

Final Report CU-1350

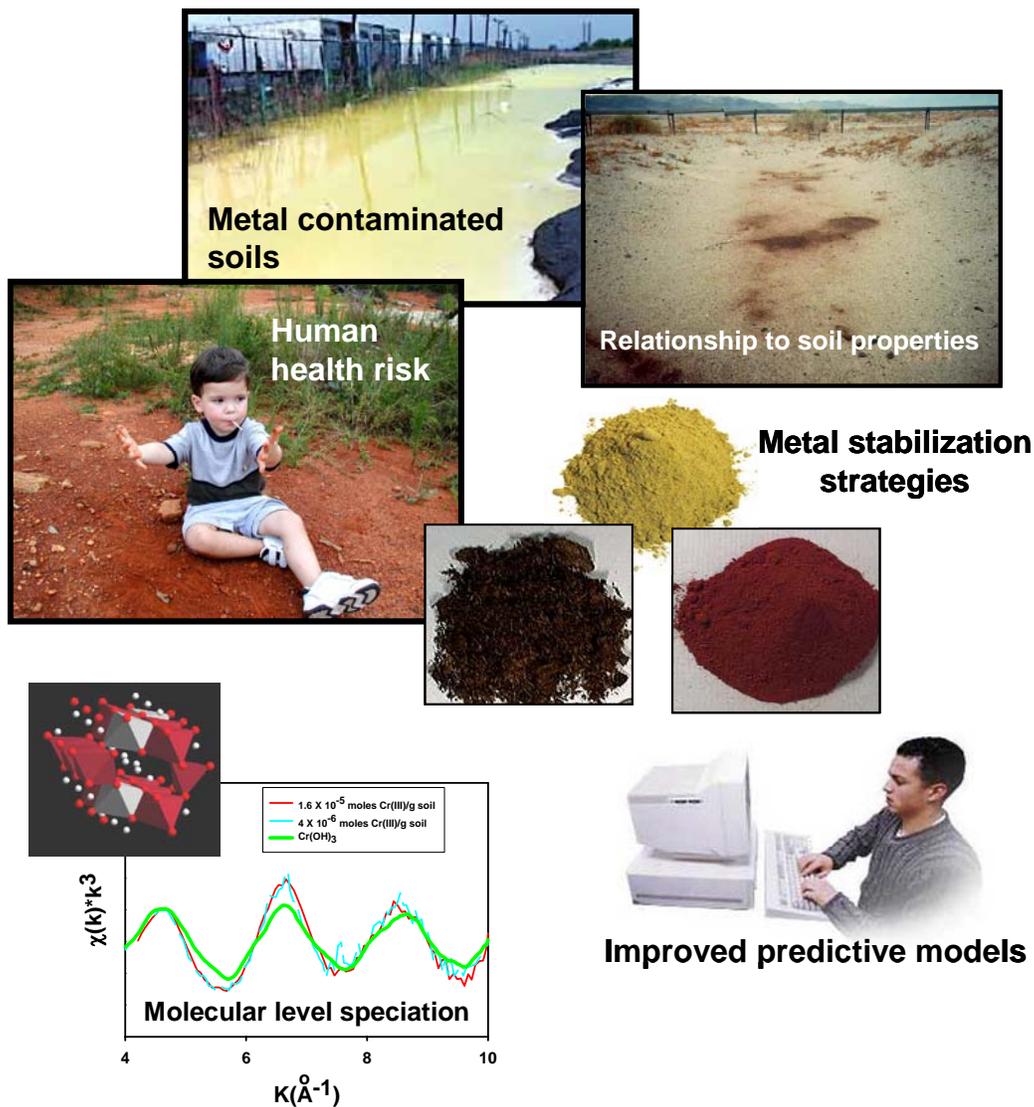
Decreasing Toxic Metal Bioavailability with Novel Soil Amendment Strategies

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PROJECT OBJECTIVES

The overall objective of this project is to develop an improved understanding and predictive capability of the enhanced immobilization and decreased bioaccessibility of hazardous metals in soil as a result of chemical amendment strategies. The specific objectives of this investigation are to:

- (1) Develop an improved understanding of the rates and mechanisms of enhanced metal sequestration in DoD soils that have been treated with various organic and inorganic amendment strategies.
- (2) Develop remedial protocols that maximize toxic metal sequestration and minimize bioaccessibility for a wide range of soil types and mixed metal systems encountered at DoD sites.
- (3) Develop an improved predictive capability for evaluating sequestration and bioaccessibility of mixed toxic metal systems for various amendments and soil types.

The proposed research is motivated by our previous SERDP-sponsored research findings (CU-1166) that indicated the conditions that reduce metal bioaccessibility in soils, and more importantly for the current research, conditions that do not favor reduced metal bioaccessibility in soils. For example, the bioaccessibility of weakly bound soil metals, such as Cd and Pb, is typically not reduced to the same extent as strongly bound metals such as As and Cr. Certain soil conditions also promote the enhanced bioaccessibility of strongly sequestered metals such as As and Cr. Thus, engineered additions of materials to soil that enhance the sequestration of toxic metals can potentially induce the formation of less hazardous metal forms, providing a practical approach to in-place inactivation. In the following research, we will show that non-toxic, low-cost, commercially available materials can be incorporated into soil to immobilize toxic metals and decrease metal bioaccessibility for long time periods. The research is an innovative response to SERDP's SON in that we integrate laboratory scale macroscopic fate and transport experiments with novel microscopic spectroscopy techniques to assess the kinetics and mechanisms of enhanced metal sequestration and decreased bioaccessibility as a function of various soil amendment strategies.

BACKGROUND

There are thousands of metal contaminated sites on DoD lands awaiting remediation and closure. The toxic metals Pb, As, Cr, and Cd are of particular concern since these metals control risk-based remedial decisions for soils at DoD sites (Exponent, 2001). Ingestion of contaminated soil by children is the exposure pathway that generally controls remediation goals (Pausterbach, 1989; Davis et al., 1990; Sheehan et al., 1991). With the exception of Pb-contaminated soils, the risk posed by soil ingestion is currently calculated from the total metal concentration and the allowed reference dose. Reference doses are available for most metals, and are typically derived from studies that have used very soluble metal species. In other words, with the exception of Pb, EPA's risk assessment guidance implicitly assumes a default relative bioavailability of 100%. The toxicity assessment for Pb is unique and is based on a pharmacokinetic model of blood Pb. The default bioavailability assumptions in EPA's blood-Pb model are 50% for food and water and 30% for soil, thus yielding a relative bioavailability in soil of 60% (30/50).

Metals in soil, however, can be relatively insoluble, and sometimes require aggressive digestion procedures for complete analytical metal recovery. As a result, reference doses developed from studies using soluble metal species may overstate the risk posed by less soluble metals in soils. Recent SERDP research within our group has shown that reference dose criteria used for soil As and Cr is often highly conservative since the indigenous metal-sequestering properties of many soils can significantly lower the bioavailability of ingested toxic metals relative to commonly used default values (Yang et al, 2002; 2003

Stewart et al., 2003 a,b). We used a relative bioaccessibility factor to show that numerous DoD soils throughout the U.S. can effectively sequester Cr(III/VI) and As(III/V) and significantly decrease metal bioavailability. Certain soil physical and chemical properties (e.g. Fe-oxide content, organic matter content, pH) were found to be highly correlated with decreased metal bioaccessibility, and statistical models were formulated to assess which soils had the greatest risk with regard to metal bioaccessibility. We also used high-resolution spectroscopic techniques, such as X-ray Absorption Spectroscopy, to quantify the chemical environment and speciation of the sequestered metals and to verify the modeling results. Studies conducted at DOE's Stanford Synchrotron Radiation Laboratory confirmed that numerous DoD soils contained natural soil constituents that could reduce mobile Cr(VI) to the less toxic Cr(III) species, and oxidize highly mobile As(III) to the less mobile As(V) species. These redox transformation processes caused a significant decrease in the toxic metal bioaccessibility. Nevertheless, certain soil conditions were also found to promote the enhanced bioavailability of these metals. For example, when the soil Fe-oxide content for a particular DoD soil fell below 0.5% on a mass basis, the bioaccessibility of As increased dramatically, particularly for alkaline soils (Yang et al., 2002, 2003). Likewise, for DoD soils low in organic and inorganic carbon, the bioaccessibility of Cr(III) and Cr(VI) is significantly higher relative to soils which possessed these mineral constituents (Stewart et al., 2003 a, b). It is these conditions for which engineered additions of soil amendments may enhance the sequestration of toxic metals and potentially induce the formation of less hazardous metal forms, providing a practical approach to in-place inactivation.

Recent SERDP research within our group on DoD contaminated soils and DOE firing range soils, also found that nearly all soil-bound Pb was bioaccessible even at very high solid phase Pb concentrations (near 1% on a mass basis). These data were in agreement with Pb-spiked DoD soils from around the country that suggested Pb bioaccessibility remained high despite the fact that it was thoroughly adsorbed to various mineral constituents in the soils (Yang et al., 2002). Molecular speciation analyses using XAS suggested that Pb(II) was weakly associated with the soil via electrostatic interactions). Apparently in these systems, the weak surface bonds between Pb and soil were easily disrupted by the acidic conditions encountered in the stomach digestive system, allowing the Pb to be much more bioavailable relative to Pb in mining soils which exist most likely as sparingly- soluble PbS.

