Metal Bioavailability and Speciation in a Wetland Tailings Repository Amended with Biosolids Compost, Wood Ash, and Sulfate

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Abbreviations: AVS, acid volatile sulfide; EC, electrical conductivity; $E_{h,}$ redox potential; EXAFS, extended x-ray adsorption fine structure spectroscopy; ICP, inductively coupled argon plasma emission spectroscopy; PBET, physiologically based extraction technique; SEM, simultaneously extracted metals.

Abstract

Lead poisoning of waterfowl from direct ingestion of wetland mine tailings has been reported at the Bunker Hill Superfund site in Idaho. A greenhouse study was conducted to evaluate the effects of surface applications of amendments on lead bioavailability from the tailings. Treatments included sediment only, and sediment with three different surface amendments: (1) biosolids compost plus wood ash ("C+A"), (2) C+A+ a lowSO_4^{2-} addition as as K_2SO_4 ("low sulfate"), and (3)C+A + a high SO_4^{2-} addition ("high sulfate"). Measured variables included growth and tissue Pb, Zn , and Cd concentration of Arrowhead [*Sagittaria latifolia* (L.)] and cattail [*Typha latifolia* (L.)] and soil pH, Eh, porewater Pb, Pb speciation by x-ray absorption spectroscopy, and *in vitro* Pb bioavailability. The C+A amendment alleviated phytotoxicity for both plant species. Bioavailability of Pb as measured by the physiologically - based extraction technique (PBET) was decreased by 24-34% (over control) in the tailings directly below the amendment layer in the compost + SO_4 treatments. The ratio of acid volatile sulfide: simultaneously extracted metals (AVS:SEM) also indicated a reduction in Pb bioavailability (1:40 control, 1:20 compost, 1:8 compost + low SO_4, and 1:3 compost + high SO_4). Extended x-ray adsorption fine structure spectroscopy (EXAFS) and x-ray absorption near edge structure (XANES) data indicated that Pb-sulfide was greater after 99 d in the treatments that included additions of sulfate. These results indicated that, under reducing conditions, a surface amendments of compost + wood ash (with or without sulfate) decreased the bioavailability of Pb in metal-contaminated mine tailings.

Introduction

Mining and milling of metal ores in the Silver Valley in northern Idaho have resulted in widespread distribution of metal contaminants. In many cases tailings were directly discharged into the Coeur D'Alene river system. In some cases, tailings were discarded in natural depressions, including on-site wetlands. This has resulted in elevated metal concentrations in river, wetland and lake sediment (Bostick et al., 2001:Harrington et al., 1998; Rabe and Bower, 1977). The widespread contamination has damaged the native ecosystem. Studies have shown toxicity to fish and waterfowl due to elevated metal concentrations in sediment and water (Beyer et al., 1998, Maxfield et al., 1974). Although ecosystem impacts due to elevated metal concentrations are not unique to the Coeur D'Alene basin, the degree and extent of contamination in this region make it an extreme example (Beyer et al, 1985; Dodds-Smith et al., 1992)

The animals that are potentially most severely impacted by the elevated metal concentrations in sediment are waterfowl. These include tundra swans [*Cygnus columbianus* (Ord)], Canada geese [*Branta canadensis* (L.)], and mallard ducks [*Anas platyrhynchos* (L.)]. These birds utilize the Coeur d'Alene River Basin as a feeding and nesting area (Beyer et al., 1998). Several dead tundra swans and other animals found in the area have tested positive for Pb poisoning (Audet, 1999). A study of waterfowl fecal matter collected within the Basin determined that direct ingestion of sediments is the primary pathway for Pb exposure (Beyer et al., 1998). Beyer et al. (1998) estimated that the diet of tundra swans in the Coeur d'Alene River Basin consists of approximately 22% sediment while Canada geese ingest approximately 9%. A direct correlation was found between sediment Pb concentrations and waterfowl exposure to Pb (Beyer et al., 1998).

Recent studies have established a relationship between the mineral forms of metals such as Pb and their bioavailability (Laperche et al., 1997;O'Day et al, 2000; Ruby et al., 1999). In aerobic soil environments, research has focused on the potential to reduce Pb availability through the formation of chloropyromorphite (Ma et al., 1993; Ryan et al., 2001; Traina and Laperche, 1999). In wetland environments, the emphasis has been on mineral changes that are associated with reducing conditions (Simms et al., 2000; Feng and Hsieh, 1998). Although chloropyromorphite is not a redox sensitive mineral, adding large quantities of P to a wetland would not be an environmentally sound practice (Sharpley et al., 2001). However, a reducing environment may form that supports the presence of sulfate reducing microorganisms may causemetals in the tailings to precipitate as highly insoluble sulfides (Simms et al., 2000).

Studies have found that a sulfate-reducing environment can be created by adding amendments that provide a food source, sulfur, and raise pH (Feng and Hsieh, 1998).

Studies on metal contaminated sediments along the Coeur D'Alene River and into Lake Coeur D'Alene have demonstrated that metal sulfides are the dominant form of Pb and Zn in the lake where a water cap is present year round. In the lake, the correlation between Fe, Pb and Zn concentrations was weak, indicating that these metals are not necessarily associated with each other. In contrast, a large fraction of both Pb (49.3%) and Zn (63.3 %) were associated with sulfides (Harrington et al, 1998). In area wetland sediments, however, the fraction of total Zn present as Zn sulfide varied seasonally with changes in water depth and temperature (Bostick et al, 2001). Bostick et al. (2001) found that the mineral species of Zn was readily altered in response to changes in environmental conditions. A study on the rate of metal sulfide dissolution found that a significant fraction of CdS, PbS, and ZnS oxidized after 300 minutes of exposure to oxygenated conditions (Simpson et al., 1998). These results, along with the actual field observations indicate that formation of sulfides may be an effective means to limit metal availability under static conditions.

Additionally, reducing conditions alone may not be sufficient to ensure that the metals of concern would be present as sulfides. An additional factor is the effect of plants on soil parameters. A study examined the influence of plant roots on metal speciation in the rhizosphere. Metal precipitates on the root surfaces of *Phalaris arundinacea* (an indigenous aquatic plant in N. Idaho) included organo-Pb complexes and Zn carbonates (Hansel et al, 2001). This observation indicates that plants can cause localized changes in redox conditions that affect metal speciation. Metal speciation may not be accurately predicted by redox measurements on bulk soil.

West Page Swamp is an 11-ha, naturally - occurring wetland located in the Coeur d'Alene River Basin near Pinehurst, ID. The area was used as a tailings repository from 1918 to 1929. The depth of tailings within West Page Swamp varies from approximately 45 cm to more than 3 m, with metal concentrations in the tailings ranging from