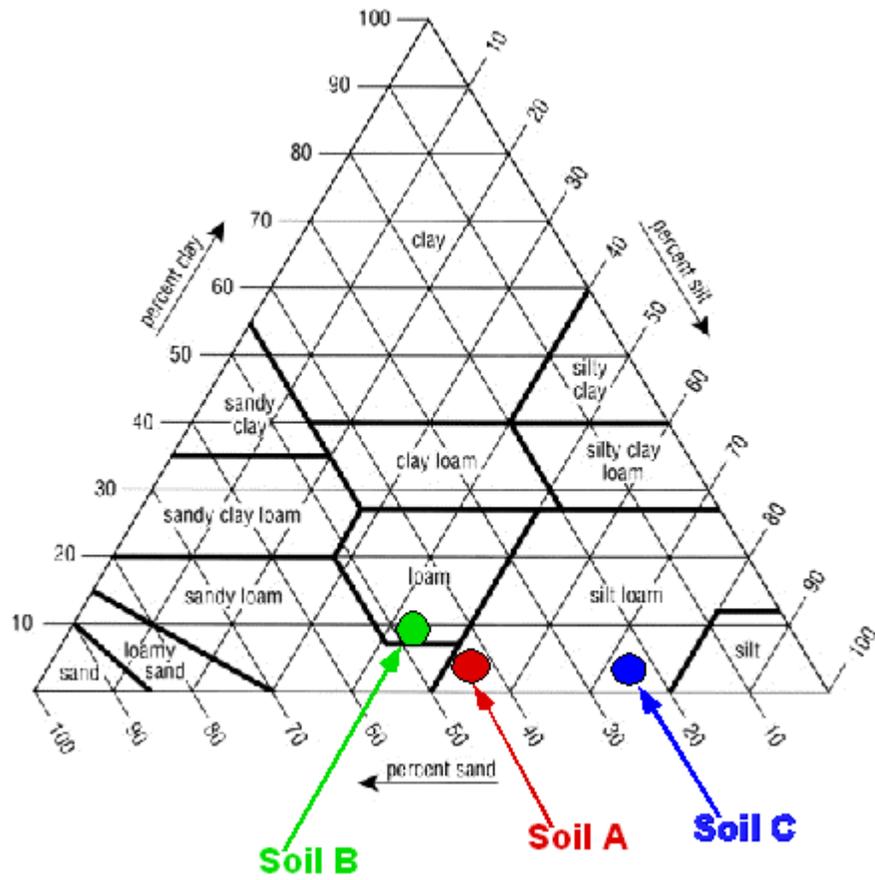


Figure 2-1 - Soil Textural Classes for the Three OLS Test Soils

### 2.1.3 Mineralogy-X-ray Diffraction

Clay mineral analyses were based on the standard method (Ref. 16). A detailed description of the methodology and results can be found in Appendix F. The bulk XRD analyses of all three soils are dominated (Figures 2-2 through 2-4) by quartz ( $\text{SiO}_2$ ), plagioclase ( $\text{Na,CaAlSi}_3\text{O}_8$ ), and microcline ( $\text{KAISi}_3\text{O}_8$ ). Soil B additionally contained a significant amount of hematite ( $\text{Fe}_2\text{O}_3$ ). Further analyses of the soils clay fraction (Figures 2-5 and 2-6) indicate that all three soils are dominated by the presence of the minerals illite, kaolinite, and smectite.

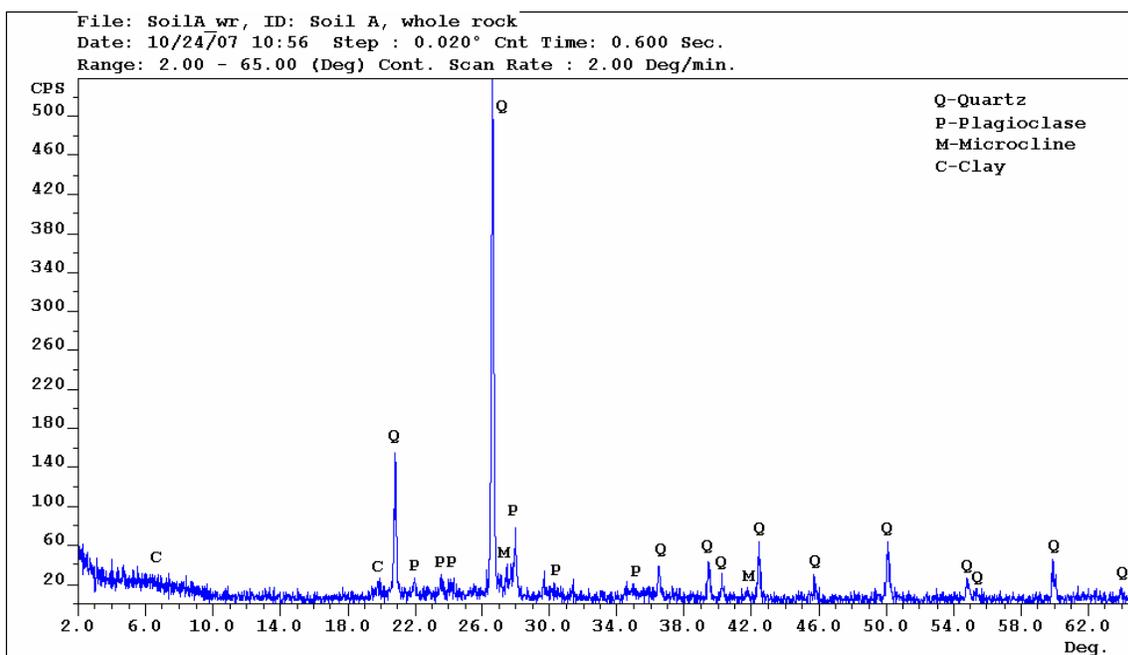


Figure 2-2 - Whole-Rock XRD Spectra for OLS Test Soils A

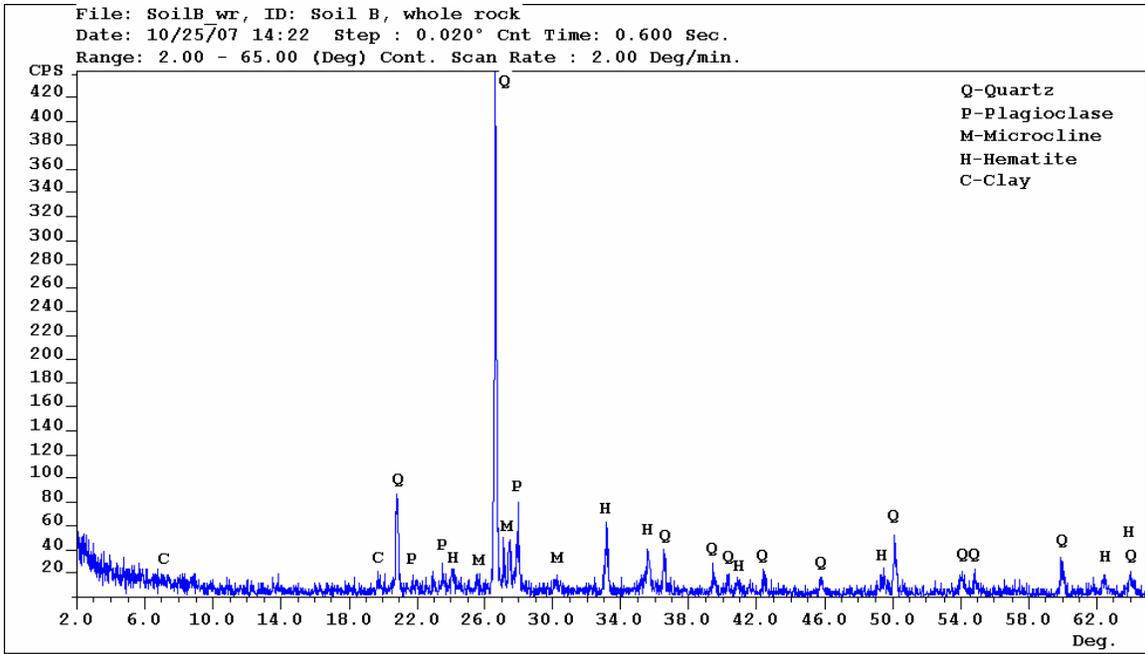


Figure 2-3 - Whole-Rock XRD Spectra for OLS Test Soils B

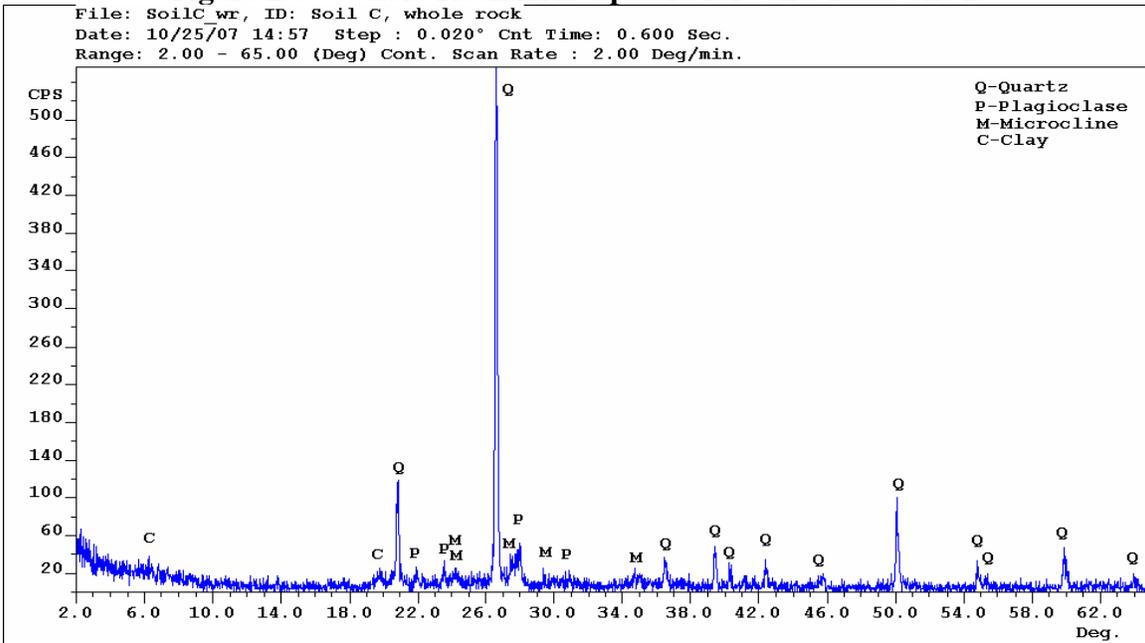


Figure 2-4 - Whole-Rock XRD Spectra for OLS Test Soils C

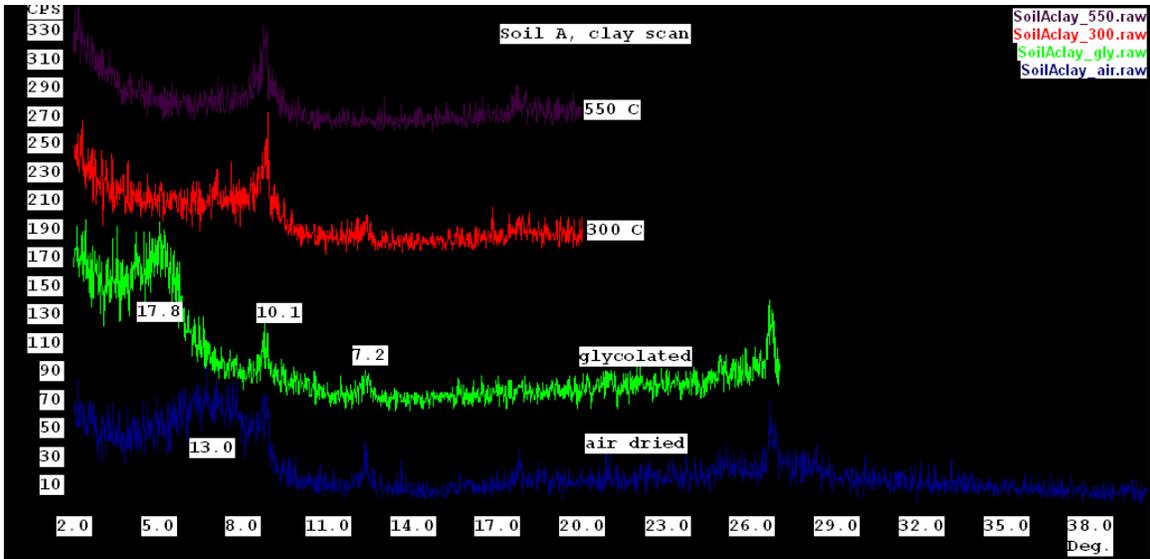


Figure 2-5 - Clay Fraction XRD Spectra for OLS Test Soils A

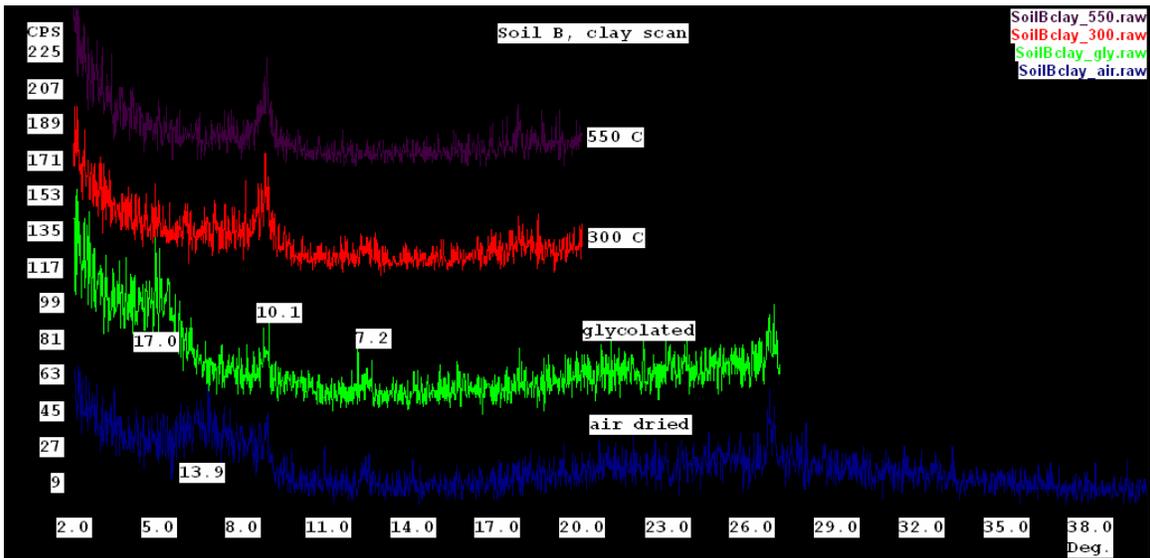


Figure 2-6. Clay Fraction XRD Spectra for OLS Test Soils B.

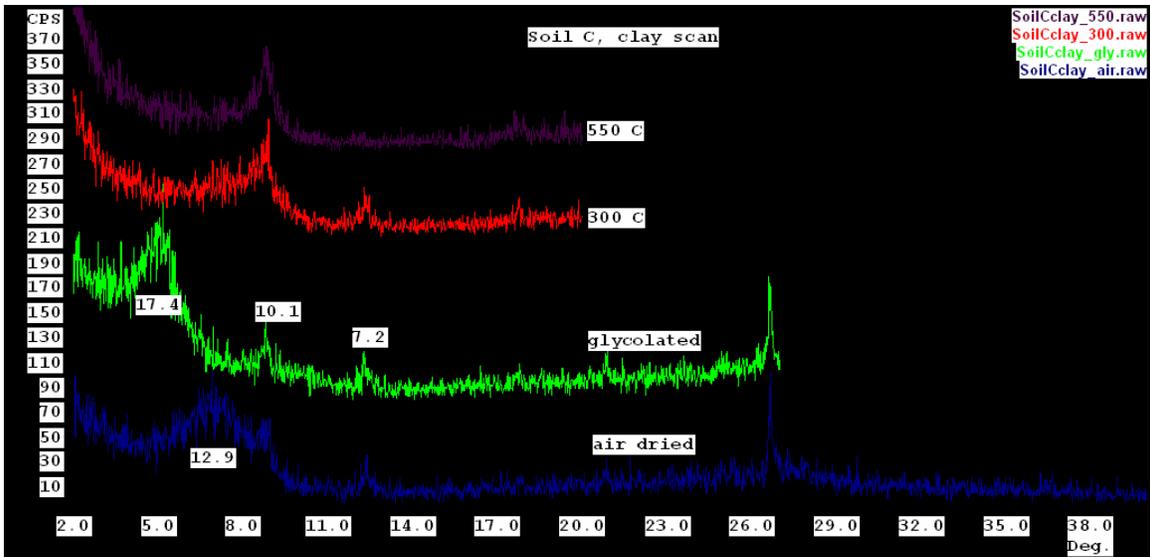


Figure 2-7 - Clay Fraction XRD Spectra for OLS Test Soils C

#### 2.1.4 Speciation- EMPA

Lead speciation on the <2mm fraction for each of the OLS soils was conducted following the LEGS method (Appendix B) at the University of Colorado. A single split was taken for each soil. Data are summarized in Tables 2-3 to 2-5 and Figures 2-8 to 2-10, while a complete particle-by-particle data set is provided in an electronic spreadsheet contained in Appendix D.

In general, the dominant lead forms in the three test soils are: cerussite ( $\text{PbCO}_3$ ), anglesite ( $\text{PbSO}_4$ ) and a lead phosphate. These are consistent with results from the *in vitro* bioassay work described later in this report.

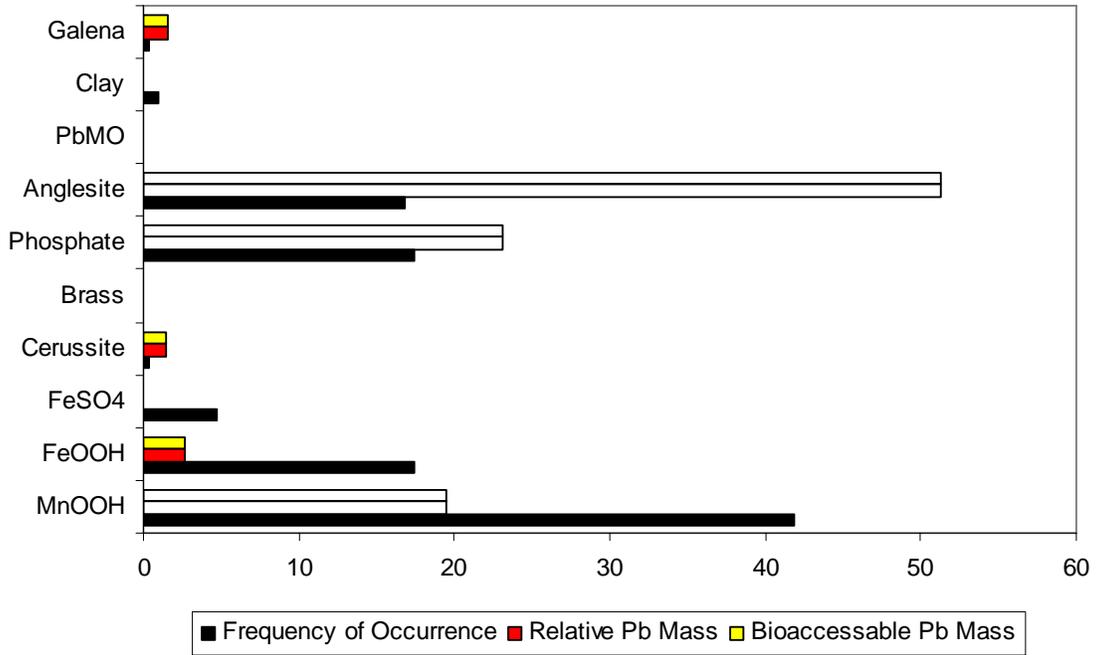
Table 2-3  
OLS Test Soil A Speciation Results.