Contaminated DoD soils lacking the ability to naturally sequester and decrease toxic metal bioavailability will remain a human health risk in their natural state. Methods for the in situ stabilization of contaminants present an attractive alternative to *ex situ* methods due to the lower cost and the potential for achieving remediation objectives. Chemical manipulation strategies are most attractive for metal contaminated soils since the redox state and chemical speciation of metals can easily be altered through changes in soil geochemistry. *In situ* incorporation of various organic and inorganic constituents, such as clay minerals and zeolites, organic matter, phosphate compounds, ferrous-iron bearing minerals, and limestone can change the chemical environment and speciation of metals in soils (GarciaDelgado et al., 1996; Traina and Laperche, 1999; Jardine et al., 1999; Lothenbach et al., 1999; Hettiarachchi et al., 2000; McGowen et al., 2001; Yang et al., 2001; Moirou et al., 2001; Wang et al., 2001). Research in this area has emphasized amendment strategies targeted at immobilizing Pb in soils, where phosphate bearing minerals such as hydroxyapatite and rock phosphates have been shown to be extremely effective (Zhang et al., 1998; Traina and Laperche, 1999; Pearson et al., 2000; Ryan et al., 2001). Despite the success of chemical manipulation strategies for immobilizing Pb in various subsurface environments, this area of research remains immature with regard to other toxic metals and the effects of varying soil type. Chemical manipulation strategies have not been investigated to a significant extent on a vast array of DoD soils or on DoD priority contaminants other than Pb (e.g. As(III/V), Cr(III,VI), and Cd). While P-compounds may work well at immobilizing Pb in soil, they do very little to stabilize Cd, and actually accelerate the movement of As(III/V) and Cr(VI) in soils (Boisson et al., 1999; Pearson et al., 2000; Seaman et al., 2001). The rates and mechanisms that control enhanced metal sequestration and decreased bioavailability in DoD soils are largely unknown, as are the costs associated with risk-reduction due to

decreased bioaccessibility of metals in amended soils. The following research seeks to address these issues through a series of hypothesis-driven tasks that seek to demonstrate that non-toxic, low-cost, commercially available soil amendment strategies can be used to immobilize toxic metals *in situ* for long time periods and decrease metal bioaccessibility.

APPROACH

The research approach of this project involves a series of multidisciplinary tasks that couple mechanistic macroscopic-scale metal immobilization studies with microscopic-scale interrogation of solid-phase interfacial processes and numerical modeling. We use field-relevant, laboratory-based metal immobilization studies that target the DoD priority metals Pb, Cd, As(III/V), and Cr(III/VI) in numerous different types of DoD soils. We utilize a unique experimental design that couples contaminant fate and transport monitoring on chemically amended soils, with metal bioaccessibility and molecular speciation using techniques such as synchrotron-generated radiation. Empirical models that relate metal bioaccessibility to soil properties and amendments have also been formulated and applied to various DoD sites.

Soil collection

For this research, we collected two types of soils: contaminated soils from DoD sites and uncontaminated soils representative of DoD sites from around the United States. The uncontaminated soils were similar to those used in the previous SERDP funded project CU-1166 where an effort was made to acquire additional soils from the western U.S. Experiments conducted with soluble metals added to uncontaminated soil allowed us to investigate the sequestration techniques for the most important operational species from a bioavailability standpoint, labile metals. Contaminated soils from a wide range of DoD sites were also used to identify the sources of the most labile and bioavailable metal species (e.g., oxide coatings on bullet fragments) and to test and validate our understanding of sequestration techniques developed in experiments with soluble metals.

TASK A: Enhanced Immobilization and Decreased Bioaccessibility of Single and Mixed Metal Soil Systems

A.1 Stabilizing redox-stable toxic metals: Cd- and Pb- soils

Pb-soils: Stabilization by precipitation

In this task we quantify the rate and magnitude of Pb immobilization on Pb-contaminated and Pb-spiked DoD soils using various phosphate sources including rock phosphate, hydroxyapatite, and triple super phosphate. The effect of amendment type, loading level, and aging were assessed on DoD soils that varied considerably in their physical and chemical properties. Laboratory amendment strategies mimicked a well-mixed tillage approach with loading levels designed for scale-up to the field. Loading levels for the various phosphate sources were 0.5, 1.0, and 5.0 % P w/w. Such treatment strategies are economical for implementing at the field scale. Rock phosphate and apatite cost \$0.25 and \$0.35 per kg, respectively, which suggests treating a 1 hectare square field soil to a depth of 10 cm would cost between \$1,800 to \$12,500 / hectare for the 1% and 5% loading levels, respectively. The rate and extent of metal immobilization and bioaccessibility were quantified on each amended soil and its control as described below.

Cd-soils: Stabilization by complexation

In this task we propose to use a novel approach that takes advantage of the low solubility of CdS precipitates. Ca-polysulfide will be added to the contaminated and Cd-spiked DoD soils. Previous research involving Hg(II), which also forms highly insoluble precipitates with S²⁻ suggests preferential

bonding of Hg(II) to reduced organic S sites (Xia et al., 1999; Hesterberg et al., 2001). The reduced S functional groups are known to be stable under aerobic conditions (Hutchison et al., 2001) and they should effectively sequester Cd from contaminated soils. Thus, strong preferential bonding of Cd to reduced sulfide ligand should result in a significant decrease in Cd bioavailability. As with the Pb system, the effect of amendment types, loading level, and aging will be assessed on the various DoD soils. Laboratory amendment strategies will mimic a well-mixed tillage approach with loading levels designed for scale-up to the field. Loading levels for Ca-polysulfide will be 0.5, 1.0, and 5.0 % w/w. As with the Pb system, the rate and extent of metal immobilization and bioaccessibility will be quantified on each amended soils and its control as described below.

A.2 Stabilizing redox-sensitive toxic metals: Cr- and As- soils

Cr-soils: Stabilization by reduction

Studies by Stewart et al. (2003 a) have already demonstrated that numerous DoD soils can effectively reduce Cr(VI) to Cr(III) with a corresponding dramatic decrease in Cr bioaccessibility. Because of its effectiveness, commercial availability, and low-cost, organic matter amendment strategies are emphasized for Cr contaminated soils. For soils with pH values above 8, Cr(VI) reduction by organic matter may be kinetically prohibitive and this was monitored using synchrotron radiation. For such conditions, alternative Cr(VI) reduction strategies may be considered. The effect of amendment loading level, aging, and soil properties were assessed for the various DoD soils. Laboratory amendment strategies mimicked a well-mixed tillage approach with loading levels designed for scale-up to the field. Loading levels for humus or sphagnum moss will be 0.5, 1.0, and 5.0 % w/w. Such treatment strategies are economical for implementing at the field scale. Premium grade humus or sphagnum moss cost \$0.10 per kg which suggests treating a 1 hectare square field soil to a depth of 10 cm would cost \$550 and \$2,700 / hectare for the 1% and 5% loading levels. The rate and extent of metal immobilization and bioaccessibility were quantified on each amended soil and it's control as described below.

As-soils: Stabilization by Oxidation

Studies by Yang et al.(2005) have already demonstrated that numerous DoD soils can effectively oxidize As(III) to As(V) with a corresponding dramatic decrease in As bioaccessibility. These finding coupled with the fact that Fe-oxides strongly sequester and decrease the bioaccessibility of both As(III) and As(V), suggest that soluble Fe or Fe(III)-oxide amendments strategies in DoD soils may be an effective, low-cost remedial strategy for As contaminated soils. Because of its effectiveness, low-cost, and ease of production and commercial availability, soluble Fe and Fe-oxide amendment strategies are emphasized for As contaminated soils. The effect of amendment surface area, crystallinity, and loading level, as well as aging and soil properties were assessed for the various DoD soils. Laboratory amendment strategies mimicked a well-mixed tillage approach with loading levels designed for scale-up to the field. Loading levels for hematite were 0.5, 1.0, and 5.0% w/w. Such treatment strategies are economical for implementing at the field scale. Commercial grade hematite cost \$0.22 per kg which suggests treating a 1 hectare square field soil to a depth of 10 cm would cost \$1,500 and \$7,800 / hectare for the 1% and 5% loading levels, respectively. The rate and extent of metal immobilization and bioaccessibility were quantified on each amended soil and its control as described below.

A.3 Quantify Soil-Metal Bioaccessibility

We used the physiologically-based extraction test (PBET) to measure contaminant bioaccessibility (a surrogate for bioavailability measured in a *in vitro* test) on chemically amended and unamended DoD soils (Stewart et al., 2003 a,b; Yang et al., 2002; 2003; 2005). The PBET is an *in vitro* leaching procedure designed to replicate the solubility-limiting conditions of a child's digestive tract. Results of the *in vitro* PBET method have been shown to correlate well with results from *in vivo* animal studies for

Pb and As (Ruby et al., 1996; Rodriguez et al., 1999). The PBET will be performed at both a pH of 1.5 and 2.3. Analytical analysis of the metals will be accomplished via ICP-MS and AA. Matrix matching is the most important aspect of the analyses since a variety of wet chemical techniques was involved in the investigation (e.g. EPA total digest method for total solid phase metals, PBET extraction). Each PBET measurement was performed on triplicate samples. A rigorous QA/QC protocol is used where triplicate analyses are performed on samples and internal standards are analyzed every 10 to 15 samples. With regard to the total digest analyses, soils from the National Institute of Standards, with known concentrations of solid phase metals, were also analyzed with each block of analyses (12 samples). On numerous occasions, samples were reanalyzed at different institutions (ORNL, Stanford, and Auburn) to ensure accuracy and precision.

A.4 Metal speciation using high-resolution spectroscopy techniques.

