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Phosphate Stabilization of Heavy Metals Contaminated Mine Waste Yard Soils, Joplin, Missouri NPL Site

By

Jay Cornish, Project Manager
MSE Technology Applications, Inc.
Mike Mansfield Advanced Technology Center
Butte, Montana 59702

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Norma Lewis, EPA Project Manager
Sustainable Technology Division
National Risk Management Research Laboratory
Cincinnati, Ohio 45268

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Notice

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Lawrence W. Reiter, Acting Director
National Risk Management Research Laboratory

Abstract

This document summarizes the results of Mine Waste Technology Project 22—Phosphate Stabilization of Heavy Metals-Contaminated Mine Waste Yard Soils. Mining, milling, and smelting of ores near Joplin, Missouri, have resulted in heavy metal contamination of the area. The Joplin site was listed on the Superfund National Priorities List in August 1990. High blood levels in young children in the area have prompted efforts to reduce soil-based lead (Pb) (and cadmium) health threats.

Previous investigations indicate that Pb bioavailability can be reduced via addition of 1% by weight phosphoric acid (PA) plus 0.05% potassium chloride. The purpose of this study was to determine if the treatment would be effective in mine waste-affected soils. Bioavailability of Pb is determined by measuring Pb levels in various tissues from young pigs following ingestion of a known quantity of Pb in treated and untreated soil or lead acetate. The data collected for the in vivo study were not sufficient to conclude (at the 95% confidence level) that PA-treatment had any particular effect on Pb bioavailability.

The results of a parallel in vitro study were more encouraging. The extractable Pb was consistently lower in PA-treated soils compared to untreated soils.

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Acronyms and Abbreviations

ABA	absolute bioavailability
As	arsenic
AUC	area under the curve
BAF	bioaccessible fraction
Ca	calcium
Cd	cadmium
CF	concentration factor
CoC	contaminants of concern
DTPA-AB	diphenylamine triamine pentaacetic acid-ammonium bicarbonate
EPA	U.S. Environmental Protection Agency
EPA/NERL	EPA=s National Exposure Research Laboratory (Las Vegas)
Fe	iron
H_3PO_4	phosphoric acid
ha	hectare
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
IEUBK	Integrated Exposure Uptake Biokinetic Model for Lead in Children
KC1	potassium chloride
kg	kilogram
km	kilometer
LSB	leaf and stalk biomass
m	meter
MDNR	Missouri Department of Natural Resources
mg	milligram
mg/kg	milligrams per kilogram
MSE	MSE Technology Applications, Inc.
MWTP	Mine Waste Technology Program
NPL	National Priorities List
O&M	operating and maintenance
OU	operable unit
P	phosphorus
Pb	lead
PA/KC1	phosphoric acid/potassium chloride
PbAc	lead acetate
PbB	blood lead levels
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RBA	relative bioavailability
ROD	Record of Decision
SBRC	Solubility/Bioavailability Research Consortium
SRC	Syracuse Research Corporation
UB	upper bound
μg	microgram
μg/dL	micrograms per deciliter
μm	micrometer
UM/VMDL	University of Missouri (Columbia), Veterinary Medical Diagnostic Laboratory
VMDL	Veterinary Medical Diagnostic Laboratory
XRF	X-ray Fluorescence Spectrometer
Zn	zinc

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The organization and execution of this project was a collaborative effort between many participants without whom this project could not have been completed. Special appreciation is given to the following individuals:

- Mr. J. Keith Nolan (President, Lima Hill Mining Co.) for allowing access to and establishment of the test plot on his property;
- Mr. Mark Doolan (EPA Region VII, Remediation Project Manager, Joplin National Priorities List Site) for arranging and obtaining funding for the in vitro bioaccessibility study;
- Mr. Dave Mosby (Missouri Department of Natural Resources, Joplin Site Project Officer) for participating in MSE document preparation, for implementing the field treatability study, and serving as liaison between MSE and EPA/State of Missouri entities involved in this project;
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- Dr. Ken Brown (EPA/National Exposure Research Laboratory) for overseeing the in vitro Pb bioaccessibility study performed by Lockheed-Martin, plus participation in MSE document review;
- Mr. Kevin Kissell (Manager, HKM Laboratory) for overseeing the analysis of test plot soil and plant samples, and follow-on soil liming investigation;
- Dr. Vicki Lancaster (Neptune and Company, Inc.) for her critical review of the draft (September 2002) report, and suggestions offered for improving the statistical analysis of the VMDL data sets; and
- Dr. Bill Brattin et al. (Syracuse Research Corporation) for their timely responses to Dr. Lancaster, and expert reanalysis of the pig dosing data.

In addition to the people listed above, the following agency and contractor personnel contributed their time and energy in completing this project: Norma Lewis and Lauren Drees, EPA/National Risk Management Research Laboratory; Gene Ashby, DOE/WETO; and Helen Joyce, Aleta Richardson, Miriam King, and Pam Mullaney, MSE.

Executive Summary

Mining, milling, and smelting lead/zinc/cadmium (Pb/Zn/Cd) ores in and around Joplin, Missouri over the past century have resulted in significant adverse impacts to land and water resources in this area. The Joplin site was assigned final listing on the Superfund National Priorities List in August 1990, and various investigations have been underway since 1991. Given that unacceptably high blood lead (PbB) levels have been observed in young children residing near the old workings, a considerable effort has been made regarding the reduction of soil-based Pb (and Cd) health threats to this population. The June 1996 Record of Decision identified a number of remedial responses to residential soils contaminated by smelter emissions within Operable Unit (OU) 2 or by mining/milling-related wastes within OU3. The major components of the selected remedy included:

- excavation and replacement of residential yard soils, with haulage of the excavated soils to a constructed repository;
- conducting a phosphate stabilization treatability study; and
- phosphate stabilization of contaminated residential soils if treatability study results are positive.

Previous (1995-1999) investigations indicate that Pb bioavailability in soils contaminated by particulate fallout (from the historic Eagle-Picher smelter) could be lowered via addition of 1% by weight phosphoric acid (PA) plus 0.05% potassium chloride. Although these results were encouraging, it was not clear whether they could be applied to the mine waste-affected soils. Such uncertainties arise, in part, from potential differences in the types and/or levels of the different minerals (e.g., cerussite) produced by weathering of smelter fallout versus residual ore particles. As funding from EPA Region VII was not available to continue these investigations, the follow-on research regarding mine waste-affected soils was supported by the Mine Waste Technology Program (MWTP).

The study's goal is to evaluate whether PA treatment can reduce the relative bioavailability (RBA), bioaccessibility, and phytoavailability of Pb in mine waste-contaminated soils at the Joplin, Missouri NPL site. The RBA of Pb is determined by measuring Pb levels in various tissues from young pigs following ingestion of a known quantity of Pb in treated or untreated soil, as compared to Pb levels observed in tissues following ingestion of a known quantity of lead acetate (PbAc). For example, a RBA of 50% means that one-half of the Pb in soil was absorbed equally as well as lead from PbAc, while the remaining one-half behaved as though it was not available for absorption. Lead bioaccessibility assessments use an in vitro approach that estimates the amount of Pb that would probably be released from a particular soil as it proceeds through a mammalian gastrointestinal tract. Phytoavailability pertains to comparison of metals levels in collocated rooting zone soil plus leaf and stalk biomass (LSB) samples collected from sites treated or not treated with PA. Metals levels in LSB are also evaluated regarding potential risk to herbivores consuming such plant material. Conventional sampling and analytical methods are used to generate the metals data. Soil and plant phytotoxicity plus herbivore "tolerance" (plant toxicity) values from the literature are then used to prepare a screening level assessment of potential adverse effects (and subsequent impact mitigation by PA-treatment) to the area's plants and herbivores.

The specific study objectives are focused on whether PA treatment lowers:

- Pb-RBA by 25% (compared to RBAs in untreated mine waste soils), which approximates the minimum RBA reductions observed during PA-treatment of smelter-affected soils;

- Pb bioaccessibility by ≥ 25%, assuming a general correspondence between the in vivo (pig dosing) and in vitro (soil extraction) results; and
- overall mobility of the target metals (Cd, Pb, Zn) from soil-plant-herbivore, to achieve an environmentally beneficial result.

With one notable exception, the methods used in the smelter soil and mine waste studies were essentially the same. Given the potential for greater Pb bioavailability in mine waste-contaminated soils, the lower dose of PA was increased from 0.5% to 0.75% by weight. The critical difference was the attempted streamlining of the pig dosing study via comparison of Pb-RBAs in 0.75 vs. 1.0% PA-treated soils, only. It was assumed that Pb-RBA in untreated (0% PA) mine waste soils would be ≥ to that observed in untreated smelter-affected soils. The consequence of this deviation from earlier work is presented and discussed below.

The MWTP-related test site was located in July 2000 on an historic mill tailings impoundment situated 3.6 kilometers northeast of Joplin. The 3 PA treatments (0%, 0.75%, and 1% by weight) were applied to test plot soils in mid-October 2000; a randomized block design was used with four 2-by-4-meter vegetated plots per treatment. After adding hydrated lime, treatment-specific pH was monitored between October and February 2001. Although pH of the treated soils was below the target range (i.e., approximately 5.3 versus ≥6.5), budget and time constraints resulted in sampling these materials in mid-March. Composite soil samples (one per treatment) were prepared by the University of Missouri=s Geological Sciences Department; these materials were then given to the University=s Veterinary Medical Diagnostic Laboratory (VMDL) for use in pig dosing and to EPA=s National Exposure Research Laboratory (NERL) at Las Vegas, Nevada, for the in vitro (bioaccessibility) studies. Finally, treatment-specific composite soil and LSB samples were collected in mid-June 2001 and sent to the HKM Analytical Laboratory for analysis. All results from these various investigations were received at MSE Technology Applications, Inc., by late September 2001.