Form	Particle Count	Size	Std-Dev	Range low	Range high
	Number	Mean			
total	103	14.65	30.12	1	250
MnOOH	39	16.18	16.19	3	85
FeOOH	25	10.52	10.36	1	50
FeSO4	10	7.2	8.28	3	28
Cerussite	1	6	ND	6	6
Brass	1	1	ND	1	1
Phosphate	20	13.1	33.94	1	150
Anglesite	2	126.5	174.66	3	250
PbMO	1	1	ND	1	1
Clay	3	5	4.36	2	10
Galena	1	5	ND	5	5

Form	(linear) freq	Bio freq	Rm Pb	Biorm Pb	Error-95%
%	%	%	%	%	
MnOOH	41.82	41.82	19.43	19.43	9.53
FeOOH	17.43	17.43	2.72	2.72	7.33
FeSO4	4.77	4.77	0.15	0.15	4.12
Cerussite	0.4	0.4	1.45	1.45	1.22
Brass	0.07	0.07	0	0	0.5
Phosphate	17.36	17.36	23.11	23.11	7.32
Anglesite	16.77	16.77	51.32	51.32	7.21
PbMO	0.07	0.07	0.16	0.16	0.5
Clay	0.99	0.99	0.12	0.12	1.92
Galena	0.33	0.33	1.53	1.53	1.11

Column headings: Frequency of occurrence weighed on the longest particle dimension = “**linear freq**”, bioaccessible frequency is the frequency of occurrence population less any particle greater than 250 microns or enclosed in another particle = “**Bio freq**”, relative lead mass based on frequency of occurrence = “**Rm Pb**”, Bioaccessible lead mass is based on bioaccessible frequency of occurrence = “**Biorm Pb**”, and counting error at the 95% confidence limit = “**Error-95%**”. All factors are more fully defined in SOP, Appendix B.

### Soil A

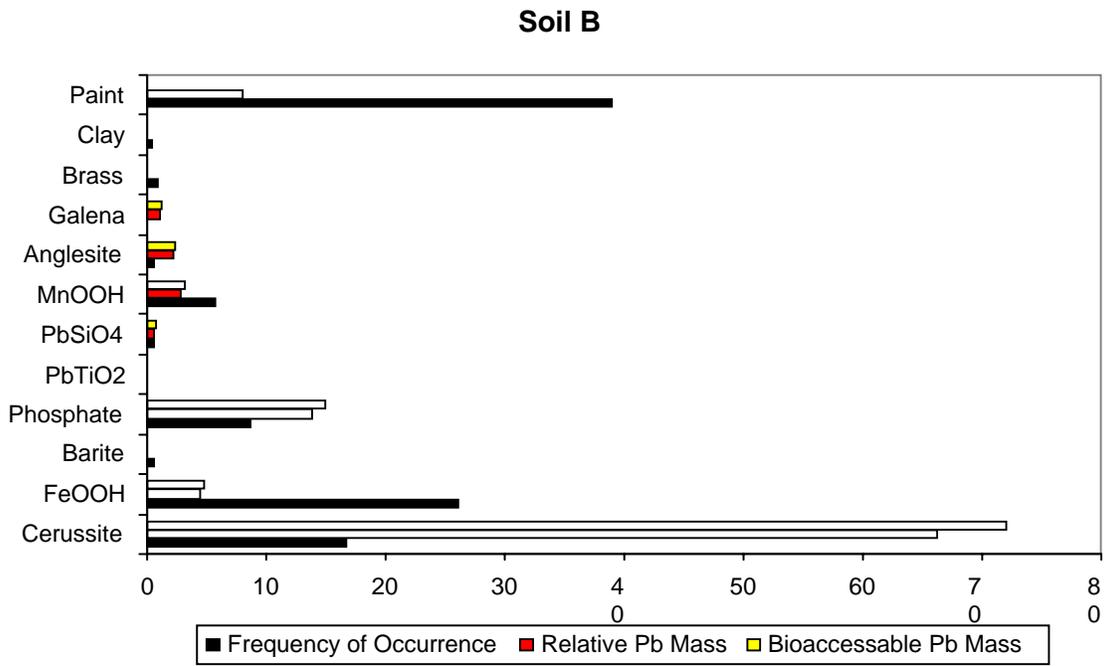


**Figure 2-8 - OLS Test Soil A Speciation Results**

Table 2-4  
 OLS Test Soil B Speciation Results.

Form	Particle Count	Size	Std-Dev	Range low	Range high
	Number	Mean			
total	135	13.12	62.09	1	690
Cerussite	63	4.71	25.03	1	200
FeOOH	24	19.29	19.53	4	75
Barite	2	5.5	3.54	3	8
Phosphate	21	7.29	9.2	1	43
PbTiO2	1	1	ND	1	1
PbSiO4	9	1.22	0.44	1	2
MnOOH	7	14.71	11.48	1	30
Anglesite	3	4	4.36	1	9
Galena	2	2	1.41	1	3
Brass	1	18	ND	18	18
Clay	1	8	ND	8	8
Paint	1	690	ND	690	690

Form	(linear) freq	Bio freq	Rm Pb	Biorm Pb	Error-95%
%	%	%	%	%	
Cerussite	16.77	27.41	66.29	72.08	6.3
FeOOH	26.14	42.87	4.45	4.85	7.41
Barite	0.62	1.02	0	0	1.33
Phosphate	8.64	14.17	13.8	15.06	4.74
PbTiO2	0.06	0.09	0.22	0.24	0.4
PbSiO4	0.62	1.02	0.7	0.77	1.33
MnOOH	5.82	9.54	2.96	3.23	3.95
Anglesite	0.68	1.11	2.25	2.46	1.38
Galena	0.23	0.37	1.13	1.24	0.8
Brass	1.02	1.67	0.01	0.01	1.69
Clay	0.45	0.74	0.06	0.07	1.13
Paint	38.96	0	8.12	0	8.23



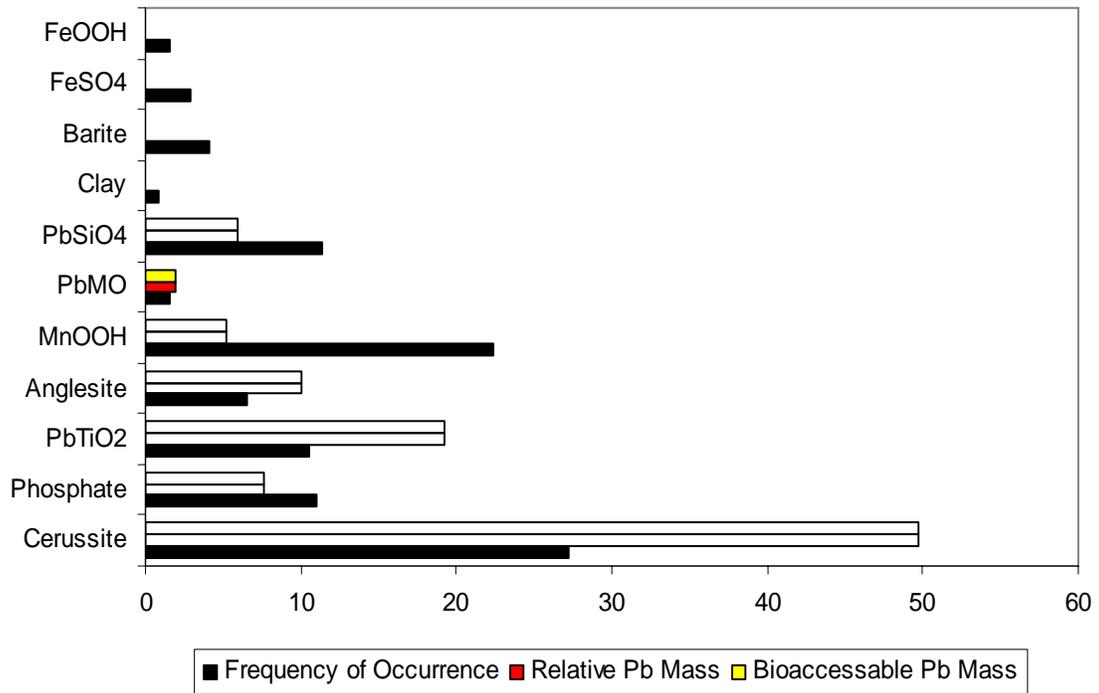
**Figure 2-9 - OLS Test Soil B Speciation Results.**

Table 2-5  
 OLS Test Soil C Speciation Results.

Form	Particle Count	Size	Std-Dev	Range low	Range high
	Number	Mean			
total	110	2.24	3.22	1	20
Cerussite	38	1.76	1.63	1	8
Phosphate	12	2.25	0.87	2	5
PbTiO2	25	1.04	0.2	1	2
Anglesite	2	8	0	8	8
MnOOH	3	18.33	2.08	16	20
PbMO	1	4	ND	4	4
PbSiO4	25	1.12	0.33	1	2
Clay	1	2	ND	2	2
Barite	1	10	ND	10	10
FeSO4	1	7	ND	7	7
FeOOH	1	4	ND	4	4

Form	(linear) freq	Bio freq	Rm Pb	Biorm Pb	Error-95%
%	%	%	%	%	
Cerussite	27.24	27.24	49.76	49.76	8.32
Phosphate	10.98	10.98	7.6	7.6	5.84
PbTiO2	10.57	10.57	19.23	19.23	5.75
Anglesite	6.5	6.5	10	10	4.61
MnOOH	22.36	22.36	5.26	5.26	7.79
PbMO	1.63	1.63	1.99	1.99	2.36
PbSiO4	11.38	11.38	5.94	5.94	5.94
Clay	0.81	0.81	0.05	0.05	1.68
Barite	4.07	4.07	0	0	3.69
FeSO4	2.85	2.85	0.05	0.05	3.11
FeOOH	1.63	1.63	0.13	0.13	2.36

### Soil C



**Figure 2-10 - OLS Test Soil C Speciation Results**

## 2.2 Bioaccessibility Testing

An *in vitro* procedure known as the “Relative Bioavailability Leaching Procedure” (RBALP) (Refs. 6 and 7) was utilized for this treatability study. The RBALP, which was developed by LEGS, has been used to estimate soil lead *in vitro* bioaccessibility (IVBA) (Refs. 8, 9, 10, and 11). Bioaccessibility testing, which is an *in vitro* test, was described in Section 2.2 of the Treatability Study Work Plan (Ref. 20).

A method of estimating bioavailability involves *in vitro* testing which is, by definition, conducted “in laboratory glassware.” The *in vitro* method is referred to as *bioaccessibility* testing to distinguish it from *in vivo* bioavailability testing which involves animal feeding studies. The *in vitro* method is significantly less resource intensive, can be performed more rapidly (weeks instead of months required for the *in vivo* test method), does not require the sacrifice of animals, and the results have been shown to correlate well with the results of *in vivo* bioavailability studies (Ref. 10).

Unlike the *in vivo* procedure, which favors soils with at least 1,000 ppm lead, the RBALP can be applied to soils with lead concentrations in the target treatment range for this project (400 to 800 ppm). For detailed information on bioaccessibility testing objectives, methods and procedures, including a discussion of how the *in vivo* and *in vitro* testing results are correlated mathematically, see Appendix C (RBALP Standard Operating Procedure).

Baseline bioaccessibility data for the OLS test soils are summarized in Tables 2-6 and 2-7. Data for both lead and arsenic are provided and represent an average of six replicate (n=6) analyses. Both the standard *in vitro* pH of 1.5 was reported in addition to data for a pH of 2.5 in order to compare results with literature values from other amendment studies. Only one detailed field study has been conducted using phosphate amendments with supporting *in vitro* and *in vivo* data. Soils from Joplin, Missouri, comprised primarily of  $PbCO_3$  and  $PbSO_4$ , (two fairly soluble forms of lead), have been studied over a time period of up to three years ( Refs. 3, 4, and 5). A reduction in IVBA and RBA-rat, (based on *in vitro* and *in vivo* data, respectively) range from 2-70%. In this study, a better comparison between (RBA-rat) results was occasionally found when the *in vitro* (IVBA) procedure was run at pH 2.2.

Also, it is important to note that all *in vitro* data is based on a sieved (<250  $\mu$ ) split of the sample, as this is the particle size that is considered bioaccessible by the EPA. Complete data package with raw data, calculations and QA/QC are provided in accompanying electronic spreadsheets in Appendix D.

Table 2-6

*In Vitro* Lead Bioaccessibility of OLS Test Soils

	<250 $\mu$ Total Pb*	IVBA-Pb pH 1.5	IVBA-Pb pH 2.5
	mg/kg	%	%
<b>Soil A</b>	831 +/- 20	80 +/- 3	41 +/- 3
<b>Soil B</b>	1406 +/- 93	86 +/- 3	49 +/- 4
<b>Soil C</b>	2284 +/- 130	88 +/- 6	61 +/- 4

\* Soil sample sieved at 60 mesh (250  $\mu$ m)

Table 2-7

*In Vitro* Arsenic Bioaccessibility of OLS Test Soils

	<250 $\mu$ Total As*	IVBA-As pH 1.5	IVBA-As pH 2.5
	mg/kg	%	%
<b>Soil A</b>	37 +/- 0.5	35 +/- 3	25 +/- 2
<b>Soil B</b>	43 +/- 0.8	37 +/- 4	24 +/- 2
<b>Soil C</b>	15 +/- 0.3	33 +/- 8	16 +/- 2

\* Soil sample sieved at 60 mesh (250  $\mu$ m)

### 3.0 Laboratory Bench Testing

Several forms of phosphate have been researched for the treatment of lead-contaminated soil including phosphate rock, triple super phosphate, and phosphoric acid. Previous studies have generally found that the bioavailability of lead is reduced by the application of phosphate amendments. Lead phosphate minerals are generally very stable with very low solubility and are expected to exhibit low bioavailability. Phosphoric acid has been evaluated in treatability studies and bench scale tests and has been shown to reduce lead bioavailability at other sites (Ref. 3, 4, and 5). Other types of amendments, including sulfate compounds and biosolids, have also yielded promising research results.

This treatability study will focus on documenting bioaccessibility changes in OLS soils resulting from phosphate amendments. One of the amendment schemes was similar to the treatment process developed for the Jasper County, Missouri, Superfund site, which utilized phosphoric acid. The treatment scheme used at Jasper County involved the following steps (Ref. 5):

- Phosphoric acid was incorporated into the soil, along with potassium chloride (KCl), in an effort to form lead phosphate minerals.
- Hydrated lime [ $\text{Ca}(\text{OH})_2$ ] was added several days after phosphoric acid amendment in order to raise soil pH and thereby promote sod rooting or grass seed growth.
- Soil samples were collected for testing at prescribed time intervals following the completion of amendment treatment.

For the OLS, laboratory bench testing followed the completion of pre-treatment soil characterization testing and was also conducted by the LEGS. The objective of this effort was to evaluate various amendment types and strategies and recommend treatment schemes and procedures for field-testing. Numerous treatment schemes were conducted on unsieved splits of soil provided to LEGS by BVSPC using three forms of phosphorus; phosphoric acid (PA), triple super phosphate (TSP), and phosphate rock (PR). The amendment concentrations ranged from 0.5 percent (for example, 0.5 PA) to 2.0 percent (for example, 2 TSP). Some scenarios included the addition of hydrous ferric oxide (HFO) in an effort to reduce arsenic mobilization under high phosphate conditions. All amendments had lime added at the end of their reactive interval to adjust the pH back to a near normal (7.5) pH value. In most instances it was not possible to adjust the pH to pre-treatment levels. The average post-treatment pH was ~ 8.7. It was determined that adding more lime for the bench-scale testing would dilute the samples to an unacceptable level, causing the lime to behave not as a pH buffer, but merely diluting the contaminated soils

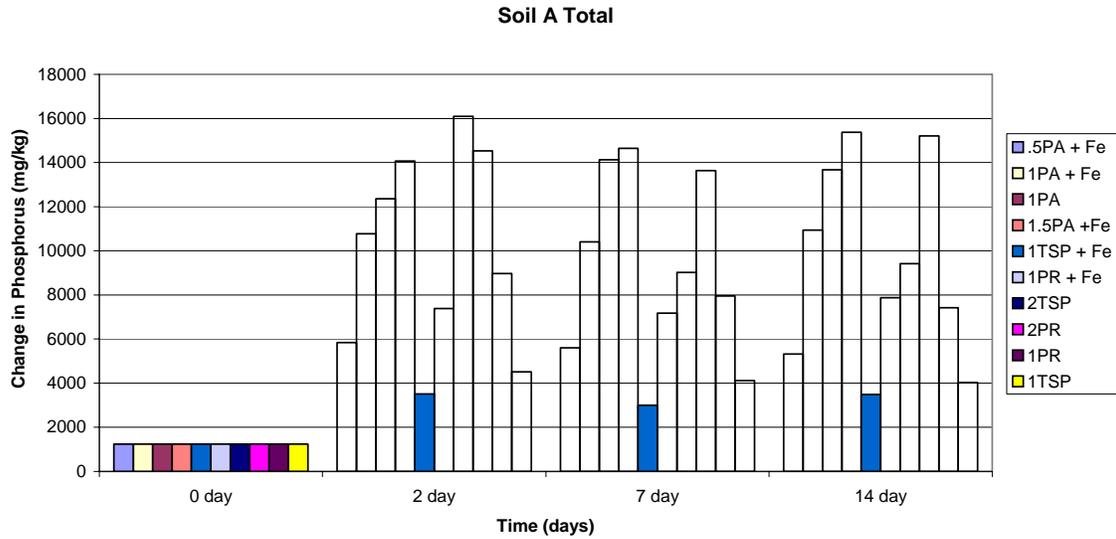
with a non-lead material. Amendments were run in duplicate (n=2) and sampled at 2, 7 and 14 days, Appendix A, (Table 2A). All analytical testing (SPLP, total P, extractable P, and RBALP) performed on the various treatment schemes are provided on accompanying electronic spreadsheets in Appendix D.