The mechanisms of enhanced metal sequestration and solid-phase metal speciation were quantified with a variety of high-resolution surface spectroscopy techniques including X-ray Diffraction (XRD), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), Transition Electron Microscopy (TEM), Raman Spectroscopy, Fourier Transform Infrared (FTIR) Spectroscopy, and X-ray Absorption Spectroscopy (XAS). Bulk XRD, SEM, and TEM measurements were conducted at the premier facilities for determining the environmental speciation of metals, located at DOE's Environmental Molecular Science Laboratory (EMSL), Pacific Northwest Laboratory, Richland, WA., which provided direct quantification of the mineralogic and crystallographic nature of solid phase contaminants that form in response to various amendment strategies. We also conducted synchrotron-based XRD at the Stanford Synchrotron Radiation Laboratory (SSRL) using beamline 2-1. The high-intensity x-ray source improved our detection limits for crystalline solids by more than an order of magnitude relative to conventional x-ray sources. The molecular-scale information provided an improved conceptual understanding of toxic metal sequestration that will be incorporated into more rigorous mechanistic models for predicting metal bioavailability in subsurface environments. This task builds upon our previous SERDP research (CU-1166) that has established baseline relationships between molecular metal speciation and bioavailability in soils, as well as the molecular scale validation of macroscopic metal bioavailability statistical models.

TASK B: Quantitative Models for Metal Sequestration and Bioaccessibility

Empirical mathematical models will be developed to predict metal bioaccessibility as a function of baseline soil properties and types and quantities of soil amendments. This approach has been extremely effective in our previous SERDP research, CU-1166, where the bioaccessibility of As(V), Cr(III), and Cr(VI) were significantly correlated with key soil properties (Yang et al., 2002, 2003; Stewart et al., 2003 a,b; Jardine et al., 2007). A multiple linear regression strategy revealed that more than 80 percent of the variability in soil-As(V) bioaccessibility could be described by the soil pH and Fe-oxide content, and that more than 70 percent of the variability in soil-Cr(III/VI) bioaccessibility could be described by the soil clay and TOC or TIC content. The validity of the models was supported with metal speciation results obtained with XAS at SSRL and the Advanced Photon Source (APS) which showed that As(V) was preferentially sorbed to soil Fe-oxides and Cr(III/VI) redox dynamics and sequestration were controlled by organic and inorganic carbon. Due to greater anticipated complexity of relationships investigated in this study, we utilized a more flexible and powerful neural network modeling technique to develop predictive models. Neural networks look for patterns in data sets, learn these patterns, and develop the ability to make forecasts and predictions in a manner that mimics the brain's problem solving process (Caudill and Butler, 1990; Specht, 1991; Chen, 1996). Neural networks initially identify linear relationships between input and output variables and then add additional model layers ("hidden neurons") to describe nonlinear relationships. The network "learns" by adjusting interconnection weights between layers until no further improvement in the model can be made. By coupling the bioaccessibility and amended soil property models, bioaccessibility may be estimated as a function of amendment and

baseline soil properties for individual metals. Based on the working hypothesis that multiple contaminants do not interact and that multiple amendment effects are linearly separable, the models may be further used to estimate bioaccessibility for multiple metal systems in response to combinations of amendments. The assumption will be tested by comparing model prediction to data from samples with multiple metal contaminants and multiple amendments.

RESULTS AND DISCUSSION

The following section has been divided into four discussion topics, namely (1) decreasing soil Pb bioaccessibility, (2) decreasing soil Cr(VI) bioaccessibility, (3) decreasing soil As(V) bioaccessibility, and (4) decreasing soil Cd bioaccessibility. Detailed discussions of each topical area are available through peer-reviewed publications and published abstracts listed in the Publication section of this text.

Decreasing Soil Lead Bioaccessibility

Soil Pb Stabilization and Decreased Bioaccessibility through Phosphate Treatments

In-situ stabilization of soil Pb using phosphorus (P) amendments, such as phosphate fertilizers and phosphate rock, have been suggested as a cost-effective and less disruptive alternative for remediating Pb in soils relative to several other commonly used methods. In the current research we examined the effect of time (0-365 days), *in vitro* extraction pH (1.5 versus 2.3), and dosage of three different phosphate-based amendments on the reduction in the bioaccessibility (as a surrogate for oral bioavailability) of Pb in

**Phosphate treated Pb contaminated DoD soils
Pb bioaccessibility at pH 1.5 and pH 2.3**

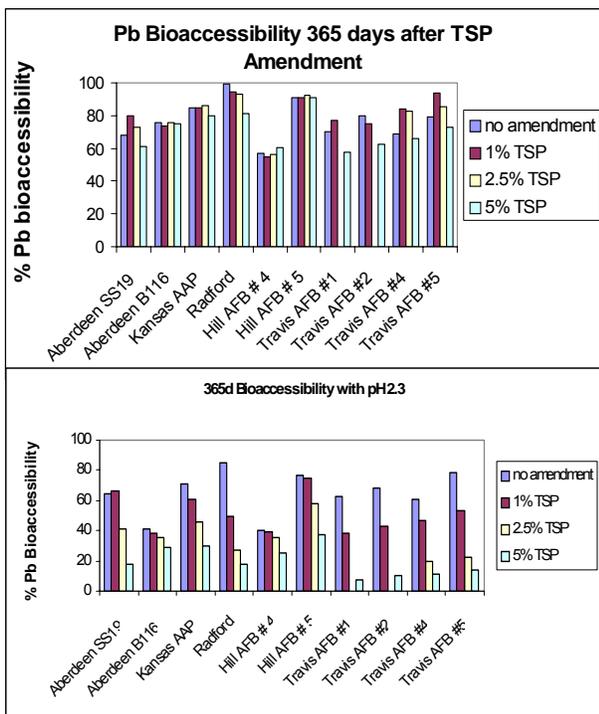


Figure 1

DoD soils with high concentrations of Pb typically did not show a decrease in soil-Pb bioaccessibility when treated with hydroxyapatite, rock phosphate, or triple super phosphate (TSP) using PBET pH 1.5.

Decreased Pb bioaccessibility by P was much more significant at a PBET pH of 2.3 vs. 1.5.

Increased mass loadings of up to 5% P on a w/w soil basis did significantly decrease Pb bioaccessibility.

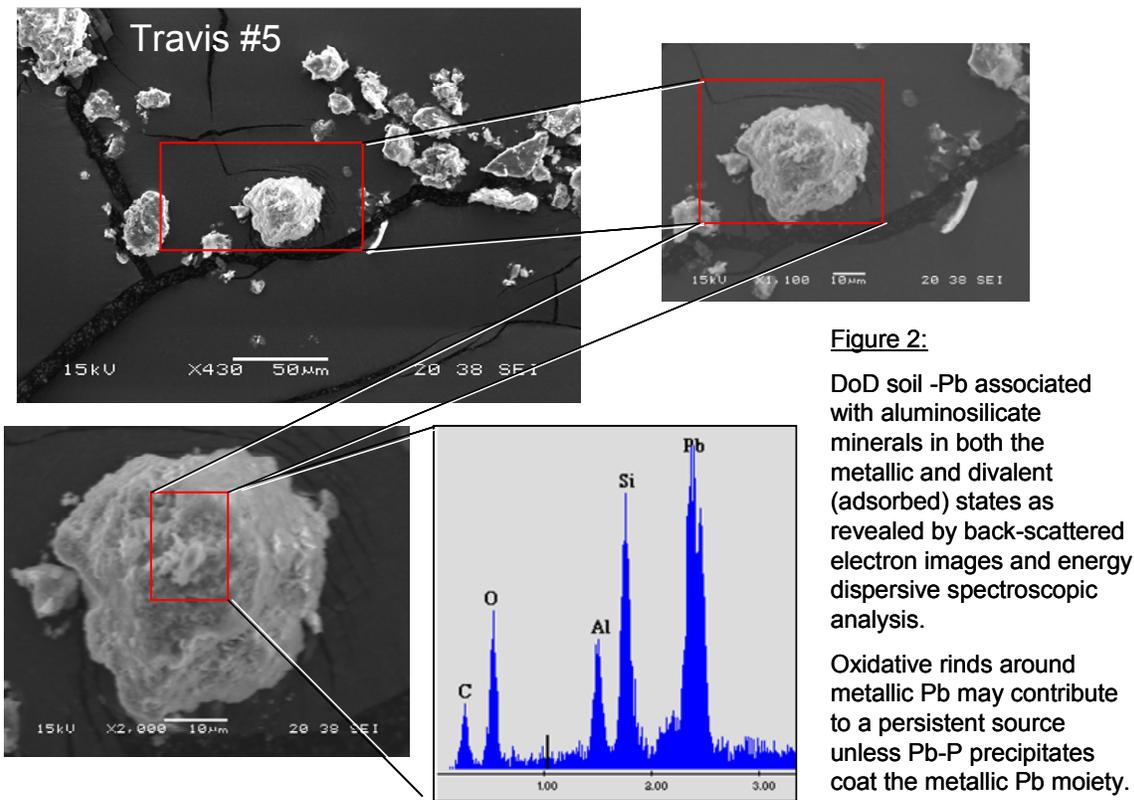
P interactions are rapid and stable with little change from 30 d to 365d.

ten soils from U. S. Department of Defense (DoD) facilities. Initial unamended soil Pb bioaccessibility consistently exceeded the U. S. Environmental Protection Agency default value of 60% relative bioavailability at a pH of 1.5 but not at a pH of 2.3 (Fig. 1). This suggested that Pb bioavailability under conditions of a fasting human stomach environment (pH=1.5) were of possible concern to induce health effects (Yang et al., 2003). The results also suggested that these potential health effects diminish when food is present within the

stomach which causes stomach pH environment to increase (e.g. >2.3). Although phosphate-based amendments statistically (statistical $p < 0.05$) reduced bioaccessibility in many instances, with reduction dependent on the amendment type and dosage, large amendment dosages (c. 20-25% by mass to yield 5% P by mass) were required to reduce average bioaccessibility by c. 25%. For most amendment

combinations, soil Pb bioaccessibility continued to decrease for periods up to one year, indicating that the observed reductions were not merely experimental artifacts of the *in vitro* extraction procedure. Although our results indicated that reductions in Pb bioaccessibility with P amendments are technically feasible, relatively large (up to 26.2% by weight) amendment masses were required to achieve relatively modest (c. 25%) reductions in bioaccessibility. The need for high P dosage levels for moderate reductions in Pb bioaccessibility most likely reflects the source of Pb in these soils which is predominately metallic Pb as bullet fragments (Fig. 2). The oxidation rinds surrounding this metallic Pb source may have occluded regimes that are inaccessible to P relative to the more aggressive action of high concentrations of hydronium ions within the PBET. These findings suggest that the cost and environmental implications of adding such large amounts of P to soil may reflect practical limitations of remediating Pb contaminated DoD soils with P-based *in situ* stabilization.