Shortly thereafter, EPA Region VII personnel determined that use of PbAc only as the experimental control in the Pb-bioavailability study produced too much uncertainty (in the results) to support defensible decision-making. Thus, VMDL performed a second pig dosing study in December 2001-June 2002; this investigation used untreated soil from the test plot and one dosing level of PbAc. However, independent statistical review (during the winter of 2002-2003) challenged the comparability of the results from the two pig soil-dosing studies. The principal concerns were that:

- the data tended to be heteroscedastic (i.e., tissue lead levels increased in variability with increasing dose of Pb in soil); and
- such occurrence indicated that the data reduction process used originally (i.e., ordinary least squares regression) was not appropriate.

Subsequently, Syracuse Research Corporation (SRC) reanalyzed the two data sets using improved data reduction methods (e.g., weighted least squares regression). They also performed qualitative and quantitative evaluation of the uncertainty associated with the estimates of Pb-RBA in treated and untreated soils from these two studies.

Table E-1 presents the best estimate (BE) plus 2.5% lower bound (LB) and 97.5% upper bound (UB) RBA values for each of the 4 measurement endpoints. These results utilized all of the data from the 2

VMDL studies, with no exclusion of outliers (i.e., data points outside the 95% prediction interval). The data set for each endpoint was fit to either a linear model (i.e., response = a + b * dose) or nonlinear model [response = a + c * (1 – exp (– d * dose))] as judged appropriate by Syracuse Research Corporation.

Table E-1. Statistical uncertainty in endpoint-specific RBA values.

	%RBA Relative to Lead Acetate								
	Untreated (0% PA) Soil			**0.75% PA-Treated Soil**			**1.0% PA-Treated Soil**		
Measurement Endpoint	BE	LB	UB	BE	LB	UB	BE	LB	UB
Blood Lead Area Under the Curve (AUC)	40	32	48	47	36	61	40	28	56
Liver Lead	17	10	25	28	21	38	21	15	28
Kidney Lead	16	9	23	35	27	44	21	15	28
Bone Lead	35	26	45	34	27	44	25	20	32

Source: SRC, 2003, Table 5 (see Appendix D).

Inspection of these results indicates that the confidence bounds for treated and untreated soils overlap considerably for each endpoint. Furthermore, with the possible exception of bone lead, there is no indication of a trend towards lower RBAs as a function of PA-treatment level.

The variabilities within endpoints (above) were then integrated so as to estimate the uncertainties in RBAs between treatments. These calculations were accomplished via:

- use of professional judgment to assign RBA weights of 9/12 to blood lead and 1/12 each to liver, kidney, and bone; then
- perform Monte Carlo simulations in which a value for RBA is drawn from the uncertainty distribution for each endpoint with a frequency proportional to the weight assigned to that endpoint.

Each uncertainty distribution was assumed to be normal, with known mean and standard deviation (e.g., the endpoint-specific BE values in Table E-1).

The uncertainty ranges in the Pb-RBA for each soil treatment level, estimated by Monte Carlo analysis as described above, are summarized in Table E-2. Inspection of these results shows no reduction in RBA due to PA-treatment of the mine waste soils.

Table E-2. Uncertainty in RBA point estimates combined across measurement endpoints.

	% RBA Relative to Lead Acetate		
Treatment Level	**2.5th**	**Mean**	**97.5th**
Untreated (0% PA)	13	36	48
0.75% PA-Treated	26	43	58
1.0% PA-Treated	18	36	51

Source: SRC, Table 6 (see Appendix D).

Therefore, the data from the two relevant VMDL pig dosing studies are not sufficient to conclude that PA-treatment of mine waste-contaminated soils had any particular effect on Pb-RBA. Subsequently, it cannot be determined presently whether the objective of 25% reduction in RBA was met by the given PA treatment levels.

The Pb bioaccessibility results from the EPA/NERL in vitro study are more encouraging than those from the VMDL's in vivo investigations. The extractable Pb concentrations in 0.75% and 1.0% PA-treated soils were 997 and 931 mg/kg, respectively, versus 2,105 mg/kg in untreated soil. These concentrations exceed the objective of reducing Pb bioaccessibility by a factor of 2 (i.e., ≥ 50% versus ≥ 25%).

The major findings for the heavy metals phytoavailability study are as follows:

- 1% PA treatment of mine waste-contaminated soils is probably sufficient to mitigate Cd and Pb phytotoxicities in tall fescue, but not necessarily for Zn, even in soils with paraneutral pH (6.9-7.2);
- only Zn appears to occur at levels in LSB that may pose a chronic ingestion hazard to domestic or wildlife herbivore species (i.e., ≥ 1,100 versus > 500 mg/kg); and
- Cd:Zn ratios of < 1:100 in PA-treated soils probably mitigates any food chain Cd transfer concern.

These findings are based upon a follow-on laboratory study (performed in Butte) that simulated metals phytoavailability in P-treated soils exhibiting the target pH (≥ 6.5). In this investigation, the pH of treated test plot soils was raised from about 5.3 to about 6.9 via addition of lime kiln dust. The soils were then extracted and analyzed in the same manner as done for the as-received (acidic) samples from the test plot.

Thus, the qualitative objective of achieving an "environmentally beneficial" result via PA treatment of these soils was met.

In conclusion, interpretation of RBA data from the MWTP-funded pig soil-dosing studies is substantially limited by the lack of simultaneous testing of treated and untreated soils within the same study. The consequent loss of statistical power precludes quantitation of any reduction in Pb-RBA due to PA treatment of mine waste-contaminated soils. However, it should be noted that:

- there is a consistent tendency for RBA to be somewhat lower in the 1% PA-treated soil than in the 0.75% PA-treated soil; and
- given the unusually low absorption of Pb (into pig tissues) from untreated mine waste soil, the RBA in such soils may be higher than that estimated by VMDL for the MWTP study.

The latter point is supported by a previous (1996) investigation by VMDL, wherein young pigs were dosed with three different soil types (including those contaminated by mine/mill wastes) from the Joplin Superfund site. The Pb-RBA results from such testing varied between 58% to 83%. If untreated mine waste soils indeed exhibit RBAs in this range, it would add credence to both NERL's bioaccessibility study results and observations of reduced Pb levels in LSB from plants grown in 1% PA-treated soils.

Therefore, further evaluation of whether ≥ 1% PA treatment of mine waste soils actually lowers Pb-RBA in young pigs, and environmental mobility of Pb in general, appears to be justifiable. Such investigations should include: direct comparisons of RBAs from pigs dosed with treated or untreated soils (plus pigs dosed with the full suite of PbAc controls); comparisons of Pb bioaccessibility in PA-treated vs. untreated soils; and heavy metals phytoavailability study for PA-treated soils having rooting zone pH values of ≥ 6.5.

1. Introduction

1.1 Project Background

1.1.1 Site History

Heavy metals levels present in residential soils affected by historic mining, milling, and smelting activities have been identified as posing significant threats to human health and the overall environment at a number of Superfund National Priorities List (NPL) sites located throughout the United States. The Oronogo-Duenweg Mining Belt NPL site is one such instance, being an inactive lead (Pb) and zinc (Zn) mineral processing area situated in the southwestern corner of Jasper County, Missouri (Figure 1-1). Mining operations began in the Joplin townsite in 1870 with subsequent establishment of numerous ore milling plus Pb and Zn smelting plants thereafter; Pb production occurred at the Eagle-Picher Smelter facility located within the northwestern corner of the city until the 1970s. Particulate fallout from smelter emissions resulted in soils contamination extending predominantly in the southeastern direction to a distance of approximately 3.6 kilometers (km), essentially bounding Operable Unit (OU) 2 (*Residential Yard Soils*) of the NPL site. In addition, many other residences (within and adjacent to Joplin) exist on or near sites contaminated by mining and milling wastes; these residences are aggregated under OU3 (*Mine Yard Wastes*). Because of the occurrence of elevated blood lead levels (PbB) >10 micrograms per deciliter (μg/dL) in children less than 7 years of age, residential soils containing $\geq$800 milligrams per kilogram (mg/kg) Pb or $\geq$75 mg/kg cadmium (Cd) in the upper 12 inches or $\geq$500 mg/kg lead (Pb) in the upper 18 inches of garden soils have been excavated and hauled to nearby repositories. The potential cost for completing these activities, including replacement of clean soils, has been estimated to be $28.6 million [and annual operating and maintenance (O&M) costs at approximately $113,000]. Because of the magnitude of such costs, the U.S. Environmental Protection Agency (EPA) Region VII and the State of Missouri are investigating the use of phosphate-based, in situ stabilization of heavy metals as an alternate treatment approach. In fact, the June 1996 Record of Decision (ROD) states that such treatment is preferable (within OUs 2 and 3), if it can meet the nine criteria associated with selecting a cleanup remedy. If implemented, total construction cost savings could vary from $5 to $24 million, depending upon the extent that this technology is applied; annual O&M costs savings are estimated to be approximately $70,000 (Ref. 1).

1.1.2 Bioavailability and Bioaccessibility of Lead (Definitions)

Bioavailability refers to that portion of a substance contacting a body portal-of-entry (e.g., via lungs, gastrointestinal tract, skin) that is then incorporated into the blood stream (Ref.2). Bioavailability is also described as absolute or relative (Ref.3). Absolute bioavailability (ABA) is the amount of a substance entering the blood via a particular route of exposure (e.g., gastrointestinal) divided by the total amount administered (e.g., soil lead ingested). Relative bioavailability (RBA) is indexed as measuring the bioavailability of a particular substance (e.g., lead carbonate or phosphate) relative to the bioavailability of a standardized reference material (e.g., water soluble lead acetate).

Essentially, bioavailability testing involves dosing of test animals (e.g., rats, pigs) with a known amount of the substance of concern per unit body weight per day (e.g., 100 μg $PbCO_3$/kg•d) over a defined interval of time. Sampling and subsequent analysis of biological materials obtained during (e.g., venous blood) and after (e.g., kidney, bone) the dosing period provides the data necessary for estimating in vivo bioavailability of the test substance. Examples of Pb RBA determinations using rats and young pigs, via oral route of exposure, are found in References 4 and 5, respectively.