### **3.1 Total Phosphorus (P)**

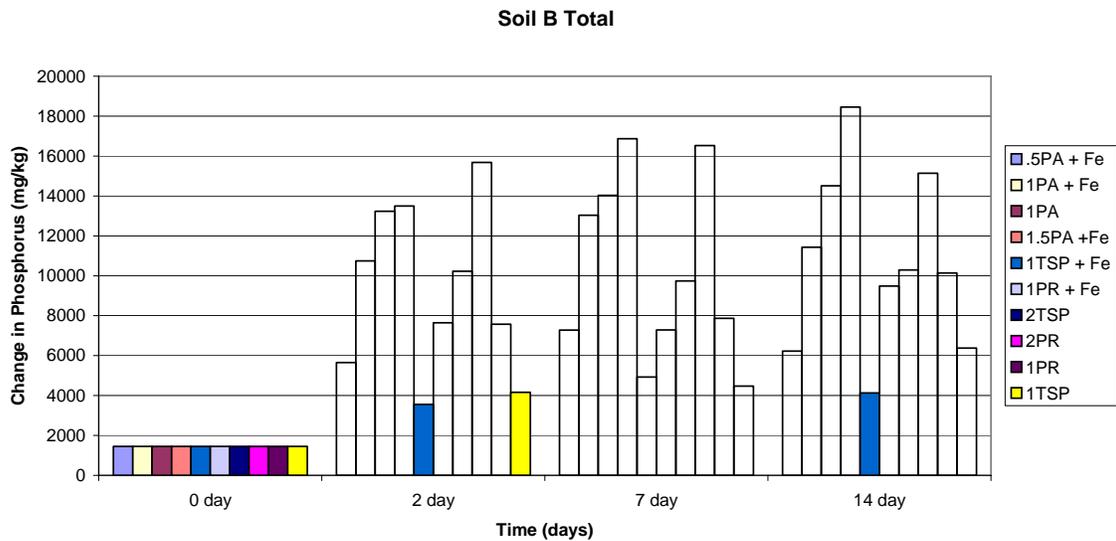
All of the amendment scenarios added considerable (1000X background) phosphorus to the OLS soils, 3,000-16,000 mg/kg P. As anticipated, the total phosphate remains generally constant, (Figures 3.1 to 3-3), throughout the 14 days testing interval. Phosphorus (P) is an essential element classified as a macronutrient for plants. Adequate P availability for plants stimulates early plant growth and hastens maturity. The soluble phosphate in the soil solution generally moves a short distance. Movement is slow but may be increased by rainfall or irrigation water flowing through the soil. As phosphate ions in solution migrate, most of the phosphate will react with other minerals within the soil. At the OLS, phosphate ions would likely react by adsorbing to soil particles or by combining with elements in the soil such as calcium (Ca), or magnesium (Mg), since soil pH is relatively high (pH >7.0), forming compounds that are solids. The adsorbed phosphate and the newly formed solids are relatively available to meet plant needs. The potential for migration of phosphorus to the water table can only be estimated once sorption isotherms for the OLS are determined; however, surface runoff of phosphorus is likely.

Although P is essential for plant growth, mismanagement of soil P can pose a threat to water quality. When lakes and rivers are polluted with P, excessive growth of algae often results. High levels of algae reduce water clarity and can lead to decreases in available dissolved oxygen (eutrophication) as the algae decays, conditions that can be very detrimental to fish populations.

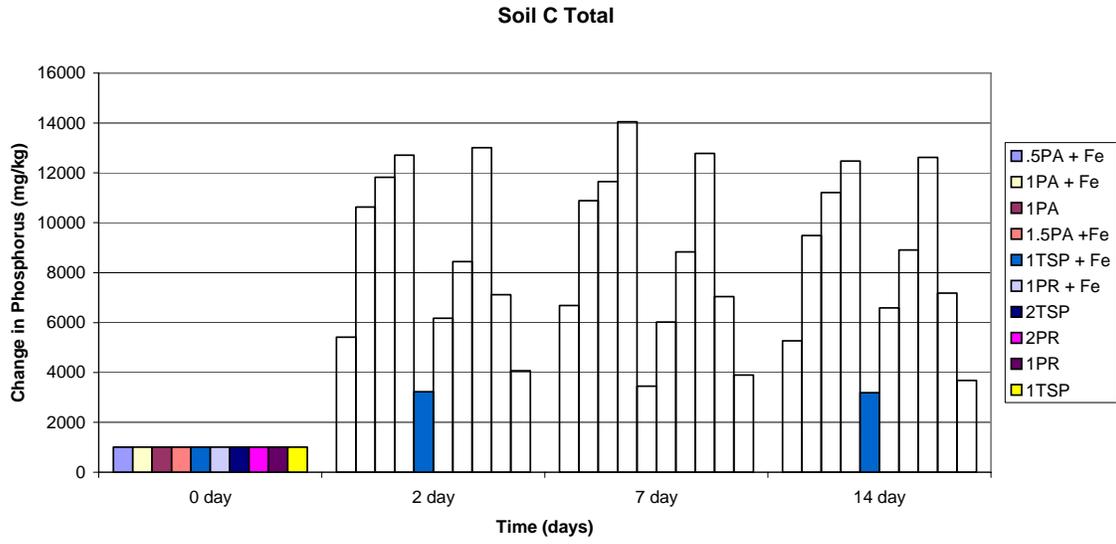
The complete data set with QA/QC can be review in the accompanying electronic spreadsheet in Appendix D.



**Figure 3-1 - Post-Treatment, Total Phosphorus from Soil A**



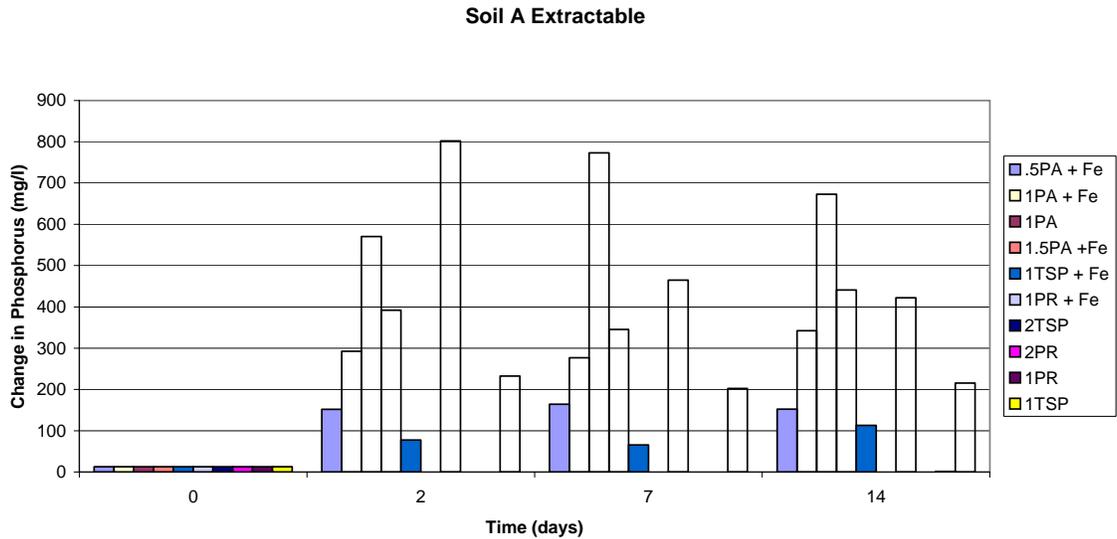
**Figure 3-2 - Post-Treatment, Total Phosphorus from Soil B**



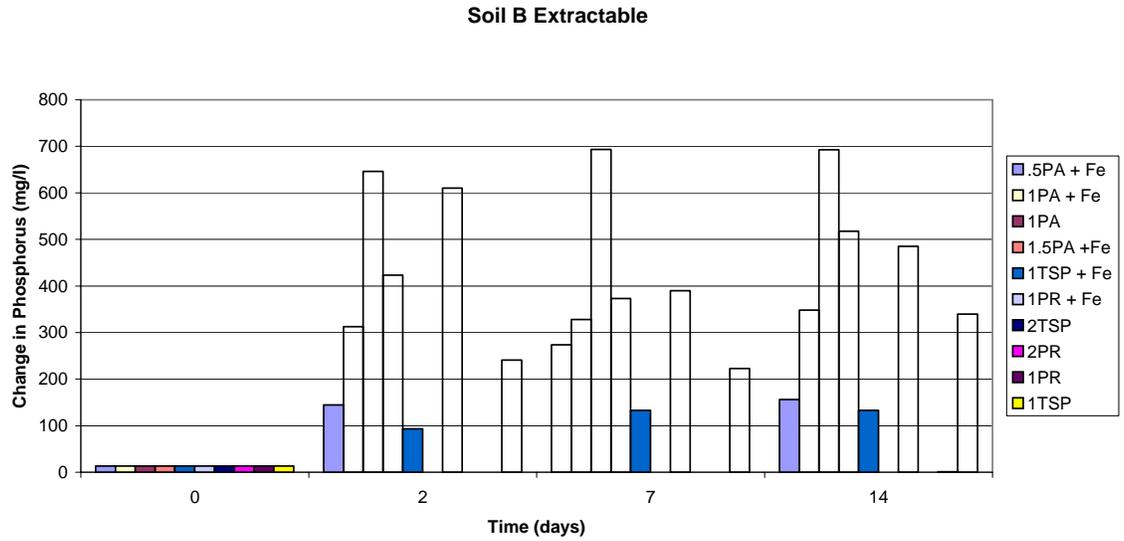
**Figure 3-3 - Post-Treatment, Total Phosphorus from Soil C**

### 3.2 Extractable P

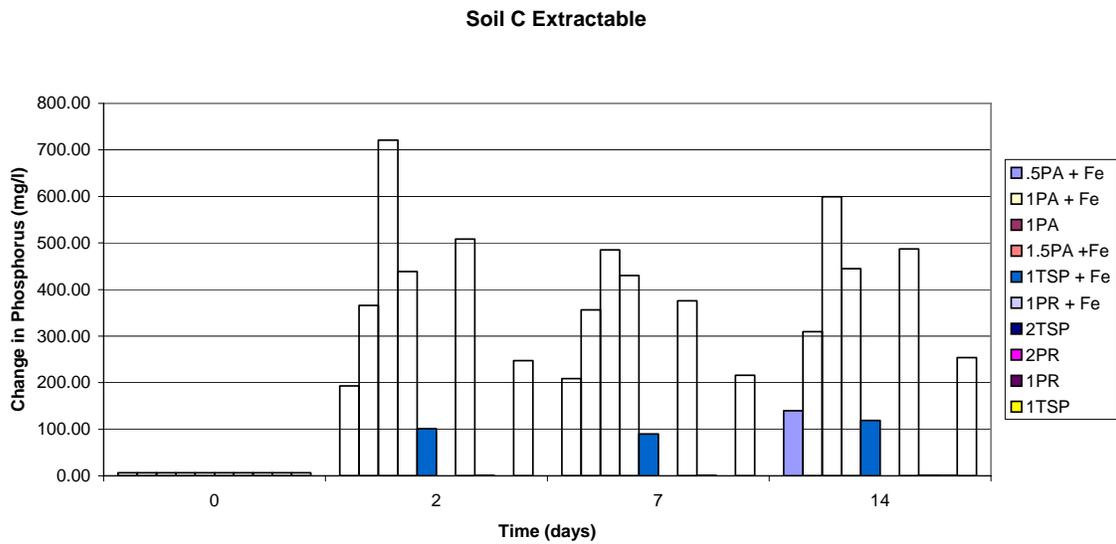
Extractable phosphate concentrations are intended to provide an indication of the sustainability of the amendment procedure. Thus, over time, as more lead becomes soluble from normal weathering, there is an issue as to whether there is sufficient phosphorous left in the soil to promote lead phosphate formation. A considerable degree of variation can be seen between the various forms of phosphate amendments and extractable phosphorus. PR yields virtually no extractable phosphate, even after 14 days (Figures 3-4 to 3-6). The other forms, TSP and PA, have 100-800 mg/l extractable P, with PA having the highest final concentrations after 14 days. The complete data set with QA/QC can be reviewed in the accompanying electronic spreadsheet in Appendix D.



**Figure 3-4 - Post-Treatment, Extractable Phosphorus from Soil A**



**Figure 3-5 - Post-Treatment, Extractable Phosphorus from Soil B**



**Figure 3-6 - Post-Treatment, Extractable Phosphorus from Soil C**

### 3.3 SPLP- Leachable P

Leachable phosphorus, (the phosphorous that will most likely impact surface runoff and groundwater) as measure by SPLP, is generally low, 2-30 mg/l, above the control soils concentrations. In general, concentrations of phosphorus decrease with time. The samples amended with 2-TSP leached from 40-120 mg/l P and remained high throughout the 14 days. The complete data set with QA/QC can be reviewed in the accompanying electronic spreadsheet in Appendix D.

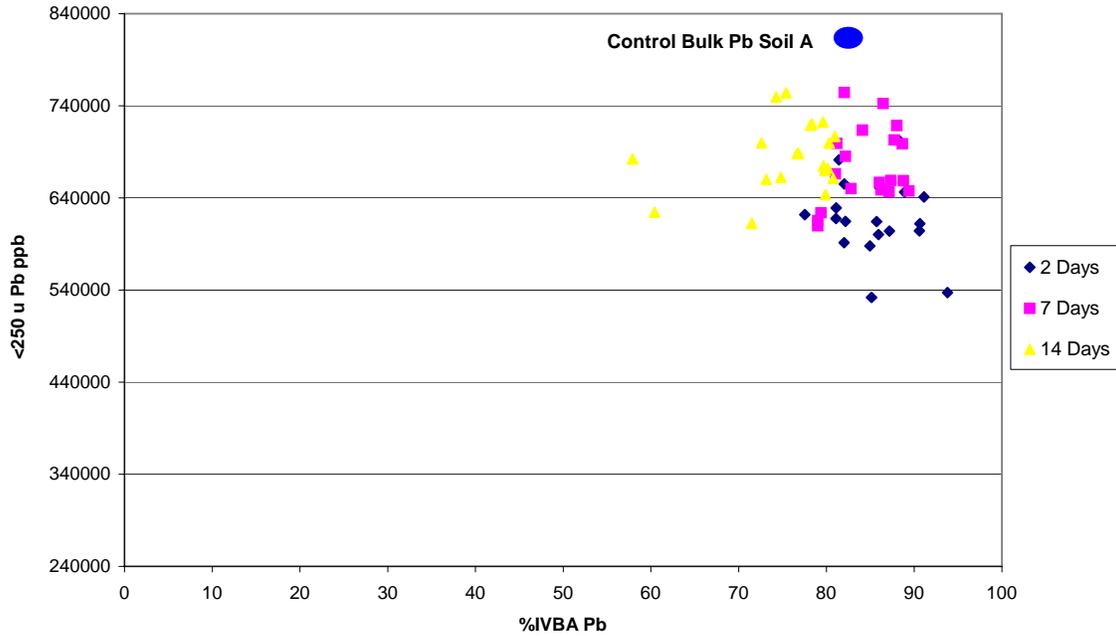
### 3.4 *In Vitro* Bioavailability

The *in vitro* bioavailability (IVBA) for lead, as measured using the RBALP, for each of the amended soils is presented in Figures 3-7 to 3-9. All of the samples show some reduction in bulk lead from the control (blue circle) samples. This change is primarily the result of dilution (from the low lead amendments) and a slight increase in particle size of the soils. The changes in IVBA are not significant and vary for each of the soils over time. In general, an average 20% reduction ( $(IVBA_{Initial} - IVBA_{Final} / IVBA_{Initial}) * 100$ ) in bioaccessibility was achieved, with the highest reduction achieved using the amendment of 1.5PA + hydrous ferric oxide (HFO). None of the amendment scenarios consistently lowered the soil IVBA's below EPA's default level (this is the value for IVBA used in the Integrated Exposure Uptake Biokinetic (IEUBK) model when no site-specific bioavailability data is available) of 60%.

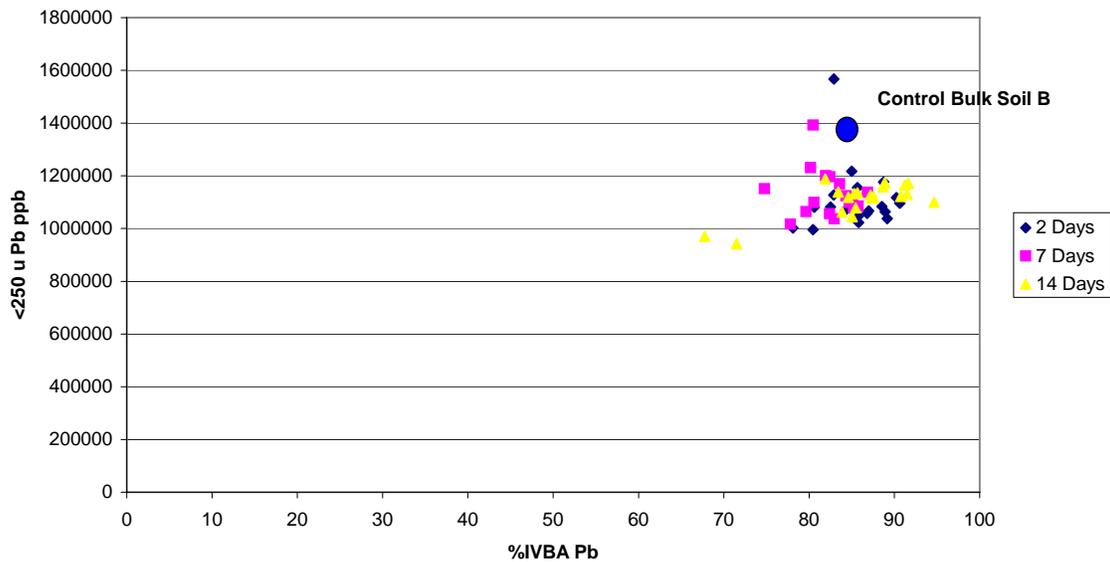
As discussed in the Treatability Work Plan (Ref.20), all samples were run with a second *in vitro* pH of 2.5 in order to be able to compare results with similar studies found in the literature. Running the RBALP at a pH of 2.5 (not a validated pH) indicates a much greater reduction in IVBA for all treated samples. As with the 1.5 pH samples, the 1.5PA + hydrous ferric oxide (HFO) amendment showed the greatest reduction, reducing IVBA to approximately 18% (11-24%) from the 50% average IVBA measured pre-treatment at pH 2.5. This represents nearly a 70% reduction in IVBA.