The speciation of DoD soil Pb contributes to the difficulty of decreasing its bioaccessibility with P amendments



Potentially Adverse Effects of Soil Pb Stabilization and Decreased Bioaccessibility Through Phosphate Treatments

The potential negative effects of adding phosphate containing fertilizers as amendments for Pb immobilization in contaminated soils were studied using column and batch experiments. Soils contaminated with high levels of lead (Pb), arsenic (As), and antimony (Sb) were amended with triple superphosphate (TSP). Sb is used as a hardening agent in Pb bullets and this is a significant problem in Europe and the U.S. since Sb is highly toxic and mobile in soils and may become a significant groundwater pollutant. Strong linear correlations were observed between Sb and Pb in both bullets collected from a small-arm firing range as well as several soils samples collected from three different metal-contaminated sites (Fig. 3). No linear correlations were observed between As and Pb at these sites,

however, indicating the presence of As to be either naturally occurring or indigenous. Results from miscible displacement studies suggested that elevated concentrations of Sb and As were present in

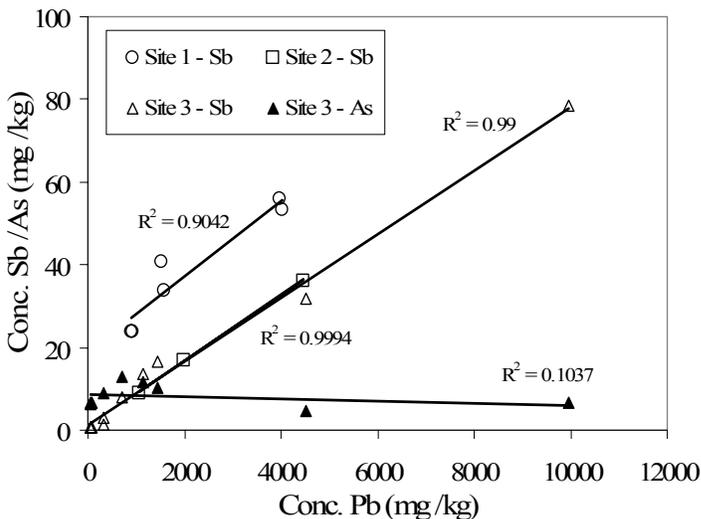


Figure 3: Correlations between Sb and Pb at three different sites and As and Pb at one site. Strong correlations were observed between Sb and Pb at all three sites ($r^2 > 0.9$), while a weak correlation was observed between As and Pb at site 3 ($r^2 = 0.1037$).

indicated that Pb migration was not accelerated when amended with 5% P via TSP addition to contaminated soils.

Batch experiments revealed bioavailability changes in both Sb and As, though these changes were not necessarily negative. In a contaminated soil with a higher sand fraction, Sb bioaccessibility increased with phosphate addition, while As bioaccessibility decreased. A contaminated firing range soil with a slightly higher clay fraction, showed a slight increase in As bioaccessibility and a decrease in Sb bioaccessibility. These results indicate varying bioavailability behavior between As and Sb at varying sites. Bioavailability studies involving various phosphate amendments and multiple contaminated soils should be conducted in order to fully make any assessments in regard to As and Sb bioavailability. With regards to Pb bioavailability, Pb bioaccessibility values were greatly decreased in both contaminated soils at the highest TSP additions.

column effluent for P amended soils vs. unamended soils (Fig. 4). Adding phosphate amendments to Pb contaminated soils can both decrease the mobility and the bioavailability of Pb, limiting its negative health impacts on humans. However, phosphate use as an amendment may have a significant impact on both the mobility and bioavailability of Sb and As. Thus, phosphate additions to lead contaminated soils that also contain elevated concentrations of Sb and As, can greatly increase the mobility of Sb and As. Because As and phosphate are known to compete for reaction sites, along with the fact that Sb is also similar to As in chemical behavior, an abundance of phosphate may lead to the increased mobility of As and Sb in a contaminated soil. With regard to Pb mobility, column studies employed in this research

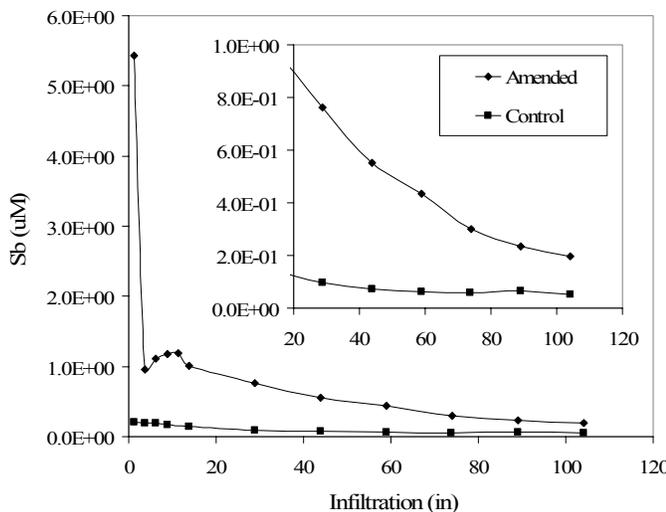


Figure 4: Antimony leachate concentrations versus infiltration through the amended and control columns for the third column test. Amended indicates soil column with TSP addition; control indicates soil column without TSP.

Decreasing Soil Chromium (VI) Bioaccessibility

Soil Cr Stabilization and Decreased Bioaccessibility through Organic Matter Treatments

In-situ stabilization of Cr(VI) in soil has been viewed as a particularly difficult challenge since Cr(VI) exist as an anion and soils are typically dominated by negatively charged minerals. Thus the retention of Cr(VI) by soils is typically poor and it remains a mobile, carcinogenic contaminant in many environmental systems. In the present research we investigated the propensity of soil organic matter amendments to enhance the stabilization of soil Cr(VI) which may in turn decrease the bioavailability of the contaminant. We examined the effect of time (0-365 days) and dosage rate of natural peat amendments on the reduction of Cr(VI) bioaccessibility (as a surrogate for oral bioavailability) in numerous DoD Cr(VI) contaminated soils and in a large number of soils with drastically differing properties that were spiked with Cr(VI). Initial unamended soil Cr(VI) bioaccessibility as determined by PBET pH=1.5 consistently exceeded the U. S. Environmental Protection Agency default value of 100 % relative bioavailability. Multiple regression analysis suggested that more than 60% of the variability in Cr(VI) bioaccessibility could be described by soil organic C and pH (Fig. 5a). Results suggested that when indigenous soil organic C fell below ~0.5% w/w the bioaccessibility of Cr(VI) increased dramatically from a low 10-20 % to nearly 65 % (Fig. 5b).

Bioaccessibility of Cr(VI) decreases as soil natural organic carbon increases

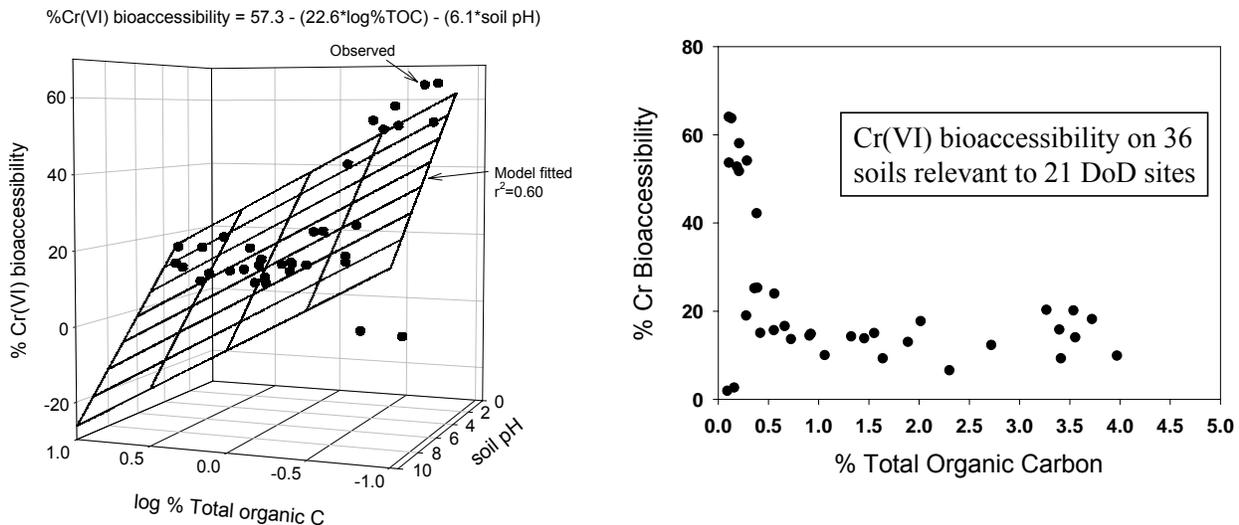


Figure 5 a: Over 60% of variability in Cr(VI) bioaccessibility described by soil organic C and pH

Figure 5 b: Cr bioaccessibility on Cr(VI) contaminated soils decreases significantly when soil organic carbon increases above ~0.5 % on a mass basis

The addition of a natural peat source to various Cr(VI) contaminated DoD soils and Cr(VI) spiked soils with drastically different soil properties resulted in a large decrease in Cr(VI) bioaccessibility in most cases (Fig. 6). Typically as the addition of soil peat increased from 1 to 5 % peat w/w, a corresponding decrease in Cr(VI) bioaccessibility was noted. The reaction kinetics of the decreased bioaccessibility was rapid such that Cr stabilization via reaction with peat was nearly complete within 60 d.