Determination of risk-based cleanup levels for Pb-contaminated soils, that are protective of young children=s health (≤6 years of age), is often dependent upon output from the Integrated Exposure Uptake Biokinetic Model for Lead in Children (IEUBK, Ref. 6). For the IEUBK model, soluble Pb in water and food is estimated to have 50% ABA. Furthermore, the model presumes that ingestion of Pb in soil results in a RBA of 60%. Thus, the ABA would be (0.60 x 0.50) or 30%. However, particle size distribution [particularly those <250 micrometers (μm) in diameter] and physicochemical form(s) of Pb present in a given soil material exert considerable influence on Pb bioavailability. These parameters have been used to explain PbB levels observed in children residing at various Pb mining and smelting sites (e.g., Refs. 7 and 8). EPA Region 8 performed studies wherein Pb-contaminated soils were fed to young pigs; the observed trends in Pb RBA are presented in Table 1-1 (Ref. 2).

In vitro methods have been developed for measuring the portion of Pb solubilized from soil materials under simulated gastrointestinal conditions (e.g., Ref. 9). These results, often referred to as the bioaccessible fraction (BAF), are thought to be an important determinant of bioavailability. Thus, BAF is not necessarily equal to RBA but depends on the relation between results from a particular in vitro test system and an appropriate in vivo model/test animal.

The in vitro tests simulate the gastrointestinal environment via sequential extraction of Pb (from soil, etc.) using strong acid and paraneutral aqueous solutions; these fluids mimic the pH conditions found in the stomach and small intestine, respectively. The extract is filtered (0.45 μm) and then analyzed for its Pb content. The mass of Pb found in the aqueous phase, divided by Pb mass introduced into the test, represents the sample-specific BAF. To date, for Pb-contaminated soils tested in the EPA pig studies, the in vitro method has correlated well with the RBA values (Ref.10).

1.1.3 Previous Soil Remediation Studies

As part of the EPA=s Remediation Technologies Development Forum (RTDF), the In-Place Inactivation and Natural Ecological Restoration Technologies (IINERT) Soils-Metals Action Team has been evaluating the reduction of Pb mobility and bioavailability at Joplin since May 1996. A consortium of federal agencies, academic institutions, and private-sector consultants has established an integrated program of laboratory and field experiments associated with treatment of the smelter-contaminated (OU2) soils. In particular, a 1-acre [0.40 hectare (ha)] test site has been developed approximately one-quarter of a mile [1550 meters (m)] west of the Eagle-Picher Smelter works (Figure 1-1). Randomized block treatments using various combinations of phosphorus compounds, iron, and organic matter (as well as at different rates of applying these materials) have been applied by various means to the 2-by-4-m plots within the test site. These field studies were tied to various laboratory investigations performed elsewhere, including those implemented at the University of Missouri (discussed below).

Laboratory treatment of OU2 soils involved adding of phosphoric acid (H_3PO_4; PA) at rates of 0, 1250, 2500, 5000 and 10,000 milligrams (mg) of P/kg soil, plus constant additions of potassium chloride (KC1) at 500 mg C1/0.75 kg soil. The reaction was followed by measurements of Pb bioaccessibility, solubility products, and electron microprobe analyses. Key results are summarized below, while details of the study are reported in Yang et al. (Ref. 11):

- the mean bioaccessible Pb concentrations in control and 1% PA-treated soils were 1789 and 564 mg/kg respectively, after 70 days incubation at room temperature (i.e., a 68% reduction in bioaccessibility);
- the microprobe analyses indicated formation of a chloropyromorphite-like mineral [$Pb_5(PO_4)_3C1$]; wherein

- the calculated and standard solubility products (-1og k = 21.0 and 25.0, respectively) suggest the reaction product is slightly more soluble and without the crystalline form associated with the *pure* compound; and
- the mean Pb concentration in the sand fraction of the 1% PA-treated soils increased from 3,483 to 6,136 mg/kg (i.e., 46% of total Pb versus 24% in untreated soil), probably due to Pb transformation into larger particles of amorphous-to-crystalline chloropyromorphite.

Collectively, these observations indicated the potential of phosphoric acid/ potassium chloride (PA/KC1) as a cost-effective means of in situ treatment of Pb smelter-contaminated soils.

Phosphoric acid treatments were administered to certain test plots at the IINERT test site in March 1997, and studies continued there through October 1998. Details pertaining to physicochemical characteristics of the soils, summaries of the field and laboratory methods used, and key results are presented in Appendix A (Ref. 12). The principal conclusions from these efforts are that:

- 0.5 to 1.0% by weight (w/w) applications of PA/KC1 can reduce Pb RBA by 26–38%, respectively, relative to RBAs in untreated soils (and probably within 90 days of field treatment); and
- 1% PA treatment reduces Pb uptake into aboveground plant biomass by about 73%, although it has no significant effects on uptake of Cd or Zn, relative to metals levels in plants grown in untreated soils.

Thus, the field studies also demonstrate that in situ PA/KC1 applications can be an effective remedial technology for cleanup of Pb smelter-effected soils.

However, further research is needed to assess the efficacy of such treatments of soils contaminated by mine/mill wastes (in OU3), as Pb RBA in these materials has been measured up to 80% (Ref.13). Such elevated bioavailability levels may be due to greater amounts of cerussite (i.e., lead carbonate either naturally occurring or as a weathering product of lead sulfide) relative to that found in smelter-contaminated soils. As funding from EPA Region VII is not available to continue these investigations using soils from OU3, the follow-on research was supported by EPA's Mine Waste Technology Program (MWTP).

1.2 Project Objectives

The overall purpose of this project was to assess the effect of PA/KC1 additions on the RBA of lead in OU3 soils at the Joplin, Missouri NPL Site. More specifically, the primary objective of the field demonstration project was to achieve an average 25% reduction in Pb RBA in PA/KC1-treated soils from OU3, as compared to Pb RBA in untreated soils contaminated by mine/mill wastes (Ref. 14). This evaluation was performed in vivo by dosing young pigs with PA-treated soils from the test plot.

1.2.1 Assess Reduction of Lead Bioavailability in Test Soils

The project is a technology demonstration effort rather than an initiation of on-site remediation of the Joplin site. However, the project will develop technical information on the ability of the P-addition technology to treat residential soils contaminated by historic mining and milling activities at this site. Therefore, the envisioned results will contribute to the ultimate cleanup of the Joplin site and surrounding area. Reduction in Pb availability should allow higher soil Pb levels to remain in residential soils, yet comply with the National Contingency Plan's two threshold criteria (i.e., be protective of public health and comply with Applicable or Relevant and Appropriate Requirements) for selecting a cleanup remedy at Joplin.

1.2.2 Assess Reduction of Lead Bioaccessibility in Test Soils

An in vitro test was also be used to analyze the treated soil samples from the site. The purpose of this testing was to compare these results to those of in vivo testing to determine whether or not the results are comparable. Previous studies have collected similar comparative data. Data from this study will be added to the overall EPA Region VII/VIII data base, which could eventually be used instead of routine in vivo testing.

1.2.3 Assess Reduction of Heavy Metals Phytoavailability in Test Soils

A third criterion is the reduction of actual or potential metals uptake of Pb, Cd, and Zn in residential soils at Joplin. Such reductions will be assessed through measurements of plant available/extractable levels of these contaminants from soil solution and analysis of acid-extractable metals levels found in aboveground plant biomass collected from the test plot site.

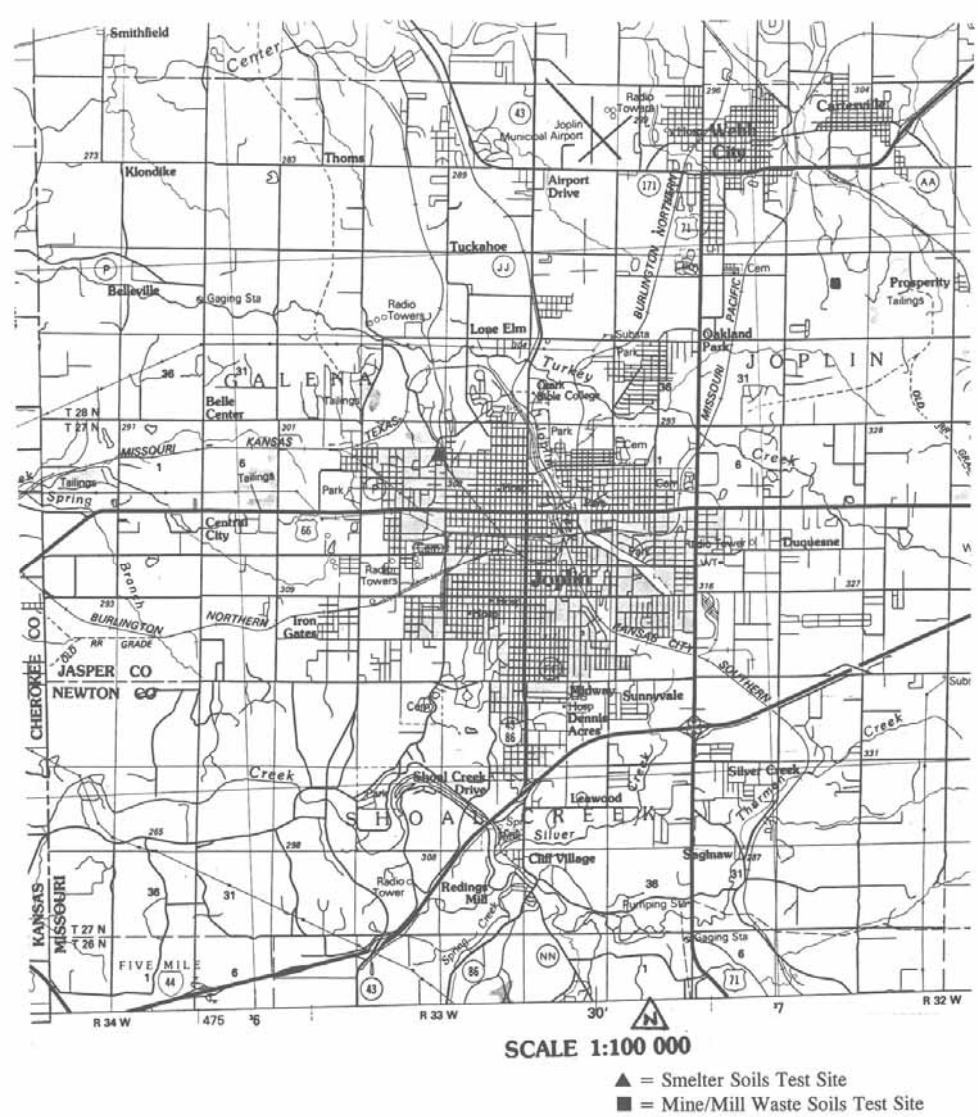

Figure 1-1. Joplin County site map.