It is very important to note that there has been no validated *in vitro* method published for phosphate-amended soils at any pH values, including pH 1.5 and pH 2.5. Studies on amended soils have limited animal data (Ref. 5 and 21) and are highly variable, indicating both increases and decreases in RBA. Additionally, the 1.5 pH IVBA data from the RBALP agrees well with the OLS *in vivo* data (Ref. 22). Average RBA estimates obtained at pH 1.5 from RBALP are 76 and 71 percent for TM-1 and TM-2

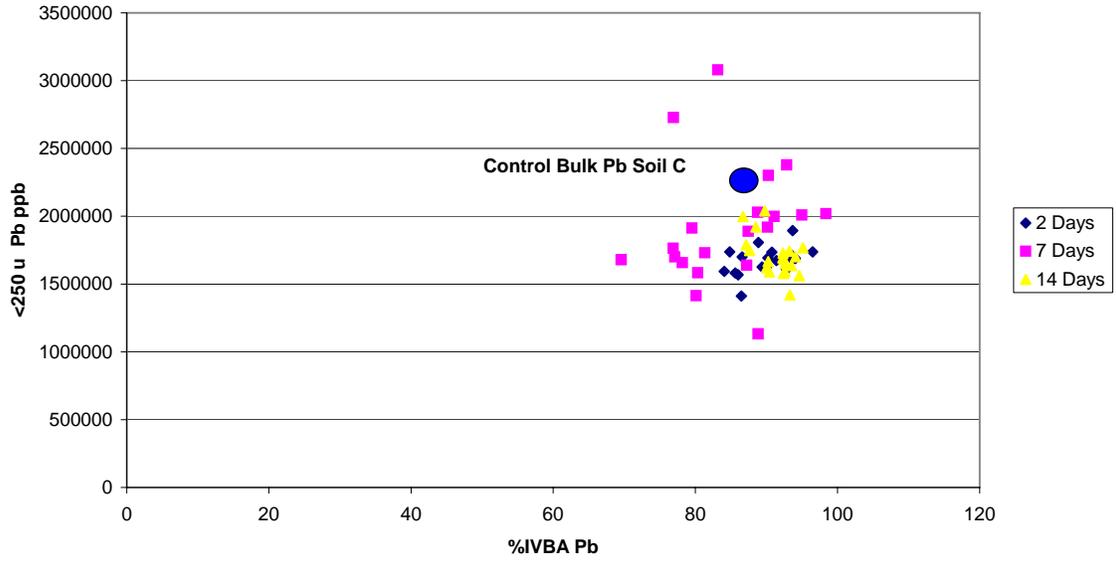
(test materials from swine OLS study), whereas measured values *in vivo* are 96 and 83 percent, respectively. Because the increase in pH from 1.5 to 2.5 standard units (su) for the RBALP would lower estimated RBA, it is clear that the use of a 2.5 pH *in vitro* solution would significantly underestimate the RBA at the OLS



**Figure 3-7 - Post-Treatment, IVBA for Lead in Soil A.**



**Figure 3-8 - Post-Treatment, IVBA for Lead in Soil B**



**Figure 3-9 - Post-Treatment, IVBA for Lead in Soil C**

### 3.5 Post Treatment Speciation

Post treatment speciation for lead is presented in Tables 3-1 to 3-3 and Figures 3-10 to 3-12. Only a single sample from the 1.5 PA + iron treatment (greatest reduction in IVBA) for each soil was speciated. It is apparent that the treatment procedure speciated is forming a phosphate product. The frequency of occurrence of lead phosphate forms increased in the treated soils to between 66 and 81% from the control soils that contained only 9-17 % lead phosphate. Two general forms of phosphate compounds are observed. The first, (labeled as phosphate) generally contain significant quantities of lead (25-60 wt% PbO) but are hydrated, with 10-25 wt% water in their structure. These phosphates, although containing lead and chloride, are clearly not pyromorphite or chloropyromorphite. They are well hydrated, and contain more chlorine and phosphorus than the pyromorphites (Figures 3-13 and 3-14). Although thermodynamically pyromorphites are the stable phase (Ref. 23), they are seldom identified and their diagenetic formation may be kinetically prevented (Ref. 24). Since the general premise of the phosphate treatment is the formation of the insoluble,  $K_{sp} = -84.4$ , chloropyromorphite, the formation of a potentially more soluble, primary or secondary orthophosphate ( $K_{sp} = -9.84, -11.43$  respectively) is significant. These phosphates would not likely be less bioaccessible than many of the original lead phases (anglesite  $K_{sp} -7.7$ , and cerussite  $K_{sp} -12.8$ ). These observations are in direct support of the limited decrease in IVBA observed in the treated soils.

The second phosphate compound, (Fe-hydrophosphate), is likely formed from the AFH (amorphous ferrihydroxide) added to the amended soils. These hydrated iron oxides have now sorbed phosphorus (1-20 wt%  $P_2O_5$ ), chlorine (1-3 wt% Cl) and lead (0.08-2.1 wt% PbO). Since they are not chemically similar to either corkite ( $PbFe_3PO_4SO_4-OH_6$ ) or drugmanite, ( $Pb_2Fe(PO_4)_2-OH_3$ ) it is unlikely they represent a stable mineral form.

Table 3-1  
Post-Treatment Lead Speciation of Soil A.

Form	Number	Mean	Std-Dev	Range low	Range high
Total	96	35.76	36.72	1	155
Phosphate	21	9.62	23.73	1	110
MnOOH	2	102.5	45.96	70	135
Brass	1	2	ND	2	2
FeOOH	14	25.64	31.72	2	90
PbTiO <sub>2</sub>	2	2.5	0.71	2	3
Fe-HydroPhosphate	55	48.33	34.36	4	155
Lead Solder	1	2	ND	2	2

Form	(linear) freq	Bio freq	rm Pb	Biorm Pb	Error-95%
%	%	%	%	%	
Phosphate	5.88	5.88	47.87	47.87	4.71
MnOOH	5.97	5.97	16.53	16.53	4.74
Brass	0.06	0.06	0	0	0.48
FeOOH	10.46	10.46	9.65	9.65	6.12
PbTiO <sub>2</sub>	0.15	0.15	1.1	1.1	0.76
Fe-HydroPhosphate	77.42	77.42	24.68	24.68	8.36
Lead Solder	0.06	0.06	0.17	0.17	0.48

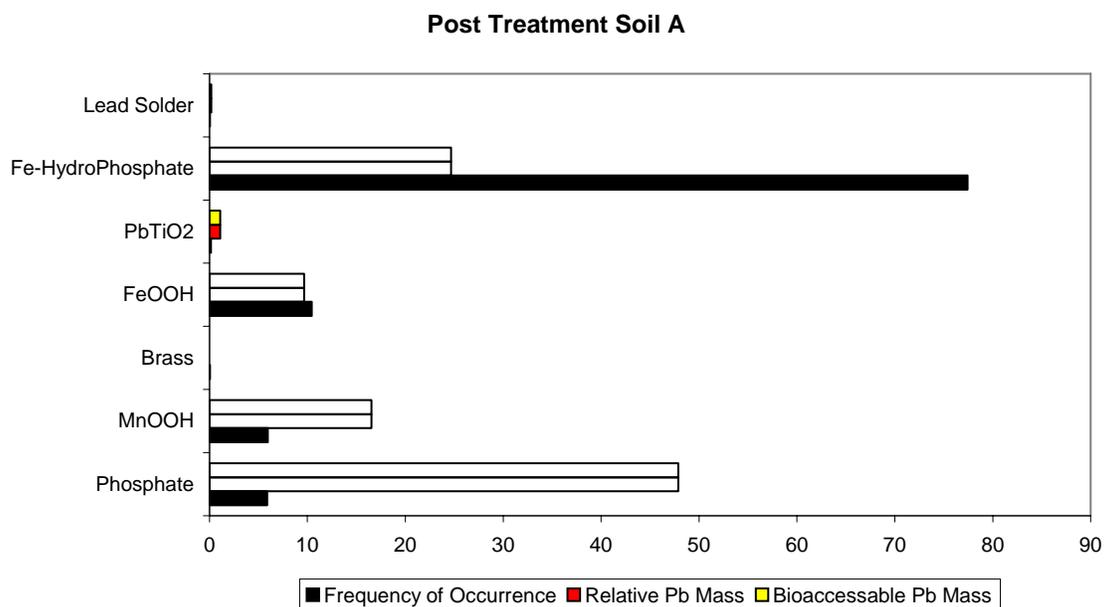
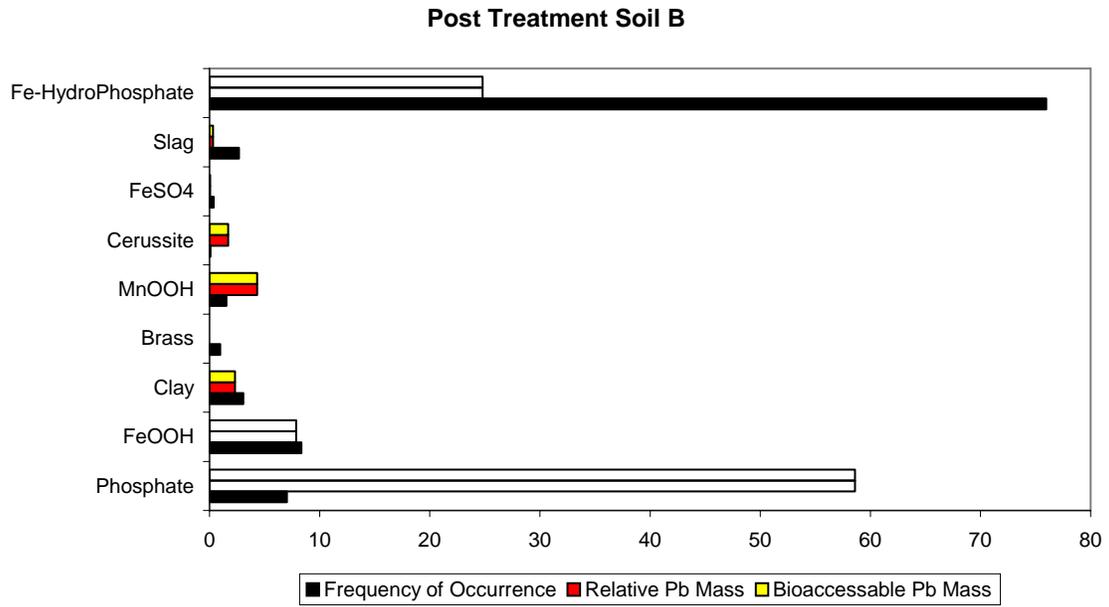


Figure 3-10 - Post-Treatment, Lead Speciation in Soil A

Table 3-2  
Post-Treatment Lead Speciation of Soil B

<b>Form</b>	<b>Number</b>	<b>Mean</b>	<b>Std-Dev</b>	<b>Range low</b>	<b>Range high</b>
Total	103	25.4	27.88	1	150
Phosphate	32	5.75	6.4	1	30
FeOOH	15	14.53	11.27	3	45
Clay	1	80	ND	80	80
Brass	1	25	ND	25	25
MnOOH	2	20	1.41	19	21
Cerussite	1	2	ND	2	2
FeSO4	1	10	ND	10	10
Slag	1	70	ND	70	70
Fe-HydroPhosphate	49	40.55	30.64	7	150

<b>Form</b>	<b>(linear) freq</b>	<b>Bio freq</b>	<b>rm Pb</b>	<b>Biorm Pb</b>	<b>Error-95%</b>
<b>%</b>	<b>%</b>	<b>%</b>	<b>%</b>	<b>%</b>	
Phosphate	7.03	7.03	58.61	58.61	4.94
FeOOH	8.33	8.33	7.87	7.87	5.34
Clay	3.06	3.06	2.32	2.32	3.33
Brass	0.96	0.96	0	0	1.88
MnOOH	1.53	1.53	4.33	4.33	2.37
Cerussite	0.08	0.08	1.68	1.68	0.53
FeSO4	0.38	0.38	0.07	0.07	1.19
Slag	2.68	2.68	0.31	0.31	3.12
Fe-HydroPhosphate	75.96	75.96	24.79	24.79	8.25



**Figure 3-11 - Post-Treatment, Lead Speciation in Soil B**

Table 3-3  
Post-Treatment Lead Speciation of Soil C

<b>Form</b>	<b>Number</b>	<b>Mean</b>	<b>Std-Dev</b>	<b>Range low</b>	<b>Range high</b>
Total	277	23.01	36.62	1	252
Cerussite	52	7.9	8.72	1	48
MnOOH	15	41.2	26.78	2	90
Phosphate	117	15.97	37.22	1	252
SnMO	1	90	ND	90	90
FeOOH	21	39.43	35.44	7	135
Fe-HydroPhosphate	50	46.94	44.45	5	205
PbMO	1	15	ND	15	15
Barite	2	6	2.83	4	8
PbTiO2	14	1.07	0.27	1	2
Clay	1	55	ND	55	55
Galena	1	4	ND	4	4
Lead Solder	1	80	ND	80	80
Paint	1	30	ND	30	30

<b>Form</b>	<b>(linear) freq</b>	<b>Bio freq</b>	<b>rm Pb</b>	<b>Biorm Pb</b>	<b>Error-95%</b>
<b>%</b>	<b>%</b>	<b>%</b>	<b>%</b>	<b>%</b>	
Cerussite	6.45	6.71	31.39	33.86	2.89
MnOOH	9.7	10.1	6.08	6.56	3.48
Phosphate	29.31	26.4	54.04	50.42	5.36
SnMO	1.41	1.47	0.46	0.49	1.39
FeOOH	12.99	13.53	2.72	2.93	3.96
Fe-HydroPhosphate	36.83	38.34	2.66	2.87	5.68
PbMO	0.24	0.25	0.77	0.83	0.57
Barite	0.19	0.2	0	0	0.51
PbTiO2	0.24	0.25	0.4	0.43	0.57
Clay	0.86	0.9	0.14	0.16	1.09
Galena	0.06	0.07	0.39	0.42	0.29
Lead Solder	1.26	1.31	0.84	0.9	1.31
Paint	0.47	0.49	0.12	0.13	0.81

Post Treatment Soil C

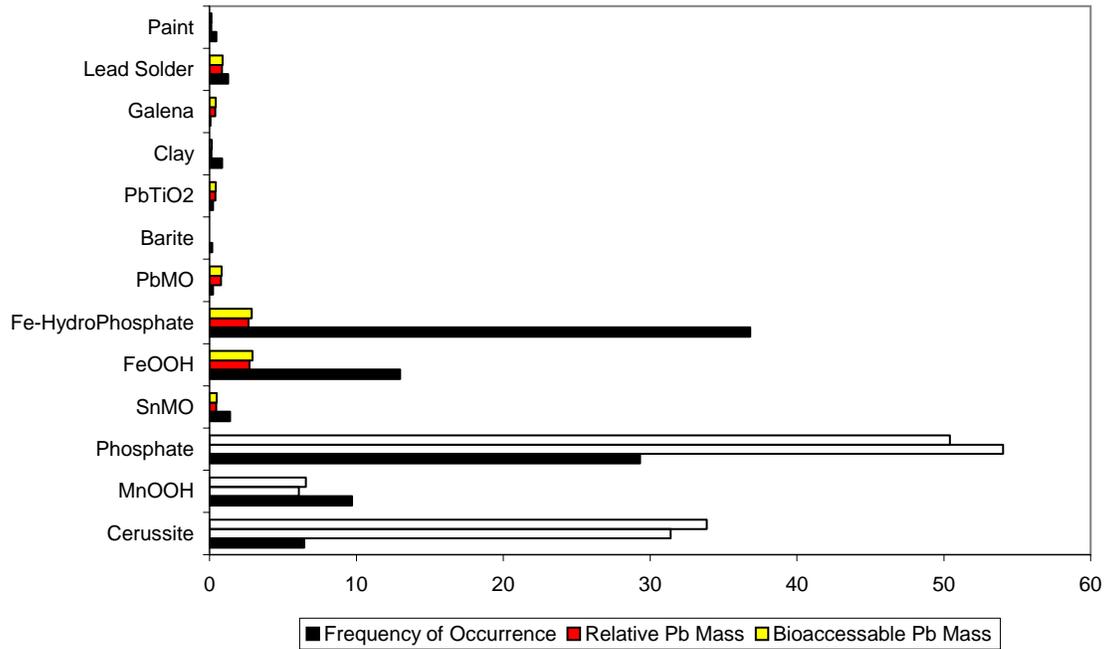
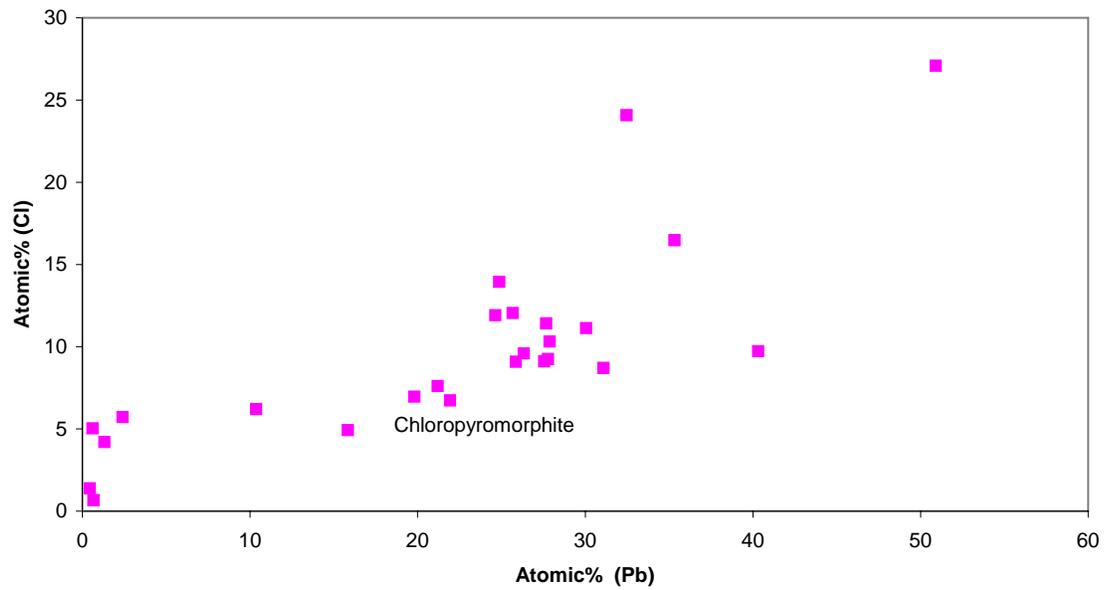
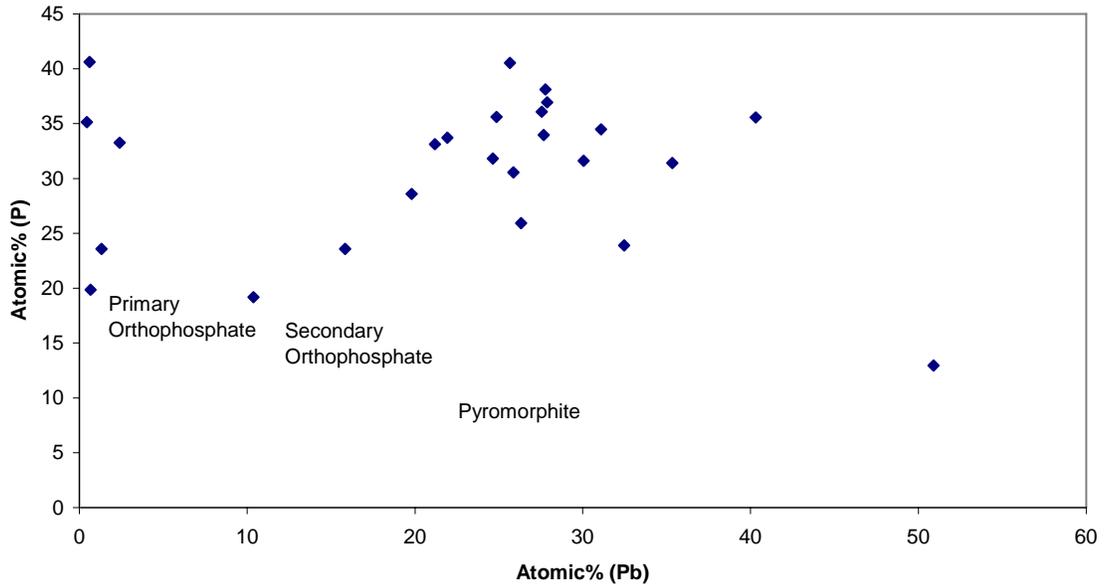


Figure 3-12 - Post-Treatment, Lead Speciation in Soil C

**Figures 3-13 & 3-14 – EMPA analyses of Post-Treatment, phosphate compounds.**



## 4.0 Conclusions

As outlined in the work plan, duplicate matrices of soils were assembled containing controls and the phosphate amendments PA, PR, and TSP, both with and without amorphous iron. The matrices were run in triplicate using 2, 7, and 14 day reaction periods. The effectiveness of the amendments were evaluated based on the relative change in IVBA as measured using the RBALP *in vitro* procedure, with extraction fluids at pH 1.5 and 2.5.

*In vivo* testing favors soils with lead concentrations greater than 1,000 ppm. Validated test methods do not exist that can measure RBA in phosphate treated soil within the lead concentration range of interest at the OLS. Although RBALP has not been validated for phosphate treated soils at either pH 1.5 or pH 2.5, the procedure may provide an indication of the potential effectiveness in reducing the RBA of lead-contaminated soils.