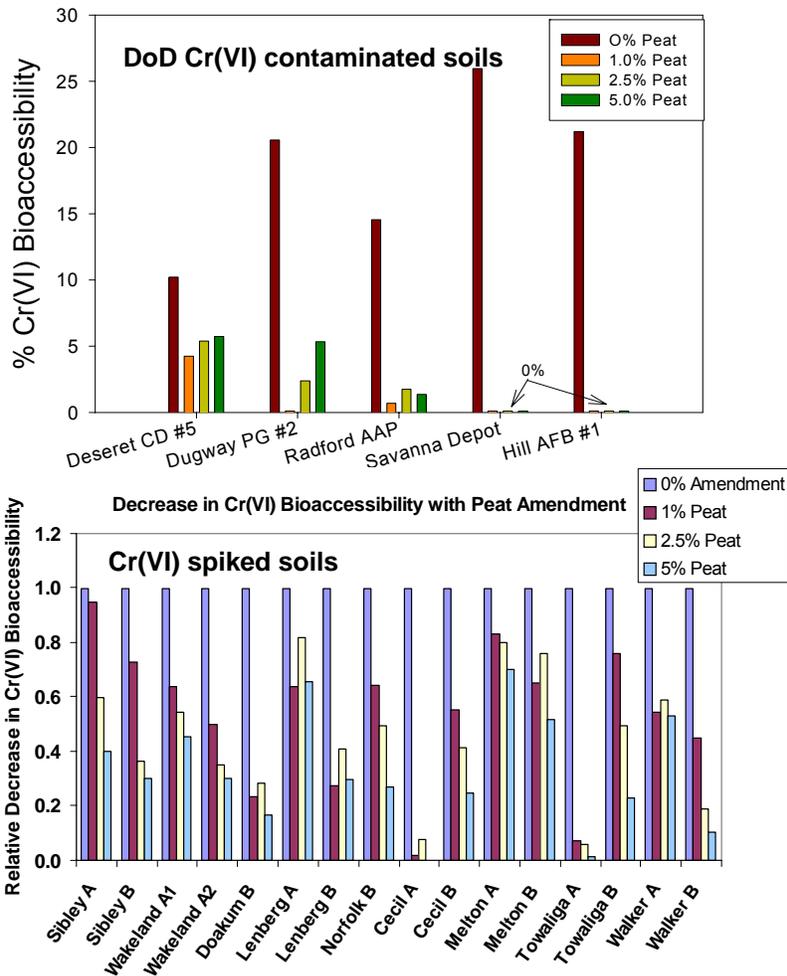


Figure 6: Peat amendments are very effective at decreasing the bioaccessibility of Cr(VI) in DoD contaminated soils and metal spiked soils.

High-resolution interfacial surface spectroscopy techniques were used to assess the mechanism of enhanced Cr stabilization and decreased bioaccessibility. X-ray Absorption Near Edge Structure (XANES) suggested that Cr(VI) was reduced to Cr(III) in the presence of organic matter or peat (Fig. 7). Extended X-ray Absorption Fine Structure (EXAFS) revealed that the reduction product Cr(III) was precipitated as sparingly soluble Cr(III)-hydroxide (Fig. 7). The trivalent cation Cr(III) is highly reactive in soil systems and tends to precipitate from solution above pH 5.0 (Stewart et al., 2003 b). The precipitation products are often surface reactive and highly resistant to reoxidation. Backscattering electron imaging confirmed that the Cr(III)-hydroxide formed in these systems was associated with soil Fe-oxides thus suggesting reoxidation of surface bound Cr(III) to Cr(VI) was highly unlikely (Fig. 8).

Therefore, the transformation of Cr(VI) to Cr(III) coupled with the surface reactivity of the latter results in a very significant decrease in Cr(VI) bioaccessibility and risk with regard to human health.

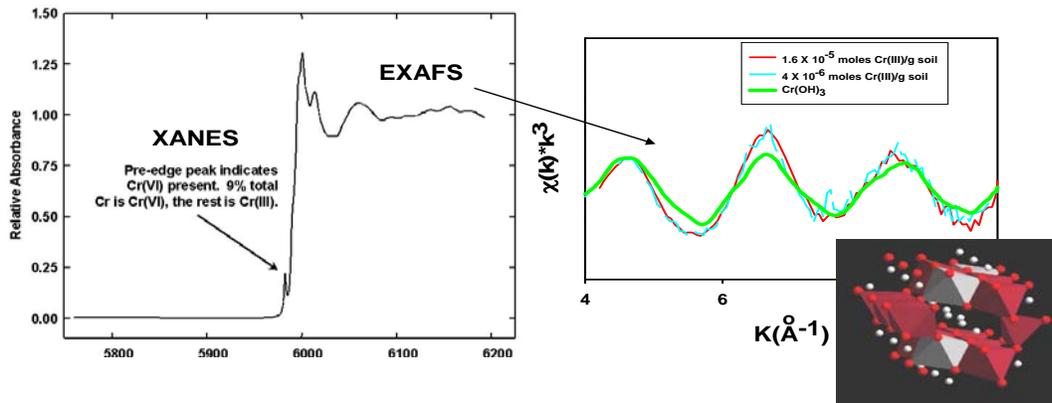


Figure 7: X-ray Absorption Spectroscopy confirms that peat amendments enhance the reduction of Cr(VI) to sparingly soluble Cr(III)-hydroxides. Reoxidation to Cr(VI) is extremely unlikely and would require the addition of powerful oxidants such as Mn-oxides. Even then, surface stabilized Cr(III) may not reoxidize.

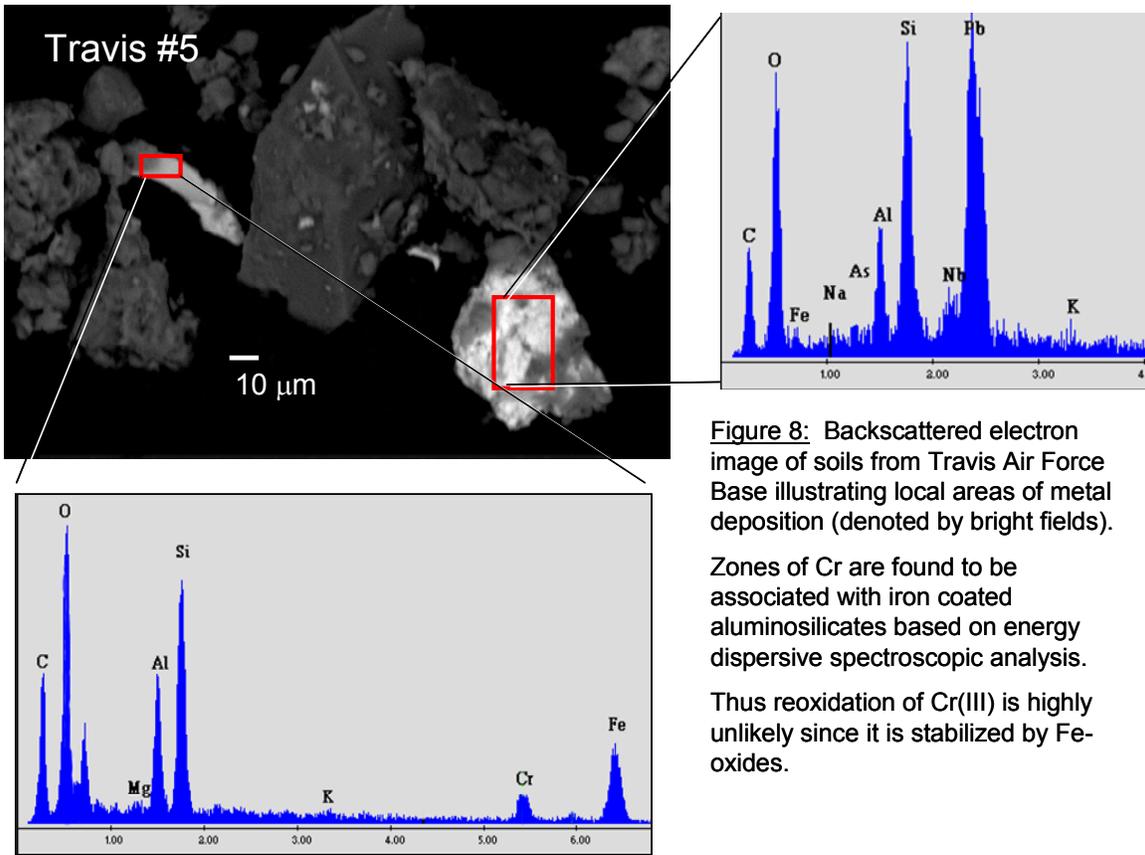


Figure 8: Backscattered electron image of soils from Travis Air Force Base illustrating local areas of metal deposition (denoted by bright fields).

Zones of Cr are found to be associated with iron coated aluminosilicates based on energy dispersive spectroscopic analysis.

Thus reoxidation of Cr(III) is highly unlikely since it is stabilized by Fe-oxides.