Table 1-1. General trends in RBA of Pb, as affected by mineral form.

Potentially Lower Bioavailability (RBA <25%)	Intermediate Bioavailability (RBA = 25%–75%)	Potentially Higher Bioavailability (RBA >75%)
Galena (PbS)	Pb Oxide (PbO)	Cerussite ($PbC0_3$)
Anglesite ($PbSO_4$)	Pb-Fe-Oxides	Pb-Mn-Oxides
Pb-Metal Oxides (Pb-M-O_x)	Pb Phosphates/Slags	
Native Lead (Pb^o)		

2. Methods

This section summarizes the design and implementation of the field and laboratory activities associated with this project. Essentially, the methods and protocols developed previously for the smelter soils-PA treatment study (see Refs. 11 and 12) were applied to the soils contaminated by Pb mine/mill wastes. Key on-site support was provided by Mr. David Mosby from the Missouri Department of Natural Resources (MDNR) Hazardous Waste Program (Jefferson City, Missouri). Mr. Mark Doolan, EPA Region VII=s Remedial Project Manager for the Joplin NPL Site, also provided technical and administrative support in executing the present study (Ref. 14).

Dr. Stan Casteel of the University of Missouri (Columbia), Veterinary Medical Diagnostic Laboratory (UM/VMDL) was the principal Investigator for the in vivo Pb bioavailability studies that dosed young pigs with soils collected from the field test plot at Joplin. Physicochemical characterization (including Pb speciation) of these soils was overseen by Dr. John Yang of UM=s Department of Geological Sciences. The in vitro Pb bioaccessibility extractions and subsequent analyses of the treatment-specific soils were performed by Lockheed-Martin and their contract laboratory, respectively. This work was overseen by Dr. Ken Brown, Director of the Technical Support Center at EPA=s National Exposure Research Laboratory (EPA/NERL), Las Vegas, Nevada. Mr. Kevin Kissell, Manager of HKM Analytical Laboratory (Butte, MT), led the extractions and subsequent analytical work pertaining to estimation of plant availability of select heavy metals in test site soils, as well as contaminant uptake into plant biomass from these soils. Interpretation of the HKM data was performed by MSE Technology Applications, Inc. (MSE).

2.1 Field Investigations

2.1.1 Experimental Design

The test site layout with plot-specific sampling locations is presented in Figure 2-1. Before beginning the treatment stage, a field XRF spectrometer was used to establish a baseline for Pb variability. X-ray fluorescence sampling locations are denoted by an "X" on Figure 2-1. The plots were laid out in randomized block design with four replications for each of the three treatments:

- Treatment A = 10 g H_3PO_4 + 500 mg KC1 per kilogram of soil;
- Treatment B = 7.5 g H_3PO_4 + 500 KC1 per kilogram of soil; and
- Treatment C = no H_3PO_4 or KC1.

Treatment C represents the control. After approximately 5 months of treatment, samples were collected from five locations within each 2- by 4-m test plot at locations denoted as "•" in Figure 2-1. These five samples were composited to obtain one representative sample from each test plot. The four samples from each treatment were then composited, resulting in three final samples: Composite A, Composite B, and Composite C. These samples were submitted to the UM/VMDL for in vivo Pb bioavailability studies in young swine and to EPA-NERL for in vitro bioaccessibility tests.

After 8 months of treatment, the sampling was repeated in the same fashion for submittal of soil samples to the HKM Analytical Laboratory for analysis. At that time, samples of fresh leaf and stalk biomass (LSB) were also collected and submitted to the HKM Analytical Laboratory to determine the plant uptake of metals during the study.

2.1.2 Implementation of Field Investigations

Mr. Mosby identified a suitable site for the PA treatment study in mid-July 2000. The site was located within a historic mill tailings impoundment, approximately 4.8 km northeast of Joplin in the SW 1/4NE1/4NE1/4 of Section 29, R32W T28N. An organic-rich horizon of soil 5–15 cm thick had developed over the top of flotation tailings that had a fine-sand to silty texture. MSE signed an access agreement with the landowner, Lima Hill Mining Company, in late August; NEPA compliance approval to proceed was received from the U.S. Department of Energy/National Energy Technology Laboratory (DOE/NETL) in early September 2000.

Before installing treatment plots, site metal concentrations were characterized with a Spectrace 9000 XRF to ensure that lead concentrations were within the desired range. XRF measurements were made in situ without sieving or other sample preparation. Lead concentrations within the selected area ranged from 1,800 to 5,000 mg/kg soil.

A total of 12 treatment plots were installed in October 2000. Two treatments plus one untreated control were installed with four replicates for each treatment (Figure 2-1). Each plot was 2 x 4 meters in area. Plots were installed by measuring the areal dimensions of the treated area, trenching to a depth of 15 cm around the borders of plots, and installing 25-cm plastic edging to prevent splashing of reagents between plots.

After the plots were installed, additional XRF measurements were made. Lead concentrations ranged from 1292 to 4375 mg/kg, with a mean 2767 mg/kg. Other important metals detected at significant concentrations by the XRF include calcium (Ca), Zn, and iron (Fe). Zinc ranged from 24,510 to 6780 mg/kg, with a mean of 16,128 mg/kg. Iron ranged from 40,830 to 16,770, with a mean of 32,358 mg/kg. Calcium ranged from 41,750 to 4,790 with a mean of 20,286 mg/kg.

Pretreatment soil characterization was beyond MDNR=s contract scope of work. Therefore, the PA application rates were predetermined from earlier treatments made on smelter-contaminated soil in Jasper County. The smelter-contaminated soil PA treatments were applied at 0.5% and 1% phosphorus (P) as PA (Section 1.1.3). Based on the high concentrations of Zn and Fe associated with XRF readings from the mill waste-contaminated plots, a field decision was made that the 0.5% P as PA treatment was not high enough to supply ample free phosphorous for the reaction with Pb. Zinc, Fe, and Ca will compete with Pb in the reactions with P (Ref. 12). The lower concentration of P was, therefore, increased to 0.75% as PA.

Phosphoric acid treatments were applied to the field soils using fertilizer grade (85%) PA (obtained from Farmer=s Chemical Co. in Joplin, MO). Soils were treated to a depth of about 15 cm. About 37.8 L of H_3PO_4 were applied to each 1% PA plot, and 28.4 L of H_3PO_4 were applied to each 0.75% PA plot. About 1.66 kg of fertilizer grade (45%) KC1 was applied to each PA plot. The plots were rototilled before applying treatment reagents. KC1 and half the volume of PA was added to each plot and rototilled into the soil, followed by adding the remaining half of the PA, followed by further rototilling. A minimum of three passes with a hand rototiller was made for each half volume of PA. The soil was moist, but sufficiently dry to till without forming significant clods.

Soil pH was measured 14 days post-treatment on composite samples of a 1:1 deionized water suspension from soil collected 0–15 cm deep. For the 1% PA plots, pH was 3.94; 4.55 for the 0.75% PA plots; and 7.58 for the control plots. Hydrated lime [$Ca(OH)_2$] was added to the plots to raise target soil pH to 6.5–7.0 on the same day to minimize mobilization of other metals. Lime was added at a rate of 3080 mg Ca^{+2}/kg soil [9.1 kg $Ca(OH)_2$] to the 1% PA plots, and 2310 mg Ca^{+2}/kg soil [6.9 kg $Ca(OH)_2$] was added to the

0.75% PA plots. A hand rake was used to work the lime into the soil to a depth of about 10 cm. Tall fescue (*Festuca arundinacea)* grass seed was hand-planted in all treatment plots the day following liming, 15 days after PA treatment.

A site visit was made in November 2000, 35 days post-treatment. Fescue seeds had germinated in all plots. Grass sprouts were most abundant on the 0.75% PA plots, and the least abundant on the control plots.

Soil pH was measured on this date to ensure sufficient lime was added to reach target pH. Grass had sprouted on all treatment plots. Mean soil pH (from 3 replicates) was 8.51 for 1% PA, and 10.39 for 0.75% PA treatment plots.

Soil pH was again measured 50 days post-treatment. Mean soil pH for the 1% PA was 8.22 and 5.61 for the 0.75% treatments.

The interpretation for this drastic pH change for the 0.75% treatment was that the soil had not enough time to reach equilibrium. The decision was made to allow more time for soil pH to stabilize and then re-measure in late winter 2001, prior to the growing season. MSE and MDNR agreed that, if soil pH had not approached the target range by that time, then lime or additional PA would be added to reach the target pH.

The pH of 1:1 deionized water:soil pastes was measured on March 2, 2001: the soils were collected from 0–15 cm below ground surface, and plot-specific subsamples composited for each PA treatment. For the 1% PA plots, the mean pH was 5.97 and 5.88 for the 0.75% plots; the control plot pH was not determined. Given the goal of project completion by September 2001, MSE directed MDNR to forego any further adjustments in soil pH, and composite samples were collected for the bioavailability/bioaccessibility studies in late March.

A plastic trowel was used to collect five subsamples of soil (0–15 cm below ground surface) from within each plot, placed in a plastic bag, and then mixed. This process was repeated until there were approximately 2 kg samples from each plot (i.e.,12 total samples from the test site). The samples were delivered to the University of Missouri, Department of Geological Sciences, and sample preparation activities commenced immediately thereafter (Section 2.2.1).