RBALP at pH 1.5 correlates well with *in vivo* RBA in untreated soils as evidenced by the close agreement of the two methods on the same soils (TM-1 and TM-2) from the OLS. RBALP at pH 2.5 would significantly underestimate the RBA when compared to *in vivo* results at the OLS.

Virtually all of the phosphate amendments showed some reduction in IVBA however, the 14-day, 1.5 PA (with iron) was the most reductive. All of the amendments behaved equally as well on the three soil-types, producing an increased presence of some phosphate form. Two negative results of the phosphate amendments, which could result in localized environmental issues is their release of both phosphate and arsenic to the vadose zone.

The measured effectiveness of the amendment techniques clearly varies between the pH 1.5 and pH 2.5 *in vitro* results. The pH 1.5 data presented in Table 4-1, which has the strongest correlation with *in vivo* RBA, shows limited reduction in IVBA, ranging from 15 percent to 26 percent reduction for the three soil types tested. The RBALP at pH 2.5 showed more significant reduction in IVBA, ranging from 61 percent to 80 percent; however the RBALP at pH 2.5 did not show good correlation with *in vivo* results on the same test soils and has not been validated by *in vivo* studies.

One sample from each of the three soil types treated with 1.5 PA plus iron was speciated. The speciation indicated that the treatment procedure was forming a phosphate product. The speciation indicated the formation of a potentially more soluble primary or secondary orthophosphate rather than the more insoluble chloropyromorphite. These orthophosphates would be more bioaccessible than the lead phases in the untreated soils and support the limited decrease in IVBA observed in the treated soils.

Finally, as pointed out previously, none of the amendment scenarios consistently lowered soil IVBA below EPA's default level of 60%, and therefore it is unlikely the data from the study would support altering EPA's cleanup decisions which are based on the IEUBK model. In addition, the long term effectiveness of the treatment scenarios has not been demonstrated at other sites and could not be assessed by this bench scale study.

Table 4-1  
Summary of Best Performing Amendments

Soil	Initial %IVBA PH (1.5/2.5)	Phosphate Amendment	Post				
			IVBA	IVBA	%Change*	%Change	
			<i>In</i> <i>Vitro</i> pH	1.5	2.5	1.5	2.5
A	80/41	1.5 PA + Iron		59%	14%	-26%	-66%
B	86/49	1.5 PA + Iron		69%	11%	-20%	-80%
C	88/61	1.5 PA + Iron		75%	24%	-15%	-61%

\*Change in IVBA = Initial IVBA-Post treatment IVBA/ Initial IVBA\*100

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**Appendix A**  
**Laboratory Testing Procedures**

# Appendix A

## Proposed Testing Procedures.

Activity	Parameter	Analysis	Method	Number of Analyses							
				Initial	30day	60 day	90 day	1yr	2 yr	3 yr	
<b>PHASE 1 Characterization</b>	Soil Properties	Particle Size	ASTM D-2487/D422	4							
		pH	SW 846 9045C	4							
		Acidity	Thomas 1982	4							
		CEC	SW 846 9080/9081	4							
	Soil Chemistry	P total	Blanchard & Stearman 1984	4							
		P extractable	SW 846 9080/9081	4							
		N	Kjeldahl	4							
		TOC	EPA 9060	4							
		Metals*	EPA 3050,6020	4							
	Mineralogy	XRD		4							
		EMPA	Drexler, 00	4							
	Bioaccessability	RBALP	Drexler and Bratin,07	4							
<b>Bench Testing</b>	Soil Properties	pH	SW 846 9045C	88							
		P total	Blanchard & Stearman 1984	88							
	P extractable	SW 846 9080/9081	88								
	Mineralogy	EMPA	Drexler, 00	4							
	Bioaccessability	RBALP	Drexler and Bratin,07	176							
		SPLP	EPA 1312	88							
	Column Leaching	Metals*	ASTM 4874	11							
<b>Field Testing</b>	Soil Properties	pH	SW 846 9045C		8	8	8	8	8	4	4
		Acidity	Thomas 1982		8	8	8	8	8	4	4
		CEC	SW 846 9080/9081		8	8	8	8	8	4	4
		Particle Size	ASTM D-2487/D422		8	8	8	8	8	4	4
	Soil Chemistry	P extractable	SW 846 9080/9081		8	8	8	8	8	4	4
		Metals*	EPA 3050,6020		8	8	8	8	8	4	4
		P total	Blanchard & Stearman 1984		8	8	8	8	8	4	4
		SPLP	EPA 1312								
		N	Kjeldahl		8	8	8	8	8	4	4
		TOC	EPA 9060				8	8	8	4	4
	Mineralogy	EMPA	Drexler, 00					8	4	4	
	Bioaccessability	RBALP	Drexler and Bratin,07	8				8	4	4	

\* Metals = Pb, As, and P.



				<b>2 day liming</b>					
<b>Sample</b>		<b>Lab ID</b>	<b>Initial Ca(OH)2 g**</b>	<b>pH 30 min</b>	<b>30 min Ca(OH)2 g**</b>	<b>pH 24hr</b>	<b>24 hr Ca(OH)2 g**</b>		
CompA-1**	Control	A2-1	0	7.24					
CompA-2	Control	A2-2	0	7.57					
CompA-3	5PA +Fe	A2-3	1	5.49	2	7.74		2	
CompA-4	5PA +Fe	A2-4	1	5.42	2	9.4		2	
CompA-5	1PA +Fe	A2-5	2	4.35	2	7.36		2	Soil A
CompA-6	1PA +Fe	A2-6	2	4.87	2	6.8		2	
CompA-7	1PA	A2-7	2	4.42	2	7.6		2	
CompA-8	1PA	A2-8	2	4.49	2	6.42		2	
CompA-9	15PA +Fe	A2-9	3	4.36	2	6		2	
CompA-10	15PA +Fe	A2-10	3	4.31	2	6.61		2	
CompA-11	1TSP	A2-11	2	7.49		8.4			
CompA-12	1TSP	A2-12	2	7.56		8.33			
CompA-13	1PR	A2-13	2	10.49		9.88			
CompA-14	1PR	A2-14	2	11.55		10.53			
CompA-15	1TSP +Fe	A2-15	2	9.16		8.29			
CompA-16	1TSP +Fe	A2-16	2	8.91		7.86			
CompA-17	1PR +Fe	A2-17	2	10.2		8.88			
CompA-18	1PR +Fe	A2-18	2	10.82		8.62			
CompA-19	2TSP	A2-19	2	7.21		7.03			
CompA-20	2TSP	A2-20	2	6.65		7.09			
CompA-21	2PR	A2-21	2	11.18		10.34			
CompA-22	2PR	A2-22	2	10.19		9.36			
CompB-1**	Control	B2-1	0						
CompB-2	Control	B2-2	0						
CompB-3	5PA +Fe	B2-3	1	6.05	2	9.48		2	
CompB-4	5PA +Fe	B2-4	1	5.88	2	8.9		2	
CompB-5	1PA +Fe	B2-5	2	4.97	2	5.22		2	Soil B
CompB-6	1PA +Fe	B2-6	2	5.43	2	7.4		2	
CompB-7	1PA	B2-7	2	6.13	2	6.59		2	
CompB-8	1PA	B2-8	2	6.34	2	6.66		2	
CompB-9	15PA +Fe	B2-9	3	6.79	2	5.26		2	
CompB-10	15PA +Fe	B2-10	3	5.33	2	5.76		2	
CompB-11	1TSP	B2-11	2	7.56		8.57			
CompB-12	1TSP	B2-12	2	7.39		8.35			
CompB-13	1PR	B2-13	2	10.15		10.26			
CompB-14	1PR	B2-14	2	10.48		10.21			
CompB-15	1TSP +Fe	B2-15	2	8.84		8.41			
CompB-16	1TSP +Fe	B2-16	2	8.53		7.62			
CompB-17	1PR +Fe	B2-17	2	9.78		9.23			
CompB-18	1PR +Fe	B2-18	2	9.22		8.99			
CompB-19	2TSP	B2-19	2	8.22		7.98			
CompB-20	2TSP	B2-20	2	8.12		8.05			
CompB-21	2PR	B2-21	2	8.67		10.43			
CompB-22	2PR	B2-22	2	7.63		9.5			
CompC-1**	Control	C2-1	0						
CompC-2	Control	C2-2	0						
CompC-3	5PA +Fe	C2-3	1	5.5	2	8.2		2	
CompC-4	5PA +Fe	C2-4	1	7.18	2	7.01		2	
CompC-5	1PA +Fe	C2-5	2	5.5	2	6.54		2	Soil C
CompC-6	1PA +Fe	C2-6	2	5.14	2	7.04		2	
CompC-7	1PA	C2-7	2	5.3	2	5.877		2	
CompC-8	1PA	C2-8	2	5.03	2	7.04		2	
CompC-9	15PA +Fe	C2-9	3	5.4	2	5.68		2	
CompC-10	15PA +Fe	C2-10	3	4.85	2	7.78		2	
CompC-11	1TSP	C2-11	2	7.14		8.32			
CompC-12	1TSP	C2-12	2	6.25		8.35			
CompC-13	1PR	C2-13	2	10.11		10.42			
CompC-14	1PR	C2-14	2	10.88		10.46			
CompC-15	1TSP +Fe	C2-15	2	9		8.43			
CompC-16	1TSP +Fe	C2-16	2	8.84		8.08			
CompC-17	1PR +Fe	C2-17	2	9.75		9.28			
CompC-18	1PR +Fe	C2-18	2	9.22		8.62			
CompC-19	2TSP	C2-19	2	7.47		7.36			
CompC-20	2TSP	C2-20	2	7.58		7.73			
CompC-21	2PR	C2-21	2	10.1		10.3			
CompC-22	2PR	C2-22	2	9.32		9.65			

				7 Day Liming			
Sample		Lab ID	Initial Ca(OH) <sub>2</sub> g**	pH 30 min	30 min Ca(OH) <sub>2</sub> g**	pH 24hrs	
CompA-1***	Control	A7-1	0				
CompA-2	Control	A7-2	0				
CompA-3	.5PA +Fe	A7-3	5	10.447		9.13	
CompA-4	.5PA +Fe	A7-4	5	10.04		8.48	
CompA-5	1PA +Fe	A7-5	5	8.738		6.94	
CompA-6	1PA +Fe	A7-6	5	8.107	+2	6.28	
CompA-7	1PA	A7-7	5	5.4		7.43	
CompA-8	1PA	A7-8	5	5.829		7.282	
CompA-9	15PA +Fe	A7-9	5	5.39	+2	6.17	
CompA-10	15PA +Fe	A7-10	5	6.024	+2	6.058	
CompA-11	1TSP	A7-11	2	7.18		8.156	
CompA-12	1TSP	A7-12	2	7.098		8.422	
CompA-13	1PR	A7-13	1	9.84		8.89	
CompA-14	1PR	A7-14	1	9.24		9.07	
CompA-15	1TSP +Fe	A7-15	2	9.31		8.25	
CompA-16	1TSP +Fe	A7-16	2	9.27		8.33	
CompA-17	1PR +Fe	A7-17	1	9.027		7.97	
CompA-18	1PR +Fe	A7-18	1	8.87		8.3	
CompA-19	2TSP	A7-19	2	6.97		7.97	
CompA-20	2TSP	A7-20	2	7.024		7.775	
CompA-21	2PR	A7-21	1	9.81		8.96	
CompA-22	2PR	A7-22	1	9.27		8.81	
CompB-1***	Control	B7-1	0				
CompB-2	Control	B7-2	0				
CompB-3	.5PA +Fe	B7-3	5	10.57		10.56	
CompB-4	.5PA +Fe	B7-4	5	10.88		10.613	
CompB-5	1PA +Fe	B7-5	5	8.46		7.5	
CompB-6	1PA +Fe	B7-6	5	10.1		8.17	
CompB-7	1PA	B7-7	5	5.42		7.83	
CompB-8	1PA	B7-8	5	5.7		8.17	
CompB-9	15PA +Fe	B7-9	5	6.97		7.05	
CompB-10	15PA +Fe	B7-10	5	11.54	ut 20 grams lime (ope	11.027	
CompB-11	1TSP	B7-11	2	10.69		9.87	
CompB-12	1TSP	B7-12	2	9.907		9.446	
CompB-13	1PR	B7-13	1	10.99		10.19	
CompB-14	1PR	B7-14	1	10.77		9.61	
CompB-15	1TSP +Fe	B7-15	2	10.62		10.36	
CompB-16	1TSP +Fe	B7-16	2	11.17		10.2	
CompB-17	1PR +Fe	B7-17	1	10.47		9.8	
CompB-18	1PR +Fe	B7-18	1	10.8		9.76	
CompB-19	2TSP	B7-19	2	9.06		8.56	
CompB-20	2TSP	B7-20	2	9.211		8.57	
CompB-21	2PR	B7-21	1	10.63		9.53	
CompB-22	2PR	B7-22	1	11.04		10.4	
CompC-1***	Control	C7-1	0				
CompC-2	Control	C7-2	0				
CompC-3	.5PA +Fe	C7-3	5	12.07		11.17	
CompC-4	.5PA +Fe	C7-4	5	12.13		11.16	
CompC-5	1PA +Fe	C7-5	5	11.61		9.27	
CompC-6	1PA +Fe	C7-6	5	11.64		10.2	
CompC-7	1PA	C7-7	5	6.88		8.98	
CompC-8	1PA	C7-8	5	6.21		8.535	
CompC-9	15PA +Fe	C7-9	5	10.75		8.92	
CompC-10	15PA +Fe	C7-10	5	10.72		9.606	
CompC-11	1TSP	C7-11	2	9.86		9.74	
CompC-12	1TSP	C7-12	2	10.188		9.739	
CompC-13	1PR	C7-13	1	10.87		10.13	
CompC-14	1PR	C7-14	1	10.76		10.77	
CompC-15	1TSP +Fe	C7-15	2	11.24		10.34	
CompC-16	1TSP +Fe	C7-16	2	11.01		10.12	
CompC-17	1PR +Fe	C7-17	1	10.851		10.48	
CompC-18	1PR +Fe	C7-18	1	11.02		10.126	
CompC-19	2TSP	C7-19	2	8.58		8.74	
CompC-20	2TSP	C7-20	2	8.4		8.428	
CompC-21	2PR	C7-21	1	10.248		9.861	
CompC-22	2PR	C7-22	1	10.6		10.32	

14 day liming						
Sample		Lab ID	Initial Ca(OH) <sub>2</sub> g**	pH 30 min		pH 24hrs
CompA-1***	Control	A 14-1	0			
CompA-2	Control	A 14-2	0			
CompA-3	.5PA +Fe	A 14-3	5	10.1		9.2
CompA-4	.5PA +Fe	A 14-4	5	9.5		9.5
CompA-5	1PA +Fe	Soil A A 14-5	5	7.7		9.1
CompA-6	1PA +Fe	A 14-6	5	6.9		9.8
CompA-7	1PA	A 14-7	5	6.8		9.4
CompA-8	1PA	A 14-8	5	7.5		7.9
CompA-9	15PA +Fe	A 14-9	5	6.9		6.5
CompA-10	15PA +Fe	A 14-10	5	7.9		7
CompA-11	1TSP	A 14-11	2	9.8		9
CompA-12	1TSP	A 14-12	2	10.6		9.9
CompA-13	1PR	A 14-13	1	9.5		9.7
CompA-14	1PR	A 14-14	1	10.1		9
CompA-15	1TSP +Fe	A 14-15	2	9.2		8.2
CompA-16	1TSP +Fe	A 14-16	2	9.4		8.6
CompA-17	1PR +Fe	A 14-17	1	9.7		8.8
CompA-18	1PR +Fe	A 14-18	1	8.5		9.2
CompA-19	2TSP	A 14-19	2	8		7.8
CompA-20	2TSP	A 14-20	2	8.9		7.7
CompA-21	2PR	A 14-21	1	9.6		9.3
CompA-22	2PR	A 14-22	1	9.5		9.1
CompB-1***	Control	B 14-1	0			
CompB-2	Control	B 14-2	0			
CompB-3	.5PA +Fe	B 14-3	5	11.6		9.8
CompB-4	.5PA +Fe	B 14-4	5	11.2		9.7
CompB-5	1PA +Fe	Soil B B 14-5	5	10.5		8.6
CompB-6	1PA +Fe	B 14-6	5	9.5		7.7
CompB-7	1PA	B 14-7	5	9.5		8.2
CompB-8	1PA	B 14-8	5	8.3		7.9
CompB-9	15PA +Fe	B 14-9	5	7.7		7.9
CompB-10	15PA +Fe	B 14-10	5	7.4		8.6
CompB-11	1TSP	B 14-11	2	9.9		9.6
CompB-12	1TSP	B 14-12	2	9.8		9.9
CompB-13	1PR	B 14-13	1	10.8		10.2
CompB-14	1PR	B 14-14	1	11		8.3
CompB-15	1TSP +Fe	B 14-15	2	9.3		8.5
CompB-16	1TSP +Fe	B 14-16	2	9.7		9
CompB-17	1PR +Fe	B 14-17	1	9.6		7.7
CompB-18	1PR +Fe	B 14-18	1	9.5		7.6
CompB-19	2TSP	B 14-19	2	8		8.4
CompB-20	2TSP	B 14-20	2	8.9		8.7
CompB-21	2PR	B 14-21	1	8.8		9.6
CompB-22	2PR	B 14-22	1	10		9.7
CompC-1***	Control	C 14-1	0			
CompC-2	Control	C 14-2	0			
CompC-3	.5PA +Fe	C 14-3	5	10.9		10.8
CompC-4	.5PA +Fe	C 14-4	5	11.5		10.8
CompC-5	1PA +Fe	Soil C C 14-5	5	10.5		9.5
CompC-6	1PA +Fe	C 14-6	5	9.9		9.2
CompC-7	1PA	C 14-7	5	9.1		11.1
CompC-8	1PA	C 14-8	5	9.3		9.2
CompC-9	15PA +Fe	C 14-9	5	8.2		8.4
CompC-10	15PA +Fe	C 14-10	5	8.5		8.2
CompC-11	1TSP	C 14-11	2	9.6		9.6
CompC-12	1TSP	C 14-12	2	9.5		9.7
CompC-13	1PR	C 14-13	1	10.4		9.8
CompC-14	1PR	C 14-14	1	10.2		9.6
CompC-15	1TSP +Fe	C 14-15	2	10.3		9.4
CompC-16	1TSP +Fe	C 14-16	2	9.4		8.9
CompC-17	1PR +Fe	C 14-17	1	9.3		8.9
CompC-18	1PR +Fe	C 14-18	1	9.4		8.8
CompC-19	2TSP	C 14-19	2	9.4		8.2
CompC-20	2TSP	C 14-20	2	8		8.1
CompC-21	2PR	C 14-21	1	9.1		9.4
CompC-22	2PR	C 14-22	1	10.6		9.5

**Appendix B**  
**Metal Speciation Standard Operating Procedure**

## Appendix B

**UNIVERSITY of COLORADO**  
**Laboratory for Geological and Environmental Studies (LEGS)**

October 11, 2007 (Rev. #2)

Title: METAL SPECIATION SOP

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**SYNOPSIS:** A standardized method for speciating metals in solid samples is described. Equipment operating conditions, sample preparation and handling, and statistical equations for data analysis and presentation are included.