This project also initiated new modeling endeavors that developed Neural Network Models (NNM) to estimate bioavailable metal concentrations for baseline conditions from site characterization data as well as to estimate bioavailable metal concentration reductions following addition of soil amendments. Due to funding constraints we did not complete tasks designed to incorporate the NNMs into spreadsheet tools for estimating baseline health risk and risk following soil amendment additions. We also did not implement uncertainty and cost analyses into the models to facilitate decision making on remedial options and data collection

Chromium VI Model

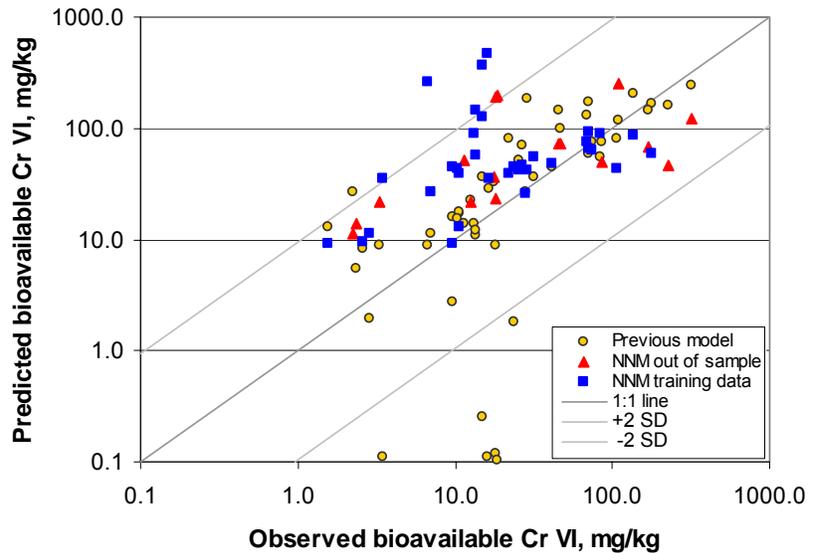


Figure 9: Neural Net Model was a better predictor and more robust than previous multiple regression model as it predicts / estimates over many orders of magnitude. This method will significantly enhance bioaccessibility spreadsheet tool (SBAT) developed in previous CU-1166.

requirements. The research did however show that that the developed NNMs were better predictors of metal bioaccessibility as a function of soil properties versus traditional multiple regression models developed in CU-1166 (Figure 9). The new NNMs were more robust and could predict bioaccessibility changes over many orders of magnitude.

Decreasing Soil Arsenic (V) Bioaccessibility

Soil As Stabilization and Decreased Bioaccessibility through Soluble Fe Treatments

We investigated the use of various iron amendments (metallic Fe and soluble Fe(II)- and Fe(III)-halide salts) to reduce arsenic (As) bioaccessibility (as a surrogate for oral bioavailability) in contaminated soils. Previous research of CU-1166 showed that As(III) and As(V) bioaccessibility in soils was controlled primarily by the soil Fe-oxide content and pH (Fig. 10 a). Bioaccessibility of As decreased significantly as the soil Fe-oxide content increased above 0.5 to 1.0% on a mass basis (Fig. 10 b).

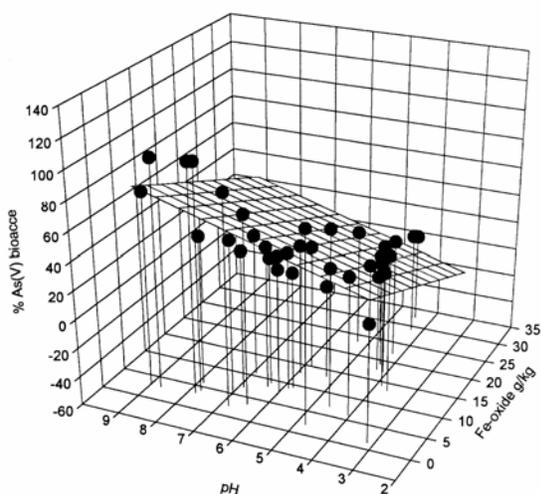


Figure 10 a: Over 75% of variability in As(V) bioaccessibility described by soil Fe-oxide content and pH

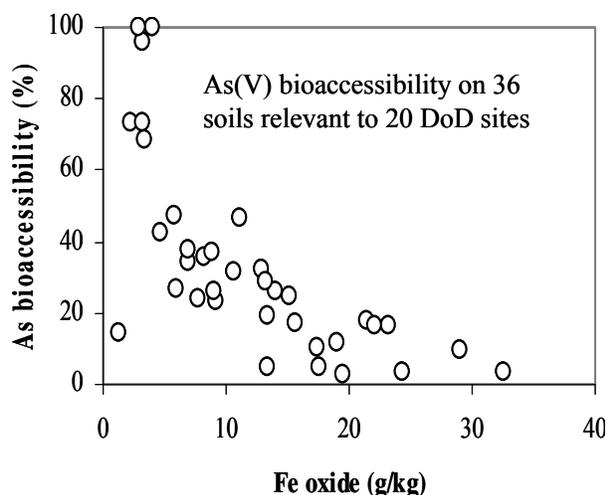


Figure 10 b: As bioaccessibility on As(V) contaminated soils decreases significantly when soil Fe-oxide content increases above 0.5 % on a mass basis

In the current study, soluble Fe(II)- and Fe(III)-salts were found to be more effective than metallic Fe in reducing As bioaccessibility. Adding soluble Fe(III)-salts to contaminated soil caused a decrease in soil As bioaccessibility by increasing the Fe(III) (hydr)oxide content via precipitation reactions. The freshly precipitated amorphous Fe-oxides provide significant surface area and charge to strongly bind As(III) and As(V), thus creating an As form that is far less bioavailable in soil. A detailed investigation into the effect of soil moisture when adding Fe(III) amendments indicated that the reaction can occur *in situ* if sufficient ($\geq 30\%$ moisture) is available. If the amendments are added to the soil without sufficient moisture, a reduction in As bioaccessibility occurs in the extraction fluid itself (i.e., an experimental artifact not reflecting a true *in situ* reduction in bioaccessibility). Adding Fe(III)-salts to nine As-contaminated DoD soils at a Fe:As molar ratio of 100:1 reduced the average bioaccessibility in the soils by a factor of approximately two (Fig. 11). Greater reductions in As bioaccessibility could be achieved by increasing the Fe:As molar ratio. Electron microprobe analysis indicated that As in contaminated DoD soils was largely associated with Fe-oxides (Fig. 12). These results were consistent with X-ray Absorption Spectroscopy analyses of DoD soils showing that As(V) was strongly bound to soil Fe-oxides via inner-sphere complexes. It is this strong complex that contributes to the decrease in As bioaccessibility. The equation developed by Yang et al. (2002), which considers Fe-oxides and pH

influences on As bioaccessibility, was found to be a good indicator of the potential effects of Fe amendments on As bioaccessibility in soil, particularly if the soil's pH buffering capacity was not exceeded due to the Fe addition (Fig. 13). The addition of alkalinity (e.g., lime) may help stabilize the pH in those soils that lack sufficient natural buffering capacity. Although site-specific, pilot-scale *in vitro* and *in vivo* bioaccessibility and bioavailability measurements will need to be conducted before adopting this remediation method at As-contaminated sites, these results suggest that such pilot-scale testing may be worthwhile, particularly at sites with large volumes of soil exhibiting high As bioaccessibility, high pH, and low native Fe concentrations. These results suggest decreasing As bioaccessibility and bioavailability in soil by adding Fe amendments may be an effective strategy to remediate As-contaminated soils.

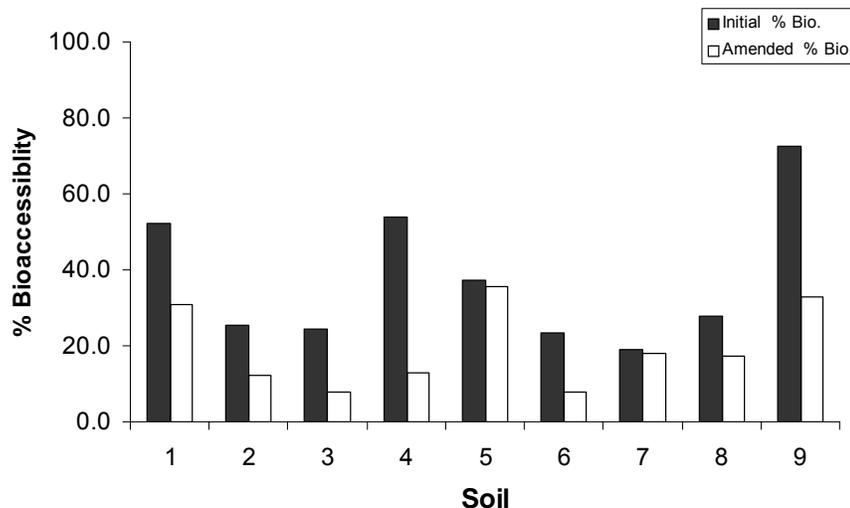


Figure 11: Adding 100 moles $\text{FeCl}_3(\text{s})$ per mole of As to nine contaminated DoD soils reduced the As bioaccessibility by approximately a factor of two on average

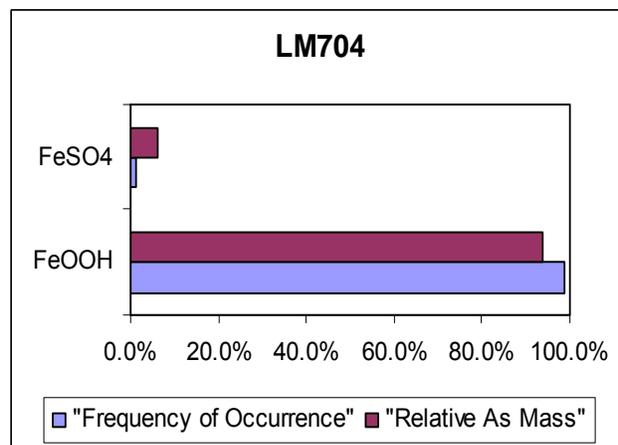
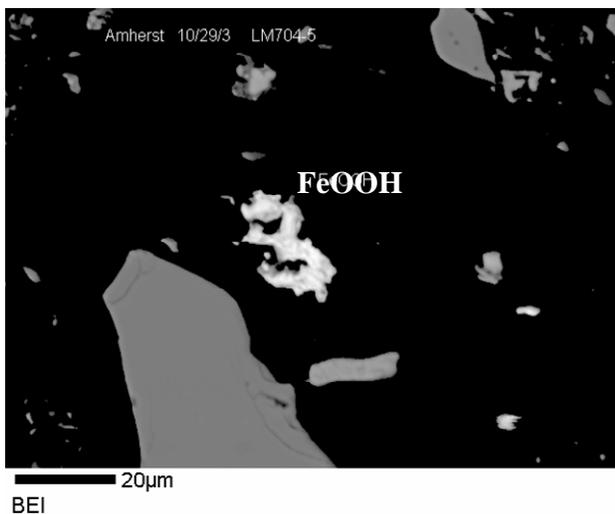