Treatment-specific composite soil and LSB samples were collected by MDNR for use in the metals mobility/uptake studies in June 2001. The soil samples were obtained via subsampling the 0–15-cm rooting zone within each treatment-specific plot and then mixing together materials from all four plots to produce the treatment-specific sample. Plant biomass samples (>3 cm above ground surface) were collected in the same manner as used for soils. The six (total) samples were shipped by overnight delivery to MSE; the soil and plant materials were then transferred to the HKM Laboratory (Section 2.2.3).

Photographs of the test site environment are presented in Figure 2-2.

2.2 Laboratory Investigations

The laboratory evaluation phase used samples collected from the field test site to determine whether project objectives were met and to assess the overall success of the PA-stabilization technology (Section 1.2). The laboratory evaluation was oriented toward the following:

- demonstrating reduction in Pb bioavailability in mine/mill waste-contaminated soils to young swine following soils treatment with phosphoric acid + KCl (in vitro studies);
- using the Solubility/Bioavailability Research Consortium (SBRC) in vitro extraction test (as performed by EPA/NERL, Las Vegas) to demonstrate reduction in Pb bioaccessibility, and comparing these results to those from the young swine study;
- evaluating changes in Pb speciation (e.g., from lead carbonate to chloropyromorphite) following soils treatment with PA and KC1; and

- evaluating changes in soil chemistry and metals uptake by the LSB using the end-of-season (test-site) samples.

2.2.1 In Vivo Lead Bioavailability Studies

2.2.1.1 First Investigation (June - September 2001)

The dosing of young pigs with Pb-contaminated soils from the test plots followed the methods previously approved by the toxicology staff of EPA Region VIII (Ref. 15), with one (critical, in retrospect) exception. In an attempt to streamline the pig dosing study, it was assumed that Pb-RBA for untreated mine waste soils would be ≥ that of the smelter-affected soils (Section 1.1.3). Thus, the initial study included only PA-treated soil types plus PbAc controls. Formal compliance with study protocols (Ref. 15) would have combined the untreated (0% PA) soil type along with each of the PA-treated soils (plus PbAc controls). Given the capacity for conducting pig dosing studies at VMDL, this approach would have required two back-to-back (i.e., 0 + 0.75% PA and 0 + 1.0% PA) investigations. Because of the perceived need to complete the project by September 2001, the project team decided to go forward with only the one (limited) study.

Critical measurements included: total Pb levels in soil; time course of pig weight, Pb dosage, and PbB levels during the 15-day dosing period; and Pb levels in kidney, liver, and femur tissues following this period (Ref. 14). The detailed study design is found in Section 2.0 of the report prepared by Dr. Casteel et al. (Ref.16; see Appendix B).

Determination of Pb levels in soils, plus ancillary agronomic soil measurements (e.g., cation exchange capacity) and Pb speciation in soils, were performed by Dr. Yang et al. as described in Ref. 11. The materials used in the Pb bioavailability and bioaccessibility studies were prepared as follows:

- soils samples from each plot were mixed, air-dried, and ground to pass a 0.25-millimeter mesh sieve;
- equal amounts of materials from the four replicate plots within each treatment were composited and thoroughly mixed; and
- subsamples of the treatment-specific composites were then digested/analyzed for Pb, as well as provided to Drs. Casteel and Brown for their respective investigations.

Sample preparation was completed by early April 2001, and the *in life* phase of the pig dosing study was completed by late April. Preparation and chemical analysis of the various biological samples, plus soil samples, occurred between mid-April through late June, followed by data validation/interpretation through late July. The draft report was prepared during August and September 2001.

2.2.1.2 Second Investigation (December 2001-June 2002)

In response to EPA Region 7 and MDNR concerns regarding lack of RBA data for untreated mine waste soils, the Pb-dosing investigation was extended into a second phase of activity.

In the second study, groups of five swine were given target average doses of 75,225, or 675 μg/kg • day of Pb in untreated mine waste soil, or 225 /kg • day of Pb from PbAc. Otherwise, the methods used were the same as in the previous study (Appendix B).

The validated, tissue-specific Pb analytical data were used to prepare best fit (linear or nonlinear) dose-response equations for the PbAc reference material plus untreated soil. Because only one dose group was incorporated into this study for PbAc, the study-specific results were combined with PbAc results from many previous studies in order to establish the dose-response relationship. The RBA results for the untreated soil from this investigation are discussed in detail in Appendix C.

2.2.1.3 Reevaluation of the VMDL Data Sets

The draft (September 2002) project report was reviewed by EPA/MWTP personnel and their contracted statistician, Dr. Vicki Lancaster (Neptune and Company, Inc.), during November-December 2002. In a letter report received by MSE in mid-December, the following concerns were expressed:

- without defined confidence intervals for each Pb-RBA estimate, one can not firmly conclude whether or not phosphate addition to mine waste soils produced a meaningful treatment effect; and
- because the analytical data tended to be heteroscedastic (i.e., the variability of Pb levels in pig tissues increased as the Pb-in-soil dosage increased), use of ordinary least squares reduction for data reduction was not appropriate.

After several months of intermittent discussions between EPA and MSE, Dr. Bill Brattin et al. of SRC were procured in late March 2003 to address the above issues. As a result of numerous verbal and written communications between EPA/Dr. Lancaster, SRC and MSE personnel, the following improvements were made to the (original) data reduction approach:

- to better accommodate the heteroscedastic nature of the data sets, weighted least squares regression was applied, where the weight assigned to each data point in a dose group is equal to the inverse of the variance in responses for all animals in that exposure group;
- to better meet the specific requirements of the linear or nonlinear modeling efforts, data sets for reference and test material were fitted simultaneously rather than step-wise;
- fewer data points were excluded from analysis via re-defining outliers at those data points having standardized weighted residual of $> \pm 3$ (vs. those outside the 95% confidence intervals, as used before);
- fiduciary limits for quantitative estimation of uncertainty for each RBA value were determined using Fieller's theorem; and
- occasional use of linear model for fitting nonlinear dose-response data (i.e., blood AUC) in those cases wherein the dataset did not extend far enough to define the shape of the curve, or to define the plateau value with confidence.

Details pertaining to the statistical methods applied to the VMDL data sets, and derivation of the uncertainty limits requested by EPA/MWTP, are presented in Appendix D.

2.2.2 In Vitro Bioaccessibility Study

This study used EPA-approved sample extraction (Ref. 10) and analysis (Ref. 17) methodologies, plus quality assurance/quality control (QA/QC) guidance (Ref.18), that were prepared by or for the SBRC. Essentially, the extraction step uses 100 milliliters of pH 1.5 fluid (prepared using concentrated hydrochloric acid and containing 0.4 moles/liter glycine) and 1.0 grams of soil. The mixture is placed in a 125-milliliter high-density polyethylene bottle, sealed, and then shaken at 30 revolutions per minute for 1 hour at 37 ^{o}C on a modified TCLP extractor. Assuming maintenance of the above pH, the solution is passed through a 0.45-μm disk filter, and the filtrate is stored at 4 ^{o}C until analyzed. The solution is then analyzed for arsenic (As) and Pb contents using ICP-AES (SW846-6010B), ICP-MS (SW846-6020), or ICP-hydride (SW846-7061A), as appropriate (Ref. 19).

Treatment-specific, composite soil samples were prepared by the University of Missouri (Dr. Yang et al.) and then sent to Dr. Brown, EPA/NERL, in April 2001. The samples were extracted in late July and analyzed in early August, with the results reported in late September.

2.2.3 Heavy Metals Phytoavailability Study

This study used methods that were either developed or approved by the EPA for evaluating heavy metals uptake into aboveground plant biomass. The methods used by the HKM

Analytical Laboratory in completing their scope of work are summarized in Table 2-1.

The soil and plant samples were received from Mr. Mosby (MDNR) at the HKM Analytical Laboratory on June 15, 2001; analytical results were received by MSE on July 11 and forwarded to Mr. Mosby the next day. Following a review and discussion of the data on July 23, additional sample processing and tests were ordered that day. The pH of the as-received, PA-treated soil samples was in the 5.2-5.4 range; as noted in Section 2.1.2, the target soil pH is 6.5-7.0. Thus, the purpose of the additional testing was determination of plant available (DTPA-AB extractable) levels in PA-treated soils having the "optimal" pH of ≥ 6.5. The data from this second round of work were received at MSE on August 10, 2001 and transmitted to MDNR shortly thereafter.