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## 1.0 OBJECTIVES

The objectives of this Standard Operating Procedure (SOP) are to specify the proper methodologies and protocols to be used during metal speciation of various solid samples including; tailings, slags, sediments, dross, bag house dusts, wipes, paint, soils, and dusts for metals. The metal speciation data generated from this SOP may be used to assess the solid samples as each phase relates to risk. Parameters to be characterized during the speciation analyses include particle size, associations, stoichiometry, frequency of occurrence of metal-bearing forms and relative mass of metal-bearing forms. This electron microprobe analyses (EMPA) technique, instrument operation protocols and sample preparation to be used during implementation of the Metals Speciation SOP are discussed in the following sections.

## 2.0 BACKGROUND

To date, numerous metal-bearing forms have been identified from various environments within western mining districts (Emmons et al., 1927; Drexler, 1991 per. comm.; Drexler, 1992; Davis et al., 1993; Ruby et al., 1994; CDM, 1994; WESTON, 1995), and industrial or agricultural (Drexler, 1999 per. comm.) settings, Table 2-1. This listing does not preclude the identification of other metal-bearing forms, but only serves as an initial point of reference. Many of these forms are minerals with varying metal concentrations (e.g., lead phosphate, iron-lead oxide, and slag). Since limited thermodynamic information is available for many of these phases and equilibrium conditions are rarely found in soil environments, the identity of the mineral class (e.g., lead phosphate) will be sufficient and exact stoichiometry is not necessary.

It may be important to know the particle-size distribution of metal-bearing forms in order to assess potential risk. It is believed that particles less than 250 microns ( $\mu\text{m}$ ) are most available for human ingestion and/or inhalation (Bornschein, et al., 1987). For this study, the largest dimension of any one metal-bearing form will be measured and the frequency of occurrence weighted by that dimension. Although not routinely performed, particle area can be determined, it has been shown (CDM, 1994) that data collected on particle area produces similar results. These measurements add a considerable amount of time to the procedure, introduce new sources of potential error and limit the total number of particles or samples that can be observed in a study.

Mineral association may have profound effects on the ability for solubilization. For example, if a lead-bearing form in one sample is predominantly found within quartz grains while in another sample it is free in the sample matrix, the two samples are likely to pose significantly different risk levels to human health. Therefore, associations of concern include the following:

- 1) free or liberated
- 2) inclusions within a second phase
- 3) cementing

### 3.0 SAMPLE SELECTION

Samples should be selected and handled according to the procedure described in the Project Plan.

### 4.0 SCHEDULE

A schedule for completion of projects performed under this Metals Speciation SOP will be provided in writing or verbally to the contractor along with monthly reporting requirements if large projects are performed. These schedules are based on an aggressive analytical program designed to ensure that the metals speciation analyses are completed in a timely period. Monthly reports are expected to reflect schedule status.

### 5.0 INSTRUMENTATION

Speciation analyses will be conducted at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder or other comparable facilities. Primary equipment used for this work will include:

Electron Microprobe (JEOL 8600) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and Geller Microanalytical data processing system. An LEDC spectrometer crystal for carbon and LDE-1 crystal for oxygen analyses are essential.

### 6.0 PRECISION AND ACCURACY

The precision of the EMPA speciation and polarized light microscopy (PLM) will be evaluated based on sample duplicates analyzed at a frequency of 10%. The precision of the data generated by the manual PLM particle count and by the "EMPA point count" will be evaluated by preparing a graph that compares the original result with the duplicate result. The accuracy of the analyses will be estimated based on a number of methods, depending on the source of the data. Data generated by the "EMPA point count" or will be evaluated statistically based on the methods of Mosimann (1965) at the 95% confidence level on the frequency data following Equation 1.

$$E_{0.95} = 2P(100-P)/N \quad (\text{Eq. 1})$$

Where:

$E_{0.95}$	=	Probable error at the 95% confidence level
P	=	Percentage of N of an individual metal-bearing phase based on percent length frequency
N	=	Total number of metal-bearing grains counted

In general, site-specific concentrations for these variable, metal-bearing forms will be determined by performing “peak counts” on the appropriate wavelength spectrometer. Average concentrations will then be used for further calculations. Data on specific gravity will be collected from referenced databases or estimated based on similar compounds.

## **7.0 PERSONNEL RESPONSIBILITY**

The analysts will carefully read this SOP prior to any sample examination.

It is the responsibility of the laboratory supervisor and designates to ensure that these procedures are followed, to examine quality assurance (QA) samples and replicate standards, and to check EDS and WDS calibrations. The laboratory supervisor will collect results, ensure they are in proper format, and deliver them to the contractor.

Monthly reports summarizing all progress, with a list of samples speciated to date with data analyses sheets (DAS), will be submitted each month.

It is also the responsibility of the laboratory supervisor to notify the contractor representative of any problems encountered in the sample analysis process.

## **8.0 SAMPLE PREPARATION**

Grain mounts (1.5 inches in diameter) of each sample will be prepared using air-cured epoxy. This grain mounting technique is appropriate for most speciation projects, however polished thin-sections, paint chips, dust wipes, or filters may be prepared in a similar manner. The grain mounting is performed as follows:

- 1) Log the samples for which polished mounts will be prepared.
- 2) Inspect all disposable plastic cups, making sure each is clean and dry.
- 3) Label each “mold” with its corresponding sample number.
- 4) All samples will be split to produce a homogeneous 1-4 gram sample.
- 5) Mix epoxy resin and hardener according to manufacturer’s directions.
- 6) Pour 1 gram of sample into mold. Double check to make sure sample numbers on mold and the original sample container match. Pour epoxy into mold to just cover sample grains.

- 7) Use a new wood stirring stick with each sample, carefully blend epoxy and grains so as to coat all grains with epoxy.
- 8) Set molds to cure at ROOM TEMPERATURE in a clean restricted area. Add labels with sample numbers and cover with more epoxy resin. Leave to cure completely at room temperature.
- 9) One at a time remove each sample from its mold and grind flat the back side of the mount.
- 10) Use 600 grit wet abrasive paper stretched across a grinding wheel to remove the bottom layer and expose as many mineral grains as possible. Follow with 1000 grit paper.
- 11) Polish with 15 um oil-based diamond paste on a polishing paper fixed to a lap. Use of paper instead of cloth minimizes relief.
- 12) Next use 6um diamond polish on a similar lap.
- 13) Finally polish the sample with 1um oil-based diamond paste on polishing paper, followed by 0.05 um alumina in water suspension. The quality should be checked after each step. Typical polishing times are 30 minutes for 15 um, 20 minutes for 6 um, 15 minutes for 1 um, and 10 minutes for 0.05 um.

NOTE: use low speed on the polishing laps to avoid “plucking” of sample grains.

- 14) Samples should be completely cleaned in an ultrasonic cleaner with isopropyl alcohol or similar solvent to remove oil and fingerprints.
- 15) To ensure that no particles of any metal are being cross-contaminated during sample preparation procedures, a blank (epoxy only) mold will be made every 20<sup>th</sup> sample (5% of samples) following all of the above procedures. This mold will then be speciated along with the other samples.
- 16) Each sample must be carbon coated. Once coated, the samples should be stored in a clean, dry environment with the carbon surface protected from scratches or handling.

## **9.0 GEOCHEMICAL SPECIATION USING ELECTRON MICROPROBE**

*All investigative samples will also be characterized using EMPA analysis to determine the chemical speciation, particle size distribution and frequency for several target metals.*

## 10.1 Concentration Prescreening

All samples will be initially examined using the electron microprobe to determine if the number of particles are too great to obtain a representative count. The particle counting will be considered representative if the entire sample (puck) has been traversed about the same time in which the counting criteria are achieved.

If this examination reveals that one metal is abundant ( $> 1\%$  of total metals concentration), clean quartz sand ( $\text{SiO}_2$ ) will be mixed with the sample material. The sand should be certified to be free of target analytes. The quartz sand should be added to an aliquot of the investigative sample, then mixed by turning the sample for a minimum of one hour, or until the sample is fully homogenized. The initial mass of the investigative sample aliquot, and the mass of the quartz addition will be recorded.

## 10.2 Point Counting

Counts are made by traversing each sample from left-to-right and top-to-bottom as illustrated in Figure 10-2. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings generally are used. One ranging from 40-100X and a second from 300-600X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of metal-bearing particles, and the complexity of metal mineralogy. A maximum of 8 hours will be spent on each analysis.

## 10.3 Data Reduction

Analysts will record data as they are acquired from each sample using the LEGS software, (Figure 10-3A) which places all data in a spreadsheet file format. Columns have been established for numbering the metal-bearing phase particles, their identity, size of longest dimension in microns, along with their association (L = liberated, C = cementing, I = included) (Figure 10-3B). The analyst may also summarize his/her observations in the formatted data summary files.

The frequency of occurrence and relative metal mass of each metal-bearing form as it is distributed in each sample will be depicted graphically as a frequency bar-graph. The particle size distribution of metal-bearing forms will be depicted in a histogram. Size-histograms of each metal-bearing form can be constructed from data in the file.

Data from EMPA will be summarized using two methods. The first method is the determination of FREQUENCY OF OCCURRENCE. This is calculated by summing the

longest dimension of all the metal-bearing phases observed and then dividing each phase by the total.

Equation 2 will serve as an example of the calculation.

$$F_M \text{ in phase-1} = \frac{\Sigma (\text{PLD})_{\text{phase 1}}}{\Sigma (\text{PLD})_{\text{phase-1}} + \Sigma (\text{PLD})_{\text{phase-2}} + \Sigma (\text{PLD})_{\text{phase-n}}} \quad (\text{Eq. 2})$$

Where:

$F_M$  = Frequency of occurrence of metal in a single phase.

PLD = An individual particle's longest dimension

$\%F_M \text{ in phase-1}$  =  $F_M \text{ in phase-1} * 100$

These data thus illustrate which metal-bearing phase(s) are the most commonly observed in the sample or relative volume percent.

The second calculation used in this report is the determination of RELATIVE METAL MASS. These data are calculated by substituting the PLD term in the equation above with the value of  $M_M$ . This term is calculated as defined below.

$$M_M = FM * SG * \text{ppm}_M \quad (\text{Eq. 3})$$

Where:

$M_M$  = Mass of metal in a phase

SG = Specific Gravity of a phase

$\text{ppm}_M$  = Concentration in ppm of metal in a phase

The advantage in reviewing the RELATIVE METAL MASS determination is that it gives one information as to which metal-bearing phase(s) in a sample are likely to control the total bulk concentration for a metal of interest. For example, PHASE-1 may comprise 98% relative volume of the sample; however, it has a low specific gravity and contains only 1,000 parts per million (ppm) arsenic. PHASE-2 comprised 2% of the sample, has a high specific gravity, and contains 850,000 ppm of arsenic. In this example it is PHASE-2 that is the dominant source of arsenic to the sample.

The third calculation is to determine the BIOACCESSIBLE MASS lead ( $\text{Bi}_{\text{OPb}}$ ). For this calculation the same procedure as outlined above is used however, the original particle-count data set has been screened to use **only** liberated and cemented particles less than 250 microns in size (BIOACCESSIBLE FREQUENCY). The reasoning behind these calculations are: 1) A particle greater than 250 microns is not bioaccessible. It will not adhere to clothes or hands. 2) A particle of lead that is enclosed within another mineral is considered far less bioaccessible, as one would need to dissolve the outer mineral or free the enclosed lead particle to make it available. 3) Finally, these data are considered likely to better reflect results observed from *invitro* or *invivo* studies.

The accuracy of an analysis will be estimated from a statistical evaluation of point counting data based on the method of Mosimann (1965) these data will be tabulated in Table 3 as  $E^{95\%}$ .

#### **10.4 Analytical Procedure**

A brief visual examination of each sample will be made, prior to EMPA examination. This examination may help the operator by noting the occurrence of slag and/or organic matter. Standard operating conditions for quantitative and qualitative analyses of most metal-bearing forms are given in Table 8-1. However, it is the responsibility of the operator to select the appropriate analytical line (crystal/KeV range) to eliminate peak overlaps and ensure proper identification/quantification of each analyte. Quality control will be maintained by analyzing duplicates at regular intervals (Section 8.5).

The backscattered electron threshold will be adjusted so that all particles in a sample are seen. This procedure will minimize the possibility that low metal-bearing minerals may be overlooked during the scanning of the polished grain mount. The scanning will be done manually in a manner similar to that depicted in Figure 8-2. Typically, the magnification used for scanning all samples except for airborne samples will be 40-100X and 300-600X. The last setting will allow the smallest identifiable (1-2  $\mu\text{m}$ ) phases to be found. Once a candidate particle is identified, then the backscatter image will be optimized to discriminate any different phases that may be making up the particle or defining its association. Identification of the metal-bearing phases will be done using both EDS and WDS on an EMPA, with spectrometers typically peaked at sulfur, oxygen, carbon and the metal(s) of concern (M). The size of each metal-bearing phase will be determined by measuring in microns the longest dimension.

As stated previously, a maximum of 8 hours will be spent in scanning and analyzing each mount. For most speciation projects the goal is to count between 100-200 particles. In the event that these goals are achieved in less than 8 hours, particle counting may continue or the analyst may move to another sample in order to increase the sample population.

#### **Quantitative Analyses**

Quantitative EMPA analyses are required to establish the average metal content of the metal-bearing minerals, which have variable metal contents as: Iron-(M) sulfate, Iron-(M) oxide, Manganese-(M) oxide, organic, and slag. These determinations are important, especially in the case of slag, which is expected to have considerable variation in their dissolved metal content.

EMPA quantitative results will be analyzed statistically to establish mean values. They may also be depicted as histograms to show the range of metal concentrations measured as well as the presence of one or more populations in terms of metal content. In the later case, non-parametric statistics may have to be used or the median value has to be established.

## **Associations**

The association of the metal-bearing forms will be established from the backscattered electron images. Particular attention will be paid in establishing whether the grains are totally enclosed, encapsulated or liberated. The rinds of metal-bearing grains will be identified. Representative photomicrographs of backscatter electron images establishing the association of the principal metal-bearing forms will be obtained for illustration purposes.

## **2Compound Identification**

As outlined in the EMPA SOP, an electron microprobe with combined EDS (energy dispersive spectrometer) and multiple WDS (wavelength dispersive spectrometers) are used to identify all metal-bearing phases of interest. A 1-2 gram split of dried sample is placed in a 2.5 cm plastic mold and impregnated with epoxy. Once the sample is hardened it is polished and carbon coated for EMPA. The EMPA is operated at 15 kV accelerating voltage, with a 20 NanoAmp current and a 1 micron focused beam. Elements of interest are standardized using certified mineral or pure metal standards and counting times are chosen to provide 3-sigma detection limits of between 100-200 ppm. Elemental concentrations are corrected using ZAF factors and concentration errors are generally less than 5% relative. For a more detail explanation of the EMPA method of analyses see Birks, 1971, or Heinrich, 1981.

Although the electron microprobe is capable of determining stoichiometries of virtually any compound composed of elements Be thru U, such a task requires a great deal of standardization and analytical time to complete. It has been determined that for the purposes these data are utilized in either risk assessments or site characterizations the term "speciation" would have a more general definition. The primary justification for this factor is that it has been shown the time required for more precise phase identification greatly impacted on the total identified-particle population. The significance to the data interpretation is highly dependent on the total number of metal-bearing phases counted. Not only would the time impact the statistical significance of sample interpretation, but it would limit the total number of samples one could study, thus the representativeness of the data to the site.

A number of phases for both lead and arsenic are considered stoichiometric. These include the following:

- Galena (PbS)
- Lead Oxide (PbO)
- Native Lead (Pb)
- Cerussite (PbCO<sub>3</sub>)

Anglesite ( $\text{PbSO}_4$ )  
Crocoite ( $\text{PbCrO}_4$ )  
Alamosite ( $\text{PbSiO}_3$ )  
Lead Arsenate ( $\text{PbAsO}$ )  
Arsenolite ( $\text{As}_2\text{O}_3$ )  
Realgar ( $\text{AsS}$ )  
Orpiment ( $\text{As}_2\text{S}_3$ )  
Arsenopyrite ( $\text{AsFeS}$ )

The author is aware that these are not all strictly stoichiometric phases. As an example, “lead oxide” would include; litharge ( $\text{PbO}$ ), massicot ( $\text{PbO}$ ), minium ( $\text{Pb}_3\text{O}_4$ ), plattnerite ( $\text{PbO}_2$ ), and scrutinyite ( $\alpha\text{PbO}_2$ ). In addition, phases such as lead hydroxide, lead isobuyrate, lead lactate, lead laurate, lead malate, lead oxalate and even lead nitrate would be grouped in this category. The phase “lead arsenate” would include; schultenite ( $\text{PbHAsO}_4$ ), paulmooreite ( $\text{Pb}_2\text{As}_2\text{O}_5$ ) as well as all the meta/ortho arsenate/arsenite phases. With very careful EMPA analyses most of these phases could be isolated; however, as the data is currently used this effort is not taken unless the client request further work.

The remaining phases that are commonly identified are far more generic. The concentration of the metal(s) of interest in these phases are thus variable and require site-specific estimates of their concentration values. These are obtained for each project by randomly collecting EMPA quantitative analyses (for lead or arsenic) for these phases and calculating average values. For these phases the first criteria used in identification is to determine if the phase is either; an oxide, carbonate, sulfide, sulfate, or phosphate. Secondly, with the exception of the “phosphates”, the major cation associated with the phase is further identified. Therefore, phases such as Fe-sulfate,  $\text{FeOOH}$ ,  $\text{MnOOH}$ ,  $\text{PbMO}$ ,  $\text{AsMO}$ , or  $\text{PbMSO}_4$  are identified. Some of these phases could represent a stoichiometric mineral forms such as allactite  $\text{Mn}_7(\text{AsO}_4)_2(\text{OH})_8$ , plumbojarosite  $\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$ , plumboferrite  $\text{PbFe}_4\text{O}_7$ , carminite  $\text{PbFe}_2[\text{OHAsO}_4]_2$ , nelenite  $(\text{Mn,Fe})_{16}\text{Si}_{12}\text{As}_3\text{O}_{36}(\text{OH})_{17}$ , or quenselite  $\text{PbMnO}_2(\text{OH})$ ; however, it is the authors belief that most of these phases are metastable and/or amorphous and have some quantity of arsenic and/or lead sorbed to their surface.

The “phosphate” group is even more generic in that the only common dominant ion is  $\text{PO}_4$ . There are many crystalline forms of phosphate that contain lead such as; pyromorphite  $\text{Pb}_5[\text{Cl}(\text{PO}_4)_3]$ , plumbogummite  $\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5\text{-H}_2\text{O}$ , orpheite  $\text{PbAl}_3[(\text{OH})_6(\text{PO}_4, \text{SO}_4)_2]$ , drugmanite  $\text{Pb}_2(\text{Fe,Al})(\text{PO}_4)_2\text{OH-H}_2\text{O}$ , and corkite  $\text{PbFe}_3[(\text{OH})_6 \text{SO}_4 \text{PO}_4]$ . Although arsenic and phosphorus are considered competitive, a number of arsenic-bearing phosphates have been identified; walentaite  $(\text{Ca, Mn, Fe})\text{Fe}_3(\text{AsO}_4, \text{PO}_4)_4\text{-7H}_2\text{O}$ , morelandite  $(\text{Ba, Ca, Pb})_5 \text{Cl}[\text{AsO}_4, \text{PO}_4]_3$ , and turneaureite  $\text{Ca}_5(\text{Cl})[(\text{AsO}_4, \text{PO}_4)_3]$ . As with previous phases, careful EMPA analyses could isolated the complete stoichiometry; however, as the data is currently used this effort is not taken unless the client request further work.