Figure 12: Electron microprobe analysis indicates that the As in this soil from Hill AFB is largely associated with Fe oxides. These results are consistent with earlier findings from CU-1166 using XAS that showed As(V) formed strong inner sphere complexes with Fe-oxides in contaminated McClellan Air Force Base soils

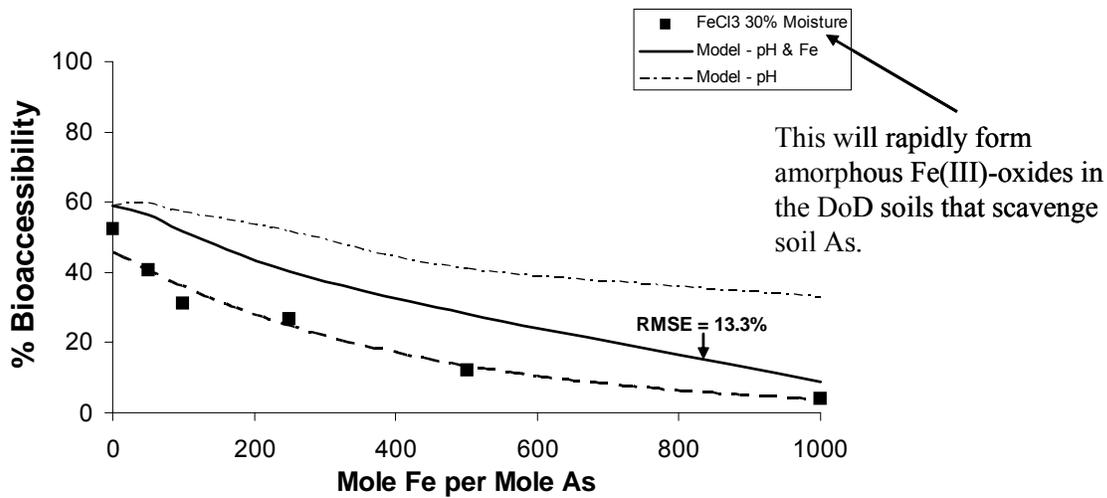


Figure 13: Effect of Fe:As molar ratio on As(V) bioaccessibility. The solid line was calculated using both the amended pH and Fe-concentration, while the dashed line was calculated using the indigenous soil Fe concentration and the amended pH. The results show the importance of newly precipitated Fe-oxides in scavenging As(V) and decreasing its bioaccessibility.

Decreasing Soil Cadmium Bioaccessibility

Soil Cd Stabilization and Decreased Bioaccessibility through Ca-polysulfide Treatment

The magnitude of Cd bioaccessibility in soil is often large since this divalent cation is often weakly bound to the soil via electrostatic surface charge interactions. Smelter soils with elevated concentrations of sulfides, or subsurface material high in P, have the propensity for decreased soil Cd bioaccessibility owing to the potential formation of strong Cd-ligand bonds with S^{2-} and HPO_4^{2-} .

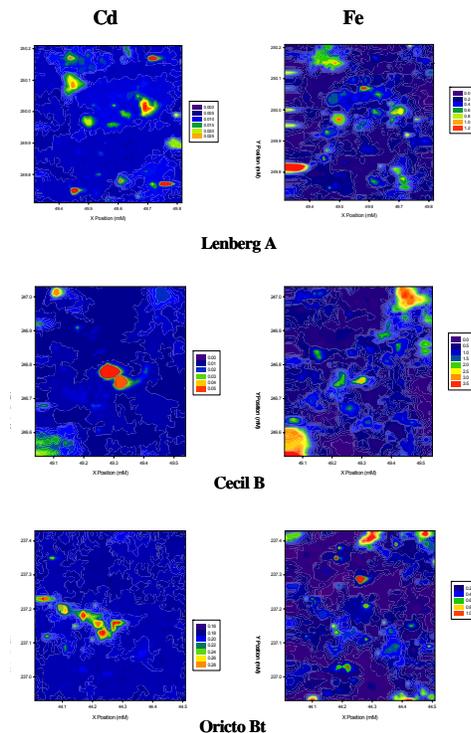


Figure 14: XAS elemental maps of Cd and Fe in three Cd spiked soils; lighter colors represent higher concentrations of specific elements. Cadmium correlations with Fe-oxides were inconsistent suggesting cadmium is weakly associated with Fe-bearing minerals. Cd bioaccessibility was greater in high Fe soils relative to than in low Fe soils. The extent of Cd adsorption was generally greater in subsurface horizons having higher CEC values, leading to a general decrease in Cd bioavailability

In this research we investigated the impact of phosphorus (P) amendments, such as phosphate fertilizers and phosphate rock, and various sulfide sources on enhanced soil Cd stabilization and decreased bioaccessibility. We examined the effect of time (0-365 days), *in vitro* extraction pH (1.5 versus 2.3), and dosage of different phosphate- and sulfide-based amendments on the reduction in the Cd bioaccessibility. Initial unamended soil Cd bioaccessibility in spiked soils and naturally contaminated DoD soils as determined by PBET pH=1.5 and 2.3 consistently exceeded the U. S. Environmental Protection Agency default value of 100 % relative bioavailability.

Elemental mapping via XAS confirmed that Cd was typically bound to the soil via weak surface bonds associated with phyllosilicates and, to a lesser extent, Fe-oxides (Fig. 14). The addition of rock phosphate, hydroxyapatite, or triple super phosphate had no effect on Cd bioaccessibility in DoD contaminated soils (Fig. 15). These results suggested that the solid phase Cd in these DoD soils was strongly bound or occluded and potentially unavailable to soluble P. We also investigated the functional group characteristics of commercially available peat (i.e. organic matter) to identify reduced organic S sites that may strongly bind Cd via CdS complexes. It was found that only about 10% of the organic matter exchange sites could strongly bind Cd, a quantity deemed too low to be considered significant enough to limit Cd bioavailability in soil (Fig. 16). Additional research is needed to determine if other organic matter sources can provide larger quantities of strong binding sites, particularly organic sources with significant amounts of sulfide functional groups.

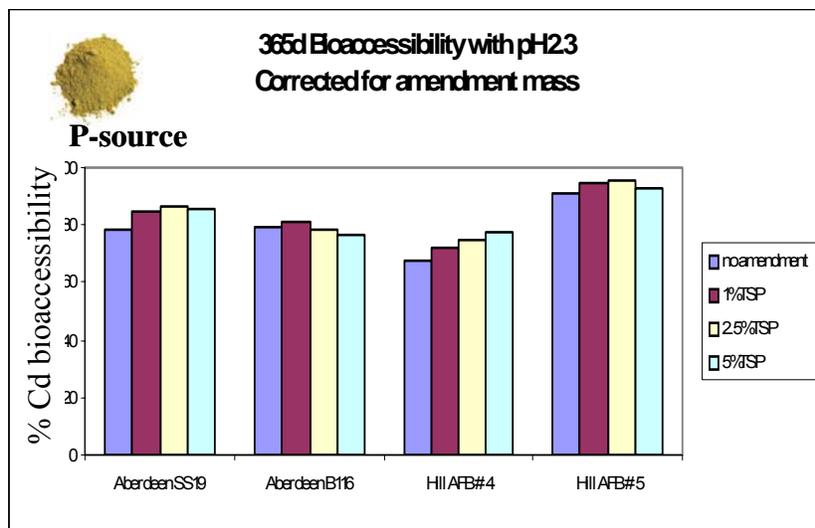


Figure 15: DoD soils with high concentrations of Cd typically did not show a decrease in Cd bioaccessibility when treated with hydroxyapatite, rock phosphate, or triple super phosphate. The strong Cd-P complex was no match for pH 1.5 or 2.3 PBET. Increased mass loadings of up to 5% P on a w/w soil basis showed no significant change in Cd bioaccessibility.

Additional research is needed to determine if other organic matter sources can provide larger quantities of strong binding sites, particularly organic sources with significant amounts of sulfide functional groups.