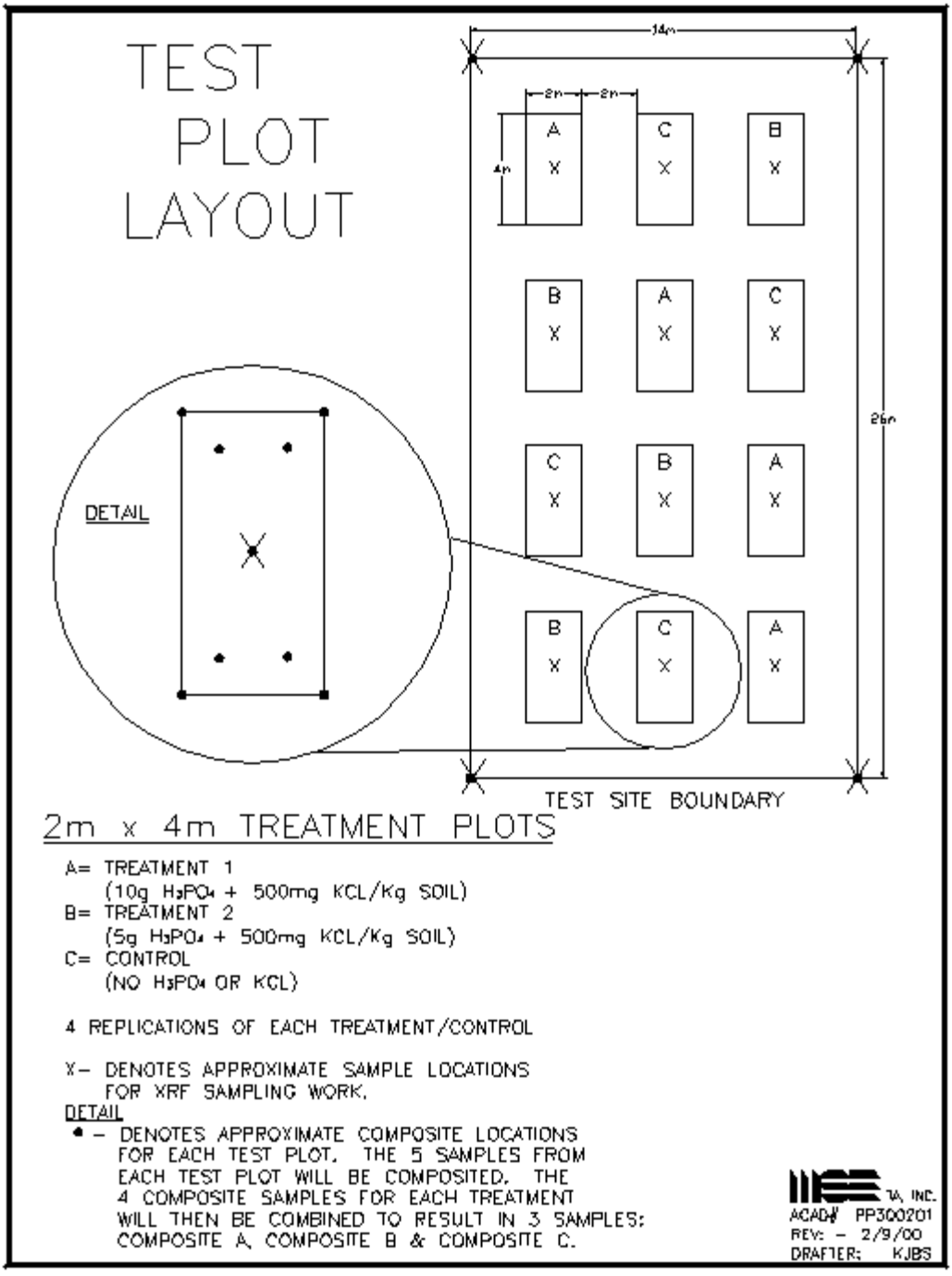

Figure 2-1. Test plot layout with sampling locations.

Figure 2-2. Photographs of the Mill Waste-Soils Test Plot Site (source: D. E. Mosby, June 2001).

Table 2-1. Laboratory methods used in the heavy metals phytoavailability study.

Parameter	HKM Standard Operating Procedure	Source (detailed method)	Comments
Preparation of soil/plant materials	SP00388/389	Ref. 20, Chap. 28	Produces soil particles <2 mm and plant particles <0.85 mm.
1:1 pH/E_h (in soil paste)	SP018A	Ref. 19 (9045C)/ Ref.20 Chap. 42	Glass electrode/probe.
Plant available metals (in soils)	SP003A/B	Ref. 20, Chaps. 26, 28; Ref. 19 (6010B)	DTPA-AB extraction, then ICP-AES.
Total metals (in soils, biomass)	SP001E	Ref. 19 (3050A/6010B)	Nitric acid-hydrogen peroxide digest, then ICP-AES.

3. Results And Discussion

This section presents the important findings associated with the Pb bioavailability, bioaccessibility, and heavy metals phytoavailability investigations. The raw data for these studies are presented in Appendices B through F, respectively. Study-specific methods used are summarized in Section 2.0. As documented in Appendix G, all reasonable efforts were made to abide by the project quality assurance project plan (QAPP) (Ref. 14).

3.1 In Vivo Lead Bioavailability Studies

The databases for VMDL's pig dosing studies (Appendices B and C) were re-evaluated by Syracuse Research Corporation using EPA-approved statistical methods (Appendix D), and the results of their work are summarized below.

Fieller's theorem was used to calculate the approximate 95% confidence interval around each tissue-specific RBA estimate. Table 3-1 presents the best estimate (BE) plus 2.5% lower bound (LB) and 97.5% upper bound (UB) RBA values for each of the 4 measurement endpoints associated with each of the PA treatment levels (including the control). These results utilized all of the data from the two VMDL studies (i.e., no exclusion of outliers), and the data set for each endpoint was fit to either a linear or nonlinear model as judged appropriate. Linear models (i.e., response = intercept + slope * dose) are used for the kidney, liver, and bone (femur) endpoints, while a nonlinear model [response = intercept + constant * (1 – exp (– constant * dose))] is used for the blood area under the curve (AUC) data. However, in the case of untreated soil, the dose-response data did not extend far enough out to define either the slope of the curve or plateau value with confidence. Thus, in this one instance, the data were fit using a linear model.

Inspection of these results (Table 3-1) indicates that the confidence bounds for treated and untreated soils overlap considerably for each endpoint. Furthermore, with the possible exception of bone lead, there is no indication of a trend towards lower RBAs as a function of PA-treatment level.

The variabilities within endpoints (above) were then integrated so as to estimate the uncertainties in RBAs between treatments. These calculations were accomplished via:

- use of professional judgment to assign RBA weights of 9/12 to blood lead and 1/12 each to liver, kidney, and bone; then
- perform Monte Carlo simulations in which a value for RBA is drawn from the uncertainty distribution for each endpoint with a frequency proportional to the weight assigned to that endpoint.

Each uncertainty distribution was assumed to be normal, with known mean and standard deviation (e.g., the endpoint-specific BE values in Table 3-1).

The uncertainty ranges in the Pb-RBA for each soil treatment level, estimated by Monte Carlo analysis as described above, are summarized in Table 3-2. Inspection of these results shows no reduction in RBA due to PA-treatment of the mine waste soils.

Therefore, the data from the two relevant VMDL pig dosing studies are not sufficient to conclude that PA-treatment of mine waste-contaminated soils had any particular effect on Pb-RBA. Subsequently, it can not be determined presently whether the objective of 25% reduction in RBA was met by the given PA treatment levels.

3.2 In Vitro Bioaccessibility Study

The statistical summary for As and Pb bioaccessibility values for the three levels of PA treatment are shown in Table 3-3; the raw data (including those associated with QA/QC) are provided in Appendix E.

Using the mean Pb values, the 1% and 0.75% PA treatments reduce Pb bioaccessibility by about 56% and 53%, respectively, as compared to the untreated mine waste soils. Regarding the 1% PA treatment level, the percent reduction in bioaccessibility is about the same magnitude as reported for smelter soils (i.e., 60% reduction), despite use of different Pb extraction methods (see Ref. 11).

Given the reasonable assumption that As loading from the PA solution is insignificant relative to As present in the receiving soils (calculations not shown), it is hypothesized that PA treatment enhances the mobility and bioaccessibility of this element. This hypothesis is supported by the relatively low (17%) recovery of As observed in the matrix spike sample (Appendix E); the As levels may be even higher than those reported in Table 3-3. It is suggested that the concentration of the $H_2PO_4^{-1}$ ion is far greater than that of the $H_2AsO_4^{-1}$ ion (at pH $\simeq$5.2, E_h $\simeq$330 millivolts) in the PA-treated soils (Ref. 22). Subsequently, the P-ion outcompetes the As-ion for adsorption sites on particles of hydrous Fe/Al oxides, aluminosilicates, etc. (Ref. 23).

3.3 Heavy Metals Phytoavailability Study

The ROD identified Pb and Cd as being the principal contaminants of concern (CoC) in residential soils at the Joplin NPL Site (Ref. 1). However, zinc ore mining/milling and smelting activities were of major economic importance also within the study area (Ref. 24). Thus, this metal was also included as a CoC in the original research proposal (Ref.13).

This section of the report first presents the CoC and ancillary laboratory data for plant and soil materials sampled during this study. These data are then interpreted from the perspectives of potential phytotoxicity and food chain concerns. Finally, the results from the present investigation are compared to those generated by the previous smelter soils-related study(ies) at Joplin.

3.3.1 Plant and Soils Data Presentation

The physicochemical characterization of untreated (0% PA) soil, plus selected physicochemical properties of 0.75% PA and 1%PA-treated soils, all from samples collected at the test site in March 2001, are presented in Appendix B (Table 2-1). The analytical results for the treatment-specific soil and plant composite samples, collected in June 2001, are presented in Table 3-4. Data from the follow- on laboratory investigations performed in Butte in late July 2001 are shown in Table 3-5. Documentation for the June and July sample analyses are found in Appendix F.

Inspection of the soils data in Table 3-4 indicates the following trends:

- pH remains $\geq$1 log unit below the target range (6.5–7.0) approximately 8 months after PA treatments;
- 1% PA treatment lowers plant available Cd to 34% of that observed in untreated soil;
- 1% PA treatment lowers plant available Pb to 18% of that observed in untreated soil; and
- 1% PA treatment lowers plant available Zn to 63% of that observed in untreated soil.

In regards to the plant data (Table 3-4, Part B), 1% PA treatment appears to reduce Cd, Pb, and Zn levels to about 42%, 34%, and 85%, respectively, of those concentrations observed in plants growing in untreated soils. Table 3-5 shows adjustment of pH to within the target range appears to further reduce plant available metals levels. The percent plant available metals levels (relative to 100% presence in the controls) in pH 7, 1% PA-treated soils are as follows: Cd, 20%; Pb, 17%; and Zn, 47%.

Overall, the effectiveness of PA treatment ($\geq$0.75% by weight, pH $\geq$6.5) in reducing CoC bioavailability/plant uptake appears to be Pb>Cd>Zn. Assuming predominance of hydroxy-chloro-phosphate mineralization under these conditions, the above ranking appears to be driven by relative solubility of these compounds. The

trend in treatment effectiveness is reflected in the solubility products (-1og K_{sp}) of such compounds, from least to most soluble: Pb (62.8–84.4), Cd (42.5–49.7), and Zn (37.5–49.1) (Ref.25).