Since the chemistry and/or sorption capacity of these categories are quite variable one should be careful in ascribing RBA (relative bioaccessability) to these metal forms. In particular, if sorption is the primary factor controlling the presence of arsenic or lead, factors such as temperature, redox, and pH can influence the metal stability significantly. However, if particle size and morphology (liberated-included) are similar, it appears, primarily from in vitro studies, that iron oxides and sulfates tend to be less bioaccessible than manganese oxides and phosphates.

## **10.5 Instrument Calibration and Standardization**

The WDS will have spectrometers calibrated for the metal of concern, carbon, oxygen and sulfur on the appropriate crystals using mineral standards. The EDS will have multi-channel analyzer (MCA) calibrated for known peak energy centroids. Calibration will be performed so as to have both low (1.0-3.0 KeV) and high (6.0-9.0 KeV) energy peaks fall within 0.05 KeV of its known centroid.

The magnification marker on the instrument will be checked once a week. This will be performed by following manufacturer instructions or by measurement of commercially available grids or leucite spheres. Size measurements must be within 4 microns of certified values.

Initial calibration verification standards (ICVs) must be analyzed at the beginning of each analytical batch or once every 48 hours, whichever is more frequent. A set of mineral or glass standards will be run quantitatively for the metal of concern, sulfur, oxygen and carbon. If elemental quantities of the ICVs do not fall within +/- 5% of certified values for each element, the instrument must be recalibrated prior to analysis of investigative samples.

The metal-bearing forms in these samples will be identified using a combination of EDS, WDS and BEI. Once a particle is isolated with the backscatter detector, a 5-second EDS spectra is collected and peaks identified. The count rates for the metal(s) of concern, sulfur, carbon and oxygen can be either visually observed on the wavelength spectrometers or K-ratios calculated.

## **10.6 Documentation**

Photomicrographs must be taken for each sample, at a rate of 5% (1 photograph per 20 particles counted), for a maximum of 10 per sample and submitted with the results . Particles selected for photography must be recorded on the EMPA graph. A 128x128 (minimum) binary image in “.tif” format may be stored. Recorded on each photomicrograph and negative will be a scale bar, magnification, sample identification , date and phase identification. Abbreviations for the identified phases can be used. Examples are listed in Table 10-2. A final list must be submitted with the laboratory report.

## **10.0 PERSONAL HEALTH AND SAFETY**

Each individual operating the electron microprobe instruments will have read the “Radiation Safety Handbook” prepared by the University and follow all State guidelines for operation of X-ray equipment.

Latex gloves and particulate masks will be worn during preparation of sample cups. All material that comes in contact with the samples or used to clean work surface areas will be placed in poly-bags for disposal.

## **11.0 FINAL REPORT**

A final laboratory report will be provided to the Contractor. The report will include all EMPA data including summary tables and figures. Individual sample data will be provided on disk.

Speciation results will include: 1) a series of tables summarizing frequency of occurrence for each metal phase identified along with a confidence limit; (Figure 11.0A) 2) summary histograms of metal phases identified for each waste type; (Figure 11.0B) 3) a summary histogram of particle size distribution in each waste type; (Figure 11.0C) and 4) a summary of metal phase associations (Figure 11.0D) . Representative photomicrographs or .tif images will also be included in the final report (Figure 11.0E).

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WESTON (Roy F. Weston, Inc.). 1995. *Metal Speciation Interpretive Report, Leadville, CO. CERCLA Site*. March, 1995.

Table 2-1  
Common Metal-Bearing Forms Found Within Mining, Smelting, Agricultural, Industrial  
and Residential Media

OXIDES

Lead Oxide  
Manganese (metal) oxide  
Iron (metal) oxide  
Lead molybdenum oxide  
Arsenic (metal) Oxide  
Lead (metal) Oxides  
Cadmium Oxide  
Copper Oxides  
Zinc Oxide  
Lead Arsenate  
Arsenic Trioxide  
Calcium (metal) oxide

SILICATES

Slag  
Lead silicate  
Arsenic silicate  
Zinc silicate  
Clays

SULFATES

Iron (metal) sulfate  
Lead sulfate  
Lead barite  
Zinc Sulfate  
Arsenic sulfate  
Copper sulfate

CARBONATES

Lead Carbonate  
Zinc Carbonate

PHOSPHATES

(metal) phosphates

SULFIDES

Lead sulfide  
Sulfur-containing salts  
Iron-arsenic sulfide  
Zinc sulfide  
Copper sulfides  
Copper-iron sulfide  
Cadmium Sulfide

OTHER

Native: Lead, Copper,  
Cadmium, Mercury, Indium,  
Thallium, Selenium  
Lead/Arsenic/Cadmium/Mercury  
Chlorides  
Paint  
Solder  
Organic lead  
Lead vanadate  
Minor telluride, and bismuth-lead  
phases

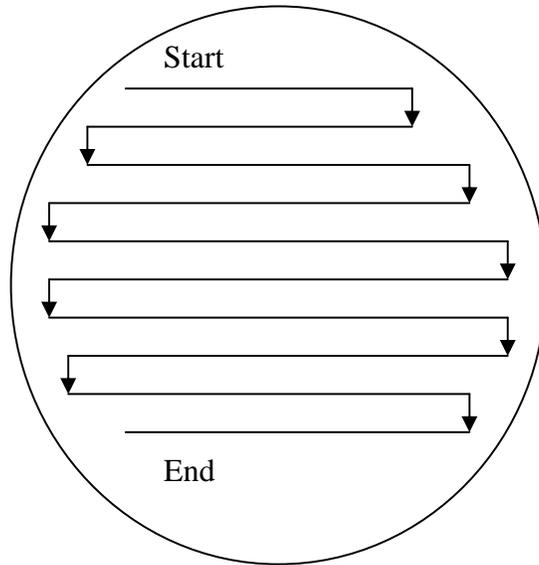


Figure 10-2

Form	Association	Size (microns)										
Cer	Liberated	5	Form	Number	Mean	Std-Dev	Range low	Range high				
Ga	Liberated	3	total	287	35.09	131.89	1	1400				
Ang	Liberated	12	Cerussite	3	18	11.79	5	28				
Ang	Liberated	13	Galena	144	9.83	9.99	1	50				
Sulf	Liberated	35	Anglesite	111	66.7	205.29	1	1400				
Ang	Liberated	9	FeSO4	6	39.33	28.23	8	90				
Ga	Cemented	5	MnOOH	8	24.13	25.86	8	85				
Ga	Cemented	5	FeOOH	11	60.27	101.4	4	350				
Ga	Cemented	5	PbBiO	3	32.67	19.4	20	55				
Ang	Liberated	21	Clay	1	8	ND	8	8				
Ang	Liberated	7										
Ang	Liberated	36	Form	(linear) freq	Bio freq	rm pb	Biorm pb					error-95%
Ang	Liberated	110	%	%	%	%	%					
Ga	Inclusion	32	Cerussite	0.54	1.32	0.65	1.73					0.84
Mn	Cemented	25	Galena	14.06	12.88	21.74	21.39					4.02
Mn	Cemented	30	Anglesite	73.51	65	75.41	71.62					5.11
Mn	Rimming	15	FeSO4	2.34	5.79	0.1	0.27					1.75
Mn	Rimming	10	MnOOH	1.92	4.73	0.8	2.14					1.59
Mn	Rimming	10	FeOOH	6.58	7.68	0.61	1.04					2.87
Mn	Rimming	10	PbBiO	0.97	2.4	0.67	1.79					1.14
Ga	Inclusion	12	Clay	0.08	0.2	0.01	0.02					0.33

Figure 10-3B

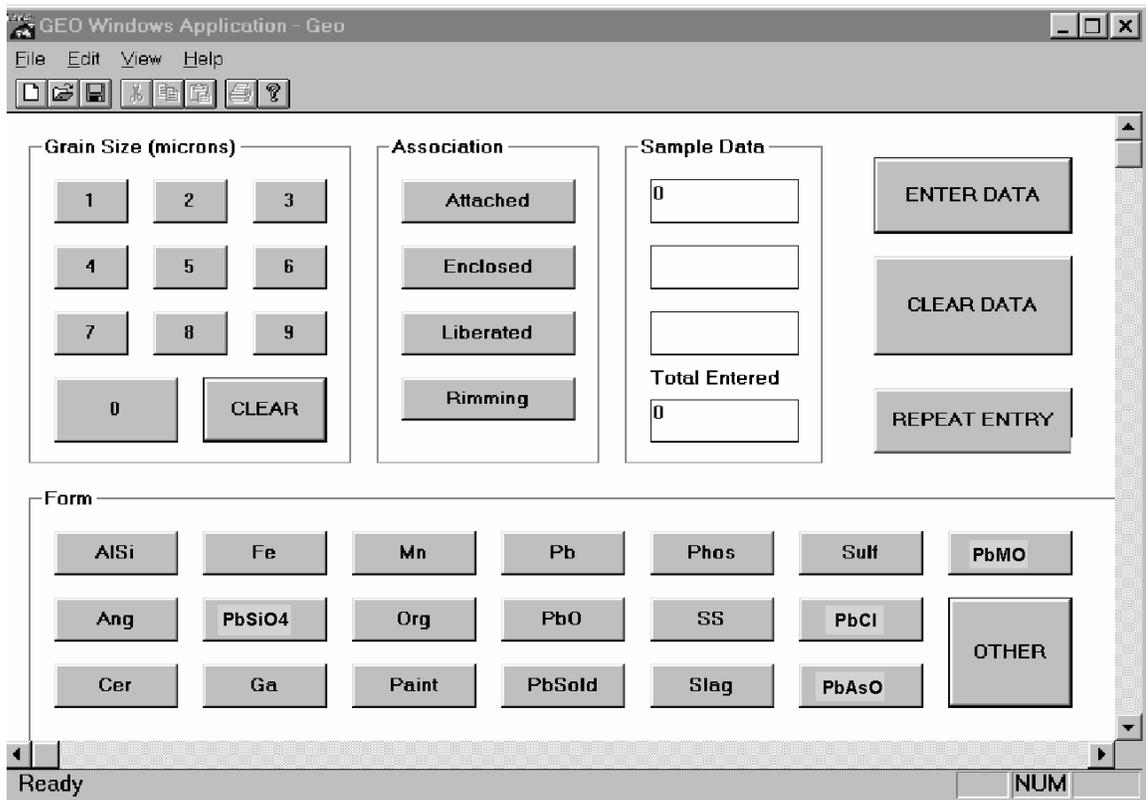


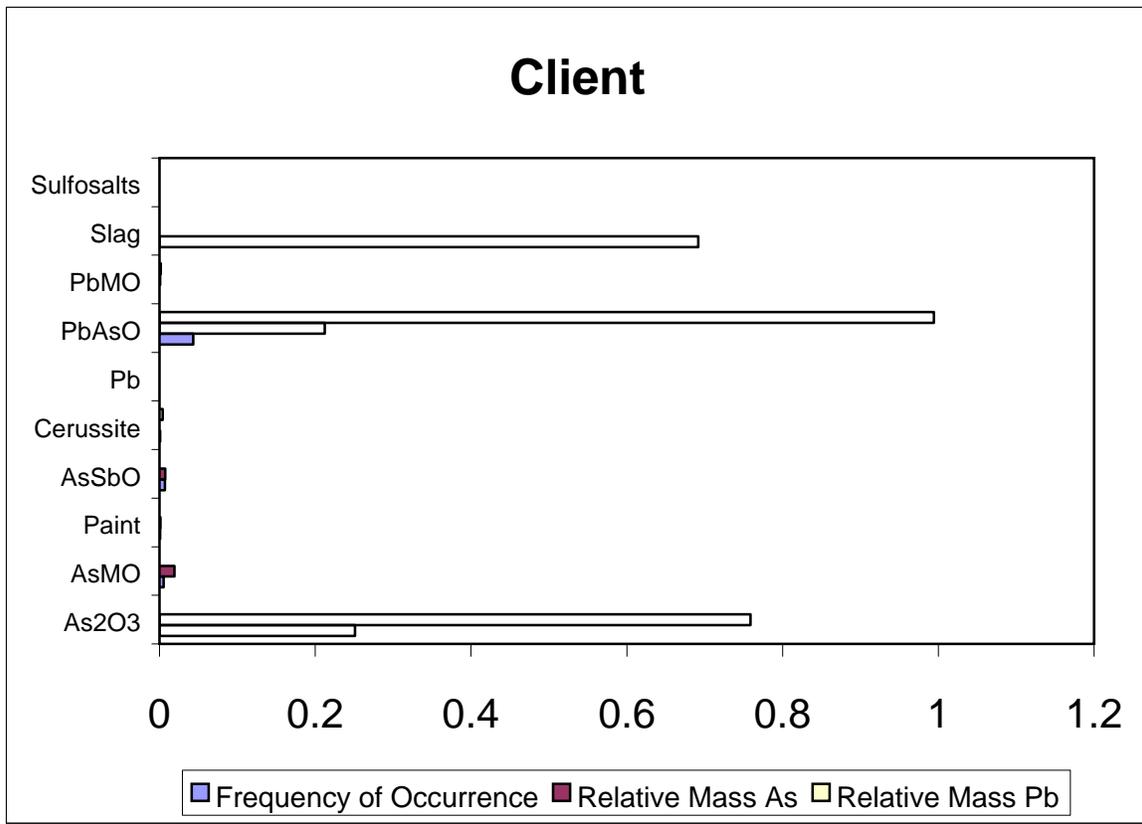
Figure 10-3A

Table 10-1  
EMPA Standard Operating Conditions

	WDS	EDS
Accelerating Voltage	15 KV	15-20 KV
Beam Size	1-2 microns	1-2 microns
Cup Current	10-30 NanoAmps	10-30 NanoAmps
Ev/Channel	NA	10 or 20
Stage Tilt	NA	Fixed
Working Distance	NA	Fixed
MCA time Constant	NA	7.5-12 microseconds
X-ray lines	S K-alpha PET O K-alpha LDE1 C K-alpha LDEC Zn K-alpha PET As L-alpha TAP Cu K-alpha LIF Cd L-alpha PET Pb M-alpha PET Pb L-alpha LIF In L-alpha PET Tl L-alpha LIF Hg L-alpha LIF Se L-alpha LIF Sb L-alpha PET	S K-alpha 2.31 KeV O K-alpha 0.52 KeV C K-alpha 0.28 KeV Pb M-alpha 2.34 KeV Pb L-alpha 10.5 KeV Zn K-alpha 8.63 KeV Cu K-alpha 8.04 KeV As K-alpha 10.5 KeV As L-alpha 1.28 KeV Cd L-alpha 3.13 KeV In L-alpha 3.28 KeV Tl M-alpha 2.27 KeV Tl L-alpha 10.26 KeV Hg L-alpha 9.98 KeV Hg M-alpha 2.19 KeV Se L-alpha 1.37 KeV Sb L-alpha 3.60 KeV

Table 10-2  
Suggested Abbreviation for Photomicrographs

Metal-bearing Phase	Abbreviation
In	In
Tl	Tl
Hg	Hg
Se	Se
Sb	Sb
Lead Sulfide	Ga
Lead Sulfate	Ang
Lead Carbonate	Cer
Mn-(M) Oxide	Mn(M)
Fe-(M) Oxide	Fe(M)
(M)Phosphate	(M)Phos
Fe-(M) Sulfate	Fe(M)Sul
Metal Oxide	(M)O
Pb-Mo Oxide	Wulf
Slag	Slag
Metallic Phase	(M)
Metal Silicate	(M)Si
Solder	Sold
Paint	Pnt
Metal-bearing Organic	(M)(Org)
(M) barite	(M)Bar
Pb arsenate	PbAsO
Pb vanadate	PbVan
As-Sb Oxide	AsSbO
Chalcopyrite	Cp
Sphalerite	Sph
Arsenopyrite	Apy



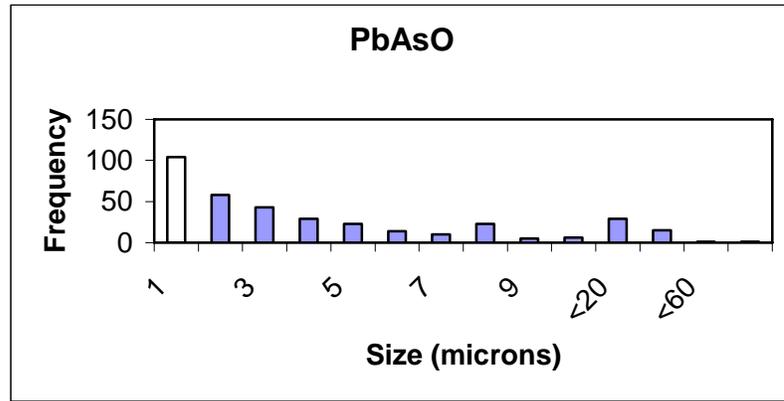
**Figure 11-0B**

Table 1  
Metal Speciation Frequency of Occurrence and Error Summary.

	Sample 1	+/-	Sample 2	+/-	Sample 3	+/-
Brass	4%	1-21				
Cerussite	8%	2-26	23%	17-30	9%	4-15
Fe-Pb Oxide	41%	23-61	64%	57-71	54%	42-61
PbMO*	5%	2-22	1%	Tr-4	Tr	
Pb Phosphate	33%	16-53	7%	4-12	24%	17-33
Fe-Pb Sulfate	10%	2-28			9%	4-16
CuAlSO4			1%	Tr-4	2%	Tr-6
Galena			3%	1-6		
Pb Vanadate			Tr		Tr	
Clays					Tr	
Particles Counted		22		173		104

\* M represents the occurrence of small quantities of Sb and Sn.