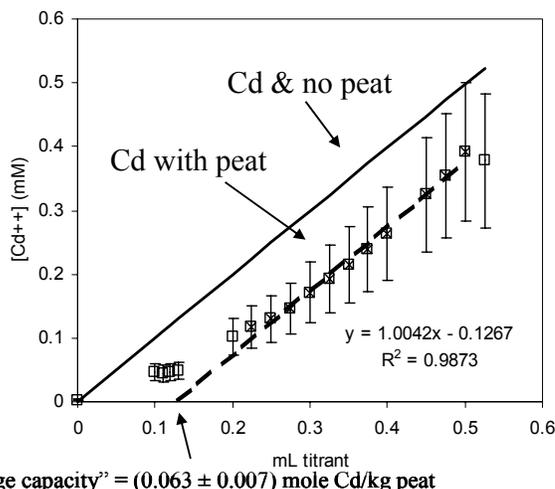
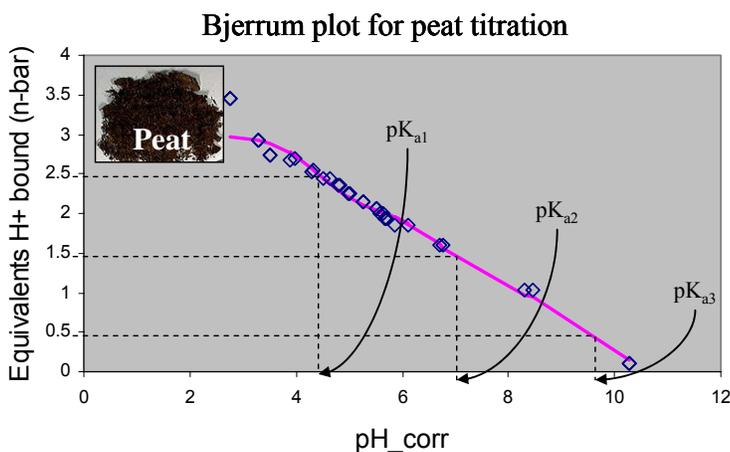


Figure 16: Examining the function group characteristics of organic matter in an effort to identify reduced organic S sites that may form low solubility CdS complexes was investigated. Only about 10% of the H⁺ exchange sites determined from Bjerrum plot will strongly bind Cd and was considered significant enough to limit Cd bioavailability in soil

Continued research used Ca-polysulfide as an additive to both Cd contaminated soils that were spiked with solution phase Cd and DoD soils containing indigenous Cd as a result of military disposal operations. The addition of polysulfide was intended to take advantage of the potential formation of sparingly soluble CdS during treatment. For spiked soils where the initial soil Cd is most likely labile (i.e. weakly bound via electrostatic interactions with the soil), polysulfide was quite effective at decreasing the bioaccessibility of Cd as estimated by the PBET method at both pH 1.5 and 2.3 (Fig. 17). The kinetics of the polysulfide reaction was rapid, as little change in Cd bioaccessibility was noted from 7 to 30 d of aging. In contrast, polysulfide additions to Cd-contaminated DoD soils had no effect on soil Cd bioaccessibility suggesting the Cd was non-labile and most likely occluded and non-reactive with the S²⁻ ligand. However, the acidic conditions of the PBET were sufficient to dissolve soil components that were responsible for the occlusion of Cd thus allowing it to become bioaccessible. Additional research is required to determine amendment strategies and conditions that are amendable for decreasing soil-Cd bioaccessibility.

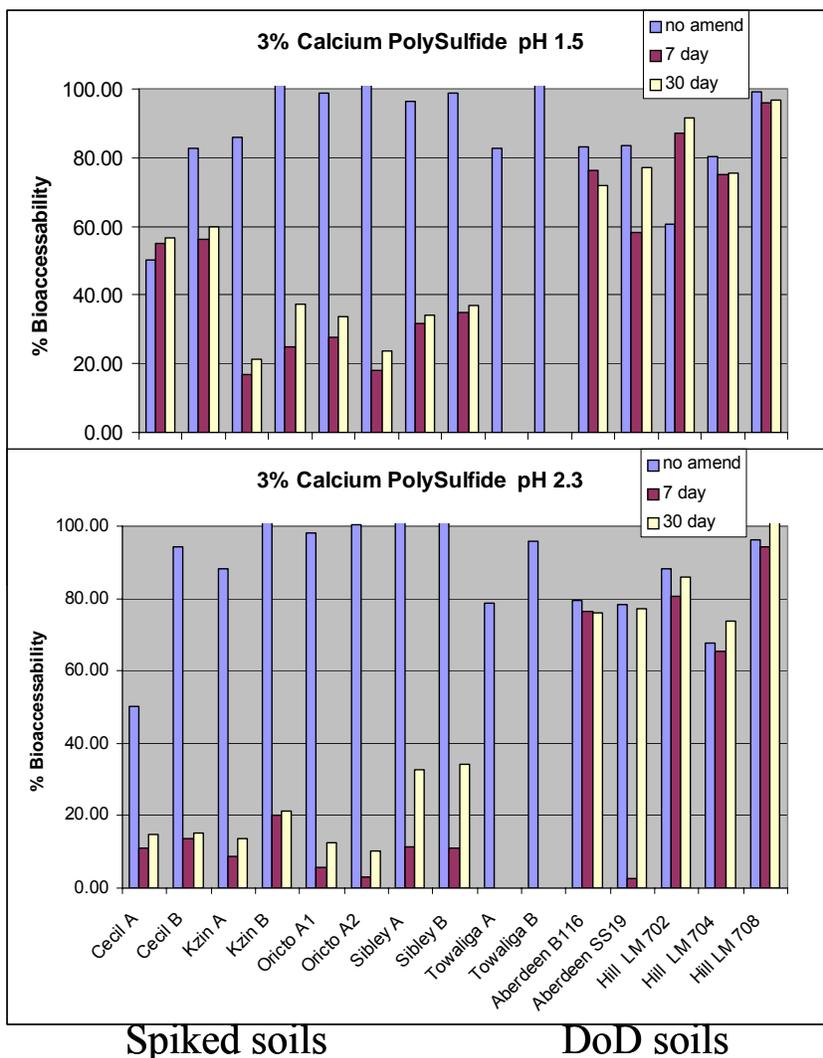


Figure 17: Polysulfide was very effective at decreasing metal bioaccessibility in Cd spiked soils for PBET pH conditions of both 1.5 and 2.3. However, Cd contaminated DoD soils showed little if any response to polysulfide additions

The results suggest that polysulfide is an effective means of decreasing Cd bioaccessibility if the soil bound Cd is labile (weak surface bonds). If the surface bound Cd is held by strong bonds or is occluded, the polysulfide is much less effective

PUBLICATIONS

Peer-Reviewed Publications resulting from CU-1350:

Yang, J.K., M.O. Barnett, J. Zhuang, S.E. Fendorf, and P.M. Jardine. 2005. Adsorption, oxidation, and bioaccessibility of As(III) in soils. *Environ. Sci. Technol.* 39:7102-7110.

Subacz, J.L., M.O. Barnett, P.M. Jardine, and M.A. Stewart. 2007. Decreasing arsenic bioaccessibility / bioavailability in soils with iron amendments. 'Special Issue' (Bioaccessibility of Soil Contaminants) of the *J. Environ. Sci. Health, Part A*, Vol. A42, No. 9 (July 2007).

Moseley, R.A., J. Zhuang, M.A. Stewart, T.L. Mehlhorn, M.O. Barnett, D.Y. Zhao, and P.M. Jardine. 2007. Decreasing Pb bioaccessibility in soils with phosphate-based amendments. *J. Environ. Qual.* (submitted).

Kilgour, D., R.A. Moseley, K. Savage, M.O. Barnett, and P.M. Jardine. 2007. Potential negative effects of adding phosphate amendments to lead-contaminated soils. *Environ. Sci. Technol.* (submitted).

Jardine, P.M., S.E. Fendorf, M.A. Stewart, and M.O. Barnett. Cr(VI) reduction and immobilization in DoD soils using organic matter amendments. *Environ. Sci. Technol.* (in preparation).

Wang, et al. 2007. Assessment PBET procedure for phosphate amendment lead-contaminated soil samples (in preparation).

Abstracts and Presentations resulting from CU-1350:

Stewart, M.A., P.M. Jardine, T.L. Mehlhorn, M. Barnett, and S.E. Fendorf. 2003 Quantifying the bioaccessibility of Cr and Cd in soils. Annual International Conference on Contaminated Soils, Sediments, and Water. Oct. 21-24, 2003, Amherst, MA.

Stewart, M.A., P.M. Jardine, S.E. Fendorf, and M.O. Barnett. 2003. Influence of soil properties on the bioaccessibility of Cr(VI) in soils. Soil Science Society of America National Meetings. Nov. 2-6, 2003. Denver, CO.

Barnett, M. O., J. K. Yang, J. L. Subacz, P. M. Jardine and S. E. Fendorf, 2003. "Estimating the oral bioavailability of arsenic in soil." Presented at the U.S. EPA Bioavailability Workshop, April 15-16, Tampa, FL.

Li, G. and S.E. Fendorf. 2003. Alteration of soil properties and their effect on the bioaccessibility of As, Cd, Cr, Pb, and Zn in soil. . Soil Science Society of America National Meetings. Nov. 2-6, 2003. Denver, CO.

Jardine, P.M., Parker, J.C., Barnett, M.O., Fendorf, S.E. 2003. Decreasing toxic metal bioavailability with novel soil amendment strategies. Partners in Environmental Technology Technical Symposium & Workshop, Washington, D.C. December 2-4, 2003.

Bioaccessibility Research Group of Europe Meeting, March 23, 2004 Hosted by British Geological Survey, Nottingham, UK. (invited).

Brooks SC, Jardine PM, Barnett MO, Fendorf S. 2004. Assessing the effects of peat amendments on the mobility of cadmium in soils. The American Chemical Society 227: U1106-U1106 009-GEOC Part 1, MAR 28 2004

Stewart, M.A., P. M. Jardine, S. E. Fendorf, M. O. Barnett. 2005. Evaluation of Soil Properties to Reduce Bioaccessibility of Heavy Metals. International Conference on the Remediation of Contaminated Sediments; New Orleans, Louisiana, January 24-27, 2005.

Stewart, M.A., P. M. Jardine, S. E. Fendorf, M. O. Barnett. 2005. Use of Soil Amendments to Reduce Bioaccessibility of Heavy Metal Contaminated Soils. 8th International Conference on the Biogeochemistry of Trace Elements; Adelaide, Australia, April 3-7, 2005 (invited).

Subacz, J.L. and J.K. Yang, J. Zhuang, M.O. Barnett, P.M. Jardine, and S.E. Fendorf. 2005. Estimating and reduction As bioaccessibility – bioavailability in soils in the U.S. Dutch National Institute for Public Health and the Environment (RIVM). April 28, Bilthoven, The Netherlands (invited).

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