3.3.2 Plant and Soils Data Interpretation

The above data were evaluated using the phytotoxicity and herbivore risk assessment criteria presented in Table 3-6. These criteria represent literature review-based judgements made by MSE; key references are cited in this table. The plant-related values are (believed to be) applicable to physiologic ecotypes of common grass and forb species that are neither intolerant or strongly tolerant of the given CoCs, and are yet able to grow in the given soil conditions. Phytotoxicity is defined in terms of >15% to 20% reduction in aboveground biomass yields, relative to those for nonstress conditions. Given their derivation, the herbivore-related criteria are probably applicable to both livestock (e.g., cattle) and wildlife (e.g., elk) species.

The element-specific strong acid extractable ("total") metals levels in soils represent interpolations between guidelines commonly reported for agricultural species (e.g., Ref. 26), and those reported for apparently metals tolerant ecotypes of uncultivated grass species present in or near the study area (Ref. 27). Similar efforts were made in developing the DTPA-AB extractable ("plant available") metals levels, using Refs. 27 and 28 for establishing the upper and lower bounds for each of the three CoCs. Given the observed CoC concentrations (Tables 3-4 and 3-5), the plant available fractions of these elements may exceed the capacity of the extraction system to reliably predict plant available concentrations (Ref. 29). Thus, the criteria in Table 3-6 (Part A) should be viewed as rough approximations of metals levels indeed toxic to the tall fescue growing in the test plot soils.

Site-specific biogeochemical interactions between rooting zone soils and the vascular plants growing in them (Refs. 30, 31), as well as species-specific physiological characteristics regarding metals uptake and processing (Refs. 32-34), greatly complicate establishment of accurate CoC phytotoxicity values in LSB. Nevertheless, general guidance developed for agricultural species (e.g., Refs. 35, 36) plus data relevant to the study area (Ref. 27) were used to generate the credible criteria shown in Part B of Table 3-6.

The criteria document prepared by the U.S. Bureau of Land Management (Ref. 37), and several of the references cited therein, served as the principal source for preparing the herbivore-related values shown in Table 3-6 (Part B). A formal ecorisk assessment using species- and contaminant-specific toxicity reference values was beyond the scope of this project.

Comparison of the laboratory (soil/plant) data in Table 3-4 with the phytotoxicity assessment criteria in Table 3-6 indicates that:

- plant available and acid extractable levels of Cd and Zn are potentially phytotoxic to plant growth in all soils sampled, even after PA treatment; while
- PA treatment probably mitigates Pb-related phytotoxicity, as judged by the reduction in plant available Pb levels; and
- 1% PA treatment may be sufficient to mitigate Cd and Pb phytotoxicity in plants, but probably not for Zn (at least in nontolerant species).

The soils data in Table 3-5 indicates that adjustment of pH to within the target range (6.5–7.0), following PA treatment, will result in the following effects:

- occurrence of further reductions in plant available Cd and Pb levels, possibly to the degree that phytotoxicity is no longer likely; while
- plant available Zn levels may remain phytotoxic to the more sensitive plant species.

Given the likelihood that plant available aluminum levels would need to be >3 mg/kg at pH ≃5.2 (Ref.

38) to be phytotoxic, this element is not believed to pose a problem in test plot soils. Furthermore, PA treatment may be precipitating out soluble aluminum species (e.g., hydrated $A1^{+2}$, $A10H^{+2}$) as Pb/Zn-aluminophosphates of varying solubility (Ref. 25). Total aluminum levels in dry leaf and shoot biomass of grass/forb species are typically ≤100 mg/kg (Ref.39) and can range up to 300 mg/kg without presenting phytotoxicity in nonaccumulator species (Ref. 40). The relatively low aluminum concentrations also supports the view that detergent/water rinsing of biomass during sample preparation removed most of the surficial soil contamination, prior to digestion and analyses of the plant materials.

Plant available (Bray-1 extractable) P is probably low for agricultural production activities (i.e., 1.2 mg/kg; Appendix A); however, total P in plant biomass taken from the "control" plot(s) does not indicate a deficiency for this element (i.e., 2900–3400 mg/kg "expected"; Ref. 40). Furthermore, total P levels in biomass collected from the PA-treatment plots are certainly elevated (i.e., ≥5500 mg/kg P) but are probably not phytotoxic to grass/forb species (i.e., >10,000 mg/kg P) (Ref. 40).

As noted previously, at least Zn may exceed phytotoxicity threshold levels in plant biomass, following PA treatment of test soils. However, the above screening level criteria are neither:

- based on long-term statistical evaluation of species-specific biomass production data acquired from the various PA treatment conditions; nor
- do they recognize potential interelement (e.g., antagonistic) effects in overall phytotoxicity response (e.g., Ref. 41).

The criteria presented in Table 3-6 are probably conservative, in the sense that they would not fail to detect an environmental condition of potential concern to regulators or public health officials. However, situations exhibiting nearly certain phytotoxicity to non-metallophyte/ hyperaccumlator plant species and/or pose unacceptable threat to herbivores will require CoC levels in soil/biomass as shown in Table 3-8 (Ref. 43).

Comparison of the test plot data (Table 3-4, Part B) with the criteria in Table 3-8 indicates that Zn levels in biomass remains of concern regarding plant production (especially for common grass/forb reclamation species) and to sheep consuming such biomass. However, such potential hazards would be self-limiting, if the quality ("taste") and quantity (i.e., dry matter/m^2) are sufficiently poor to discourage use of such lands for grazing purposes.

The calculated Cd:Zn ratios in test plot soils are approximately 0.5:100, 0.6:100, and 0.5:100 for the 0% PA, 0.75% PA and 1% PA treatments, respectively (Table 3-4, Part A). There is no evidence that soil Cd can cause the first human health effect (renal tubular proteinuria) when Cd:Zn is <1.5:100, "even when smelters have contaminated soils to as high as 100 mg/kg" (Ref. 44, Abstract). Chaney and Ryan also argue that co-occurrence of Zn strongly reduces Cd retention in animal (particularly muscle) tissues, (Ref. 44, Abstract). Assuming the above Cd:Zn ratio applies equally to monogastric (human) and digastric (elk, cattle) species then:

- the CoC levels in test plot biomass (Table 3-4, Part B) are probably safe;
- the CoC levels in biomass from PA-treated soils (pH≥6.5) are probably acceptable for consumption by herbivores; and
- the above Cd:Zn ratios in PA-treated soils mitigates the food chain transfer concern, footnote *d* in Table 3-6.

Although the database is presently small, the overall weight-of-evidence indicates that PA treatment of mine/mill waste-contaminated soils exhibits significant positive effects on reducing the environmental mobility of the 2 principal CoCs (Cd and Pb). Therefore, as the benefits of in situ PA treatment/ revegetation (i.e., reduced

contaminant transport via wind/water erosion) exceed the subsequent environmental risks, such approach to remediation of the OU3 soils appears to be technically viable.

3.3.3 Brief Evaluation of the Soil and Plant Data from the Smelter Soils Test Plot

Comparison of the smelter plot soils data (Appendix Table A-1) with that from the present study (Table 3-4) indicates that:

- the mean-of-the-mean acid extractable Cd levels are slightly higher, while Pb and Zn levels are slightly lower, in the smelter soils (versus mill waste soils); and
- the untreated smelter soil has somewhat higher total organic carbon and cation exchange capacity levels than does the untreated mill waste soil (Appendix B, Table 2-1).

The latter observation may indicate slightly lower bioavailability of Pb (and possibly Cd) in smelter plot soils; the suggested mechanism would be preferential displacement of small cations (e.g., Ca^{+2} and Mg^{+2}) by larger ones (e.g., Pb^{+2} and Cd^{+2}) on both organic and inorganic (mineral) ion exchange sites (Ref. 45). Alternatively, if plant available CoC levels in mill waste-contaminated soils far exceed those in smelter soils, then such differences in soil characteristics would be immaterial; the "excess" metal ions available for plant uptake would be reflected in higher CoC levels in aboveground biomass due to mass action effects alone (i.e., "swamping out" the above exchange sites). There are no plant available or metals-specific partitioning data presently available to test these hypotheses.

Nevertheless, the concentration factor (CF) data presented in Table 3-8 indicates that Cd and Pb are more readily taken up into plants growing in mill waste, than smelter soils. Inspection of these data also shows that CF values for Cd and Pb decrease with increasing levels of PA treatment at both test sites. This observation provides additional evidence (to that found in Section 3.3.2) that such treatment significantly reduces plant availability of these two elements. It is possible that some benefit is achieved also for Zn, particularly when present at relatively low bioavailable concentrations (as is surmised for smelter plot soils). At 1% PA, there also appears to be sufficient molar excess of reagent to ensure nearly equal effectiveness in immobilizing Cd and Pb at potentially "low" and "high" plant available levels of these metals.

Finally, comparison of soil/plant data from the smelter plot against relevant screening criteria found in Table 3-6 indicates that:

- acid extractable metals levels in soils may be phytotoxic, especially Pb and Zn;
- acid extractable metals levels in leaf and shoot biomass are probably not phytotoxic, even in plants grown in untreated soil; and
- CoC levels in the biomass sampled are probably safe for long-term consumption by most domesticated and undomesticated herbivore species.

Therefore, in situ PA treatment/revegetation of OU3 soils would have at least neutral environmental benefit, and no appreciable environmental risks, following its implementation.

Table 3-1. Statistical uncertainty in endpoint-specific RBA values.

	%RBA Relative to Lead Acetate								
	Untreated (0% PA) Soil			0.75% PA-Treated Soil			1.0% PA-Treated Soil		
Measurement Endpoint	BE	LB	UB	BE	LB	UB	BE	LB	UB
Blood Lead Area Under the Curve (AUC)	40	32	48	47	36	61	40	28	56
Liver Lead	17	10	25	28	21	38	21	15	28
Kidney Lead	16	9	23	35	27	44	21	15	28
Bone Lead	35	26	45	34	27	44	25	20	32

Source: SRC, 2003, Table 5 (see Appendix D).

Table 3-2. Uncertainty in RBA point estimates combined across measurement endpoints.