**Figure 11-10A**



**Figure 11-0C**

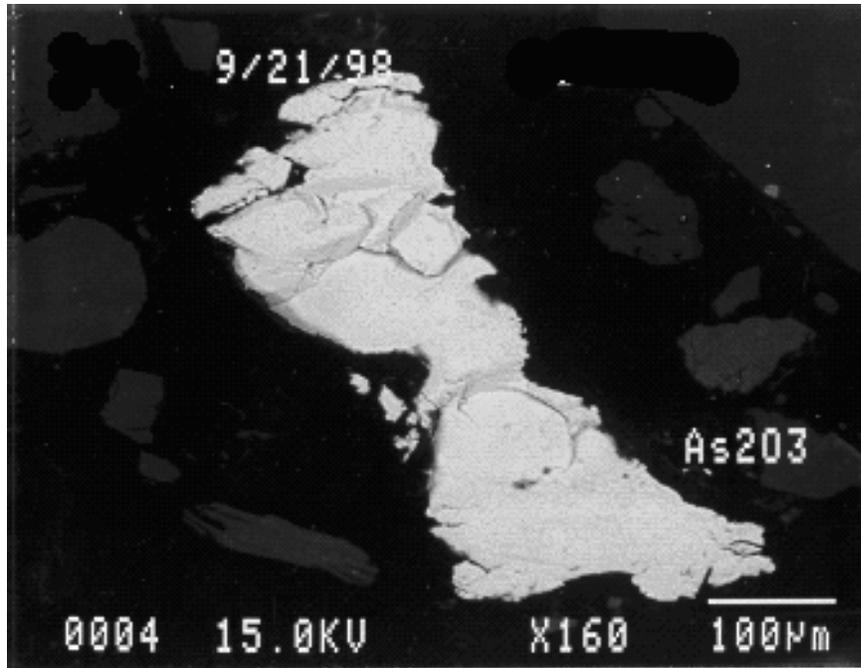


Figure 11-0E

**Appendix C**  
**Relative Bioavailability Leaching Procedure**

# Relative Bioavailability Leaching Procedure (RBLP)

## Standard Operating Procedure

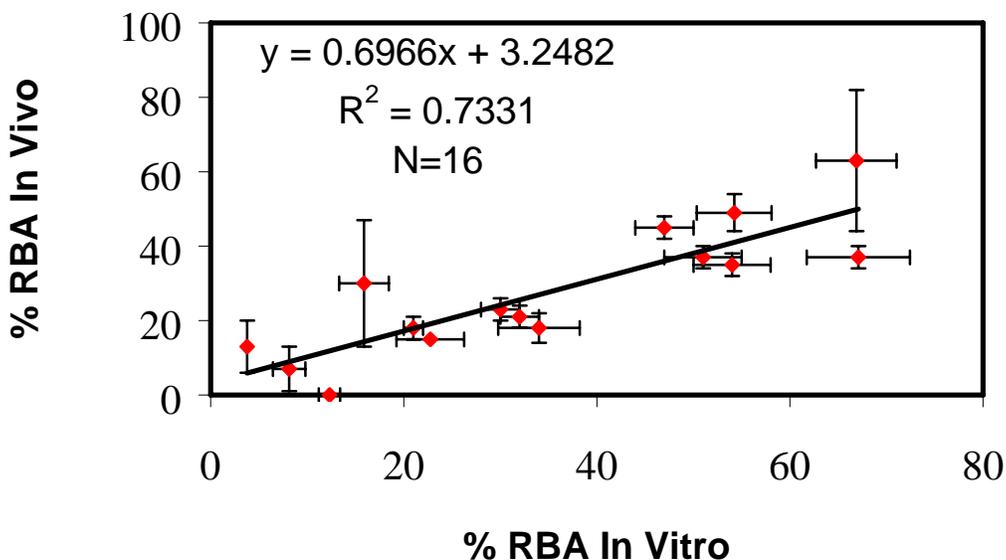
### 1.0 Purpose

An increasingly important property of contaminated media found at environmental sites is the bioavailability of individual contaminants. Bioavailability is the fraction of a contaminant that is absorbed by an organism via a specific exposure route. Many animal studies have been conducted to experimentally determine oral bioavailability of individual metals, particularly lead and arsenic. During the period 1989-97, a juvenile swine model developed by USEPA Region VIII was used to predict the relative bioavailability of lead and arsenic in approximately 20 substrates (Weis and LaVelle 1991; Weis et al. 1994). The bioavailability determined was relative to that of a soluble salt (i.e. lead acetate trihydrate or sodium arsenate). The tested media had a wide range of mineralogy, and produced a range of lead and arsenic bioavailability values. In addition to the swine studies, other animal models (e.g. rats and monkeys) have been used for measuring the bioavailability of lead and arsenic from soils.

Several researchers have developed in vitro tests to measure the fraction of a chemical solubilized from a soil sample under simulated gastrointestinal conditions. The in vitro tests consist of an aqueous fluid, into which the contaminant is introduced. The solution then solubilizes the media under simulated gastric conditions. Once this procedure is complete, the solution is analyzed for lead and/or arsenic concentrations. The mass of the lead and/or arsenic found in the filtered extract is compared to the mass introduced into the test. The fraction liberated into the aqueous phase is defined as the bioavailable fraction of lead or arsenic in that media. To date, for lead-bearing materials tested in the USEPA swine studies, this in vitro assay has correlated well ( $R^2 = 0.93$ ,  $p = .0001$ ) with relative bioavailability. Arsenic has yet to be fully validated but shows a promising correlation with in vivo results.

It has been postulated that a simplified in vitro method could be used to determine

## ARSENIC



bioavailability of lead and arsenic. The method described in this SOP represents a simplified in vitro method, which is currently being subjected to a formal validation.

### 2.0 Scope

This procedure has been developed to test contaminated media in animal studies, to determine the correlation between in vitro and in vivo. Only samples from which mineralogy has been fully characterized by EMPA techniques and for which bioavailability results from acceptable animal studies are available have been used for this study. A total of 20 substrates have been tested in validating the relative bioavailability leaching procedure (RBLP).

### 3.0 Relevant Literature

Background on the development and validation of in vitro test systems for estimating lead and arsenic bioaccessibility can be found in; Ruby et al. (1993, 1996); Medlin (1972); Medlin and Drexler, 1997; Drexler, 1998; and Drexler et al., 2003.

Background information for the USEPA swine studies may be found in (Weis and LaVelle, 1991; Weis et al. 1994; and Casteel et al., 1997) and in the USEPA Region VIII Center in Denver, Colorado.

#### **4.0 Sample Preparation**

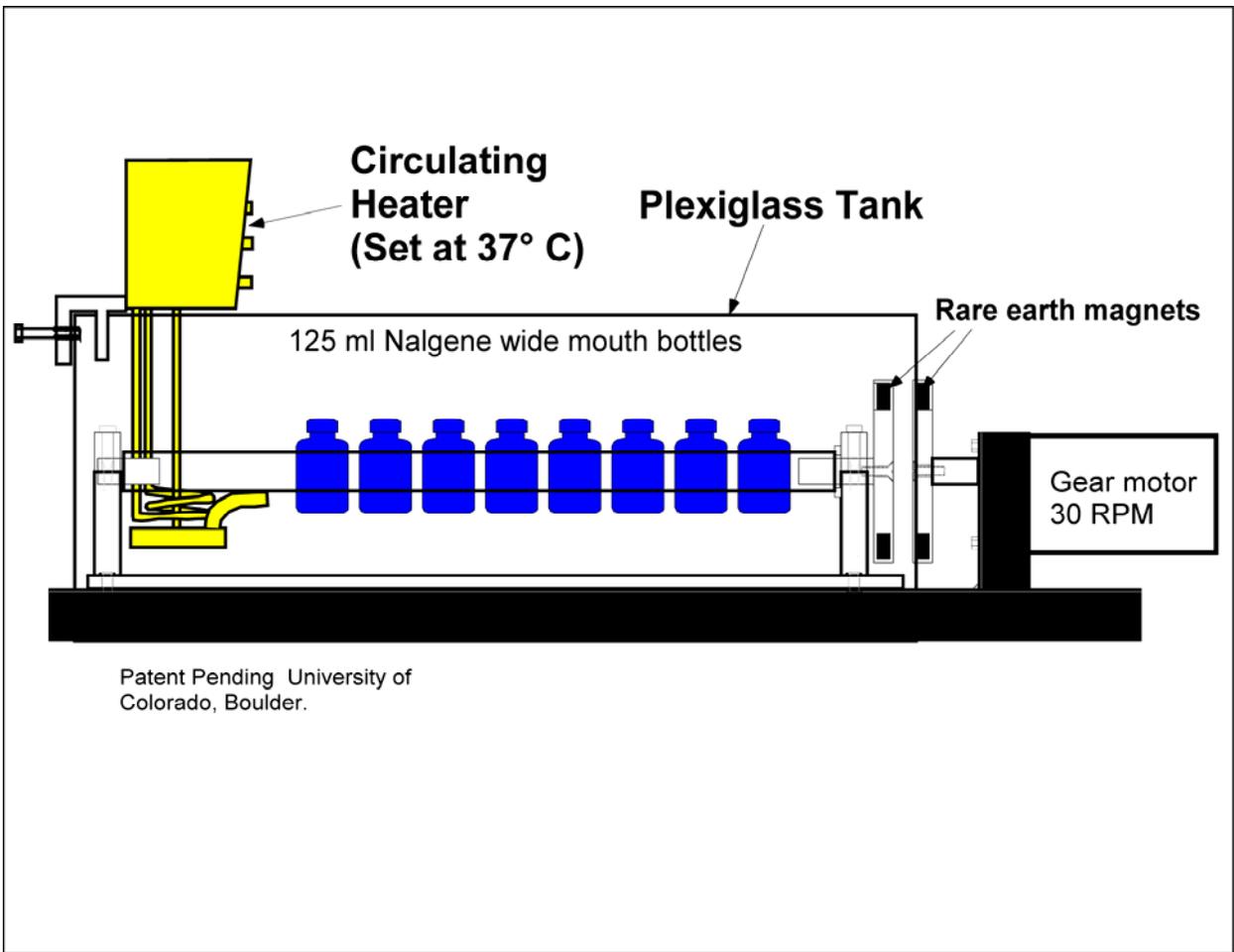
All media are prepared for the in vitro assay by first drying (<40 °C) all samples and then sieving to < 250 m. The <250 micron size fraction was used because this is the particle size is representative of that which adheres to children's hands. Samples were thoroughly mixed prior to use to ensure homogenization. Samples are archived after the study completion and retained for further analysis for a period of six months unless otherwise requested. Prior to obtaining a subsample for testing in this procedure, each sample must be homogenized in its sample container by end-over-end mixing.

#### **5.0 Apparatus and Materials**

##### **5.1 Equipment**

The main piece of equipment required for this procedure is the extraction device illustrated in Figure 1. The device can be purchased from the Department of Geological Sciences, University of Colorado. For further information contact Dr. John W. Drexler, at (303) 492-5251 or [drexlerj@spot.colorado.edu](mailto:drexlerj@spot.colorado.edu). The device holds ten 125 ml, wide-mouth high-density polyethylene (HDPE) bottles. These are rotated within a Plexiglas tank by a TCLP extractor motor with a modified flywheel. The water bath must be filled such that the extraction bottles remained immersed. Temperature in the water bath is maintained at 37 +/- 2 °C using an immersion circulator heater (Fisher Scientific Model 730).

The 125-ml HDPE bottles must have an airtight screw-cap seal (Fisher Scientific #02-893-5C), and care must be taken to ensure that the bottles do not leak during the extraction procedure.



## 5.2 Standards and Reagents

The leaching procedure for this method uses an aqueous extraction fluid at a pH value of 1.5. The pH 1.5 fluid is prepared as follows:

Prepare 2 L of aqueous extraction fluid using ASTM Type II demonized (DI) water. The buffer is made up in the following manner. To 1.9 L of DI water, add 60.06 g glycine (free base, reagent grade), and bring the solution volume to 2 L (0.4M glycine). Place the mixture in the water bath at 37 °C until the extraction fluid reaches 37 °C. Standardize the pH meter ( one should use both a 2.0 and a 4.0 pH buffer for standardization) using temperature compensation at 37 °C or buffers maintained at 37 °C in the water bath. Add trace metal grade, concentrated hydrochloric acid (12.1N) until the solution pH reaches a value of 1.50 +/- 0.05 (approximately 60 mL).

All reagents must be free of lead and arsenic, and the final fluid must be tested to confirm that lead and arsenic concentrations are less than one-fourth the project required detection limits (PRDLs) of 100 and 20 µg/L, respectively (e.g., less than 25 µg/L lead and 5µg/L arsenic in the final fluid).

Cleanliness of all materials used to prepare and/or store the extraction fluid and buffer is essential. All glassware and equipment used to prepare standards and reagents must be properly cleaned, acid washed, and finally, triple-rinsed with demonized water prior to use.

## 6.0 Leaching Procedure

Measure 100 +/- 0.5 mL of the extraction fluid, using a graduated cylinder, and transfer to a 125 mL wide-mouth HPDE bottle. Add 1.00 +/- 0.5 g of test substrate (<250 m) to the bottle, ensuring that static electricity does not cause soil particles to adhere to the lip or outside threads of the bottle. If necessary, use an antistatic brush to eliminate static electricity prior to adding the media. Record the mass of substrate added to the bottle. Hand-tighten each bottle top and shake/invert to ensure that no leakage occurs, and that no media is caked on the bottom of the bottle.

Place the bottle into the modified TCLP extractor, making sure each bottle is secure and the lid(s) are tightly fastened. Fill the extractor with 125 mL bottles containing test materials or QA samples.

The temperature of the water bath must be 37 +/- 2 °C.

Turn on the extractor and rotate end-over-end at 30 +/- 2 rpm for 1 hour. Record the start time of rotation.

When extraction (rotation) is complete, immediately stop the extractor rotation and remove the bottles. Wipe them dry and place upright on the bench top.

Draw extract directly from the reaction vessel into a disposable 20 cc syringe with a Luer-Lok attachment. Attach a 0.45 µm cellulose acetate disk filter (25 mm diameter) to the syringe, and filter the extract into a clean 15 mL polypropylene centrifuge tube (labeled with sample ID) or other appropriate sample vial for analysis.

Record the time that the extract is filtered (i.e. extraction is stopped). If the total time elapsed is greater than 1 hour 30 minutes, the test must be repeated.

Measure the pH of the remaining fluid in the extraction bottle. If the fluid pH is not within  $\pm 0.5$  pH units of the starting pH, the test must be discarded and the sample reanalyzed as follows:

If the pH has changed more than 0.5 units, the test will be re-run in an identical fashion. If the second test also results in a decrease in pH of greater than 0.5 s.u. this will be recorded, and the extract filtered for analysis. If the pH has increased by 0.5 s.u. or more, the test must be repeated, but the extractor must be stopped at specific intervals and the pH manually adjusted down to pH of 1.5 with dropwise addition of HCl (adjustments at 5, 10, 15, and 30 minutes into the extraction, and upon final removal from the water bath { 60 min}). Samples with rising pH values might better be run following the method of Medlin, 1997.

Store filtered samples in a refrigerator at 4 °C until they are analyzed. Analysis for lead and arsenic concentrations must occur within 1 week of extraction for each sample.

Extracts are to be analyzed for lead and arsenic, as specified in SOP #2, following EPA methods 6010B, 6020, or 7061A.

### **6.1 Quality Control/Quality Assurance**

Quality Assurance for the extraction procedure will consist of the following quality control samples.

Reagent Blank-extraction fluid analyzed once per batch.

Bottle Blank-extraction fluid only run through the complete procedure at a frequency of 1 in 20 samples.

Duplicate sample-duplicate sample extractions to be performed on 1 in 10 samples.

Matrix Spike-a subsample of each material used will be spiked at concentrations of 10 mg/L lead and 1 mg/L arsenic and run through the extraction procedure (frequency of 1 in 10 samples).

National Institute of Standards and Testing (NIST) Standard Reference Material (SRM) 2711 will be used as a control soil. The SRM will be analyzed at a frequency of 1 in 25 samples.

Control limits and corrective actions are listed in Table 1.

	<b>Analysis Frequency</b>	<b>Control Limits</b>
Reagent Blank	once per batch	< 25 $\Phi$ g/L lead
<b>Bottle blank</b>	5%	<50 $\Phi$ g/L lead
<b>Blank spike*</b>	5%	85-115% recovery
<b>Matrix spike*</b>	10%	75-125% recovery
<b>Duplicate sample</b>	10%	+/- 20% RPD**
<b>Control soil***</b>	5%	+/- 10% RPD

\* Spikes contained 10 mg/L lead. \*\* RPD= relative percent difference. \*\*\*

The National Institute of Standards and Technology (NIST) Standard Reference Material (SRM)

## 7.0 Chain-of-Custody Procedures

All media once received by the Laboratory must be maintained under standard chain-of-custody.

## 8.0 Data Handling and Verification

All sample and fluid preparation calculations and operations must be recorded on data sheets, Figure 3. Finally all key data will be entered into the attached EXCEL spreadsheet for final delivery and calculation of Bioavailability.

## 9.0 References

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**Appendix D**  
**Mineralogy by X-Ray diffraction**

## Appendix D

### Mineralogy by X-Ray Diffraction

X-ray diffraction (XRD) has long been regarded as a definitive tool for identifying minerals in geological materials, especially those containing significant proportions of clay minerals (Ref. 18). XRD analysis of clay-bearing substances may be based on the evaluation of a bulk sample of the whole material mounted in randomly oriented powder form. Analyses of clay-fractions themselves, however, may use oriented aggregate samples of the clay fraction subjected to XRD after saturation with ethylene glycol to isolate expandable clay minerals and after heating to collapse any expandable lattice structures. The samples were prepared following standard procedures (Refs. 16 and 13). Splits of the bulk sample were used for characterization of the whole rock mineralogy. Approximately 5 g of each soil sample was ground with a "shatter-box" crusher to obtain a homogenous powder with particle sizes  $<40\mu\text{m}$ .

Clay mineral analyses were based on the standard method (Ref. 16). A split of the powdered soil was mixed with de-ionized water (pH 7-8) and agitated. The carbonate fraction was removed with the addition of HCl (0.5 N) at  $< 80^{\circ}\text{C}$  temperature for 30 minutes or more until all the carbonate was dissolved. Ultrasonic desegregation is accomplished during 3 minute intervals. The insoluble residue was washed and centrifuged (5-6 times) until a neutral suspension was obtained (pH 7-8). Separation of the clay-size fractions were obtained by the timed settling method based on Stokes law. The selected fraction was then dispersed onto glass slides and air-dried at room temperature. XRD analysis of oriented clay samples were made after air-drying at room temperature, treating with ethylene-glycol, and heat treated steps.

All samples were analyzed on a Scintag PAD V X-ray diffractometer. Scanned from  $3^{\circ}$  to  $65^{\circ}2\theta$  at the following parameters: radiation =  $\text{CuK}\alpha$ ; scan rate =  $2^{\circ}/\text{min}$ ; step size = 0.02; voltage = 40 kV; current = 30 mA; and slits = 0.2 mm. To correct for misalignments of the goniometer a diffractogram of quartz (100) reflection at  $4.26 \text{ \AA}$  was obtained. The methods described by Refs. 12,14,15,16, and 19 were used. The bulk XRD analyses of all three soils are dominated (Figures 2.2-2.4) by quartz ( $\text{SiO}_2$ ), plagioclase ( $\text{Na,CaAlSi}_3\text{O}_8$ ), and microcline ( $\text{KAlSi}_3\text{O}_8$ ). Soil B (93206) additionally contained a significant amount of hematite ( $\text{Fe}_2\text{O}_3$ ). The further analyses of their clay fraction (Figures 2.5-2.6) require greater interpretation, however, it appears all three soils are dominated by the presence of the minerals illite, kaolinite, and smectite as described below.

### ***Illite***

Illite is distinguished by the peak series; 10Å, 5Å, and 3.33Å. It is unaffected by glycolation and heat treatment to (550°C). It is perhaps the easiest to identify. The only possible misidentification is with palygorsite at 10.4Å and hydrated halloysite at 10Å but these minerals lack the characteristic illite peaks at 5Å, and 3.33Å.

### ***Kaolinite***

Kaolinite is a large class of clay minerals that range from the very ordered (narrow and intense diffraction peaks) to the very disordered (weak and broad diffraction peaks). The characteristic lines of kaolinite are 7.1Å and 3.57Å. These are possibly confused with chlorite (14Å, 7Å and 3.53Å), but the loss of the 7Å peak at 550°C rules out chlorite. Kaolinite survives heat treatment to 350°C, but not to 550°C. Kaolinite is unaffected by glycolation.

### ***Smectite***

Smectite is a diverse group. Members of the smectite group include the dioctahedral minerals montmorillonite, beidellite, and nontronite, and the trioctahedral minerals hectorite (Li-rich), saponite (Mg-rich), and sauconite (Zn-rich). In air-dried samples it has a peak in the range 12Å to 15Å which on glycolation it expands uniformly to 17.2Å (the peak usually sharpens and increases in intensity with glycolation - also an often observed 002 peak occurs at 8.5Å— there is no 002 peak in the air-dried oriented samples). Confirmation was obtained by heating to 300°C - the first diffraction peak collapses to an illite-like 10Å peak.