	% RBA Relative to Lead Acetate		
Treatment Level	**2.5th**	**Mean**	**97.5th**
Untreated (0% PA)	13	36	48
0.75% PA-Treated	26	43	58
1.0% PA-Treated	18	36	51

Source: SRC, Table 6 (see Appendix D).

Table 3-3. Bioaccessibility results for the PA-treated mine waste soils (Ref. 21).

	Bioaccessibility (mg/kg)[a]	
Treatment Level	**As**	**Pb**
0% PA	0.7 ± 0.1 (2)[b]	2105 ± 7 (2)
0.75% PA	2.8 ± 0.1 (3)	997 ± 124 (3)
1% PA	2.8 ± 0.1 (3)	931 ± 148 (3)

Notes: [a]shows arithmetic mean ± standard deviation and (sample number).
[b]the mean of duplicate samples LM201 and LM211 was used in calculating this statistic.

Table 3-4. Laboratory data for the soil and plant samples collected in June 2001.

Part A. Soil Samples

	Parameters[a]					
Treatment	**1:1 pH/E_h**	**P/T A1**	**P/T Cd**	**P/T P**	**P/T Pb**	**P/T Zn**
0% PA	7.2/299	0.737/4100	51.7/122	18.3/1240	66.7/3850	982/23,800
0.75% PA	5.2/343	0.174/4170	26.1/123	505/16,600	15.7/3540	659/20,900
1% PA	5.4/315	0.113/3900	17.4/89	602/16,000	12.1/3390	619/16,900

Part B. Plant Samples

	Parameters[b]				
Treatment	**T Al**	**T Cd**	**T P**	**T Pb**	**T Zn**
0% PA	191	22.4	3100	118	1300
0.75% PA	91.1	14.4	5800	50.7	1250
1% PA	64.2	9.5	6500	40.7	1100

Notes: [a] pH/E_h of 1:1 soil:water extract are in standard units and millivolts, respectively; plant available (P; DTPA-AB) and strong acid extractable (T) levels are in mg/kg, oven dry weight.
[b] strong acid extractable (T) levels are in mg/kg, oven dry weight.

Table 3-5. Laboratory data for the soil liming investigation performed in July 2001.

	Parameters[a]				
Treatment	**1:1 pH Before Liming**	**1:1 pH After Liming**	**P Cd**	**P Pb**	**P Zn**
0.75% PA	5.26	6.90	8.8	9.8	474
1% Pa	5.08	6.86	10.1	11.3	464

Note: [a] pH values are in standard units; plant available (DTPA-AB extractable) metals in mg/kg, oven dry weight.

Table 3-6. Numerical criteria for evaluating the analytical laboratory results.

Part A. Phytotoxicity of Rooting Zone Soils		
Analytical Parameter	**Acid Extractable Levels[a]**	**Plant Available Levels[b]**
Cd	10–80	4–12
Pb	400–600	10–25
Zn	500–7000	70–800
Part B. Acid Extractable Levels in Leaf and Shoot Biomass		
Analytical Parameter	**Phytotoxicity[c]**	**Herbivore (Plant Ingestion) Risk[d]**
Cd	5–15 (≤1)	>5.0
Pb	20–40 (≤15)	>40.0
Zn	250–450 (≤100)	>500

Notes: [a] Levels are in mg/kg dry soil (Refs. 26 and 27).
[b] Levels are in mg/kg dry soil (Refs. 27 and 28).
[c] Levels are in mg/kg dry plant material (Refs. 27, 35, and 36); "expected" concentrations for plants growing in uncontaminated, but somewhat mineralized, soil are shown in parentheses.
[d] Levels are in mg/kg dry plant material (Ref. 37); dietary limitations of 0.5 mg/kg Cd and 30 mg/kg Pb (e.g., in cattle feed) have been suggested, based on human food residue considerations (Ref. 42.)

Table 3-7. Additional criteria for evaluating toxic effects of the CoCs on plants and herbivores (Ref. 43).

Part A. Likely upperbound phytotoxicity threshold criteria for nonmetallophyte species.			
	CoC Levels in Biomass[a]		
Analytical Parameter	**Cd**	**Pb**	**Zn**
Acid extractable metals[b]	50	200	500
Part B. Likely upperbound metals-tolerance criteria (chronic intake) for livestock species.			
	CoC Levels in Biomass[a]		
Livestock Species	**Cd**	**Pb**	**Zn**
Cattle	50–500	5–300	>2500
Horses	not determined	80–1000	>1500
Sheep	50–500	5–300	>1000

Notes: [a]in mg/kg of leaf and shoot biomass, dry weight.
[b]determined by such methods as strong acid digestion followed by ICP-AES.

Table 3-8. Calculated CoC-specific concentration factors for the smelter- and mill-waste test plots.[a]

Part A. Smelter Soils Test Plot[b]

	PA Treatment Level (pH)			
CoC	**0% PA (7.1)**	**0.5% PA (5.6)**	**1% PA (6.3)**	**% CF Reduction (1% PA vs. 0% PA)**
Cd	0.071	0.043	0.041	42
Pb	0.003	0.002	0.001	67
Zn	0.053	0.108	0.042	21

Part B. Mill Waste Soils Test Plot [c]

	PA Treatment Level (pH)			
CoC	**0% PA (7.2)**	**0.75% PA (5.2)**	**1% PA (5.4)**	**%CF Reduction (1% PA vs. 0 % PA)**
Cd	0.184	0.117	0.107	42
Pb	0.031	0.014	0.012	61
Zn	0.055	0.060	0.065	C

Notes: [a]Concentration factor = acid extractable CoC level in dry plant material ÷ acid extractable CoC level in dry soils (both in mg/kg).
[b]Soil and plant data are found in Appendix Tables A-1 and A-3, respectively.
[c]Soil and plant data are found in Table 3-4.

4. Conclusions And Recommendations

4.1 In Vivo Lead Bioavailability Studies

Data produced by the two MWTP-funded pig soil-dosing studies (by VMDL) are not sufficient to conclude, with any statistical confidence, that PA treatment(s) significantly lowered Pb-RBA in mine/mill waste-contaminated residential (OU3) soils from the Joplin, Missouri Superfund site. Such conclusions are precluded due to performing separate, rather than simultaneous, dosing of young swine with untreated versus PA-treated soils. The basis for this finding is presented below.

Historical data for Pb-RBA in OU3 soils indicates point estimates of about 80%, as compared to those around 58% in residential soils affected by smelter stack fallout (with OU2) (Ref. 51). Thus, an attempt was made to streamline the initial (2001) study by dosing young swine with PA-treated soils, only; the historical data (RBAs ≥ 58%) from previous investigations would serve as the untreated controls.

Given the variability of Pb-RBA observed in Joplin site soils, the project team decided to perform a second investigation in 2002. This abbreviated study used untreated soil from the field plot, plus one level (225 μg/kg.d) of PbAc dosing as compared to the 3 levels utilized in the initial study.

During review of the draft (September 2002 report), EPA/MWTP personnel identified concerns regarding methods used for statistical analysis of the 2 data sets, plus absence of 95% confidence limits around each of the treatment-specific Pb-RBA point estimates. Subsequently, the VMDL data were reanalyzed using improved, and more defensible, statistical methods. The key finding was that overlap in confidence limits between treatments prevents firm conclusions regarding effectiveness of PA treatment in lowering Pb-RBAs in OU3 soils. However, the higher RBAs observed historically, plus unusually low Pb absorption from untreated study plot soils (into pig tissues), suggests that 1% PA treatment does reduce Pb bioavailability in these soils.

In retrospect, study design should have involved direct comparison of RBAs from untreated soil to 0.75% PA-treated soil, first; this effort would be followed by comparison of RBAs from untreated soil to those treated with ≥ 1% PA. In both studies, all 3 dosing levels of PbAc would also be used. Performing such investigations, particularly on soils treated with PA at least 2 years ago, would provide the evidence needed regarding long-term viability of this in situ technology at Joplin.

4.2 In Vitro Lead Bioaccessibility Study

The mean Pb bioaccessibility results for the 1% and 0.75% PA soil treatments of OU3 soils were about 44% and 47%, respectively, of that observed in untreated soils. Regarding the 1% PA treatment level, the 56% reduction in Pb bioaccessibility is similar to the 44% reduction observed for Pb RBA (Section 4.1). It is also about the same magnitude as reported for smelter soils (i.e., 60% reduction), despite use of different Pb (in vitro) extraction methods.

Therefore, these study results lend credence to the potential for PA treatment of the smelter- and mine waste-affected residential soils.

4.3 Heavy Metals Phytoavailability Study

Treatment of OU3 soils with 1% PA is probably sufficient to mitigate Cd and Pb phytotoxicities in tall fescue, but probably not for Zn phytotoxicity, even at optimal pH (> 6.5). Only Zn appears to occur at levels in leaf and shoot biomass that may pose a chronic ingestion hazard to domestic or wildlife herbivore species. However, the Cd:Zn ratios in PA-treated soils probably mitigates any food chain Cd transfer concerns.

Although the phytoavailability database is presently small, the overall weight-of-evidence indicates that PA treatment of mine/mill waste-contaminated soils exhibits significant positive

effects on reducing the environmental mobility of Cd and Pb. Therefore, as the benefits of in situ PA treatment/revegetation (i.e., reduced contaminant transport via wind/water erosion) exceed the subsequent environmental risks, such approach to remediation of the mine waste-affected soils to appears to be technically viable. However, additional confidence in this conclusion would be gained by implementing at least some of the following activities:

- continued monitoring of field pH plus plant vigor, canopy cover, aerial biomass production and CoC levels in LSB over one to several additional growing seasons;
- evaluation of metals partitioning in untreated and treated soils, plus ecotoxicity evaluations using alternative test species, while using more sophisticated methods than applied during this study (e.g., Refs. 46–48); and
- correlating these findings (above) with metals speciation data generated by electron probe microanalysis of particles retrieved from treated and untreated soil samples.

Collectively, this information would provide considerable insight into the likely variation in treatment effectiveness over both time and space, and subsequently, be useful for optimizing treatment effectiveness at the Joplin (or other Pb-contaminated) site.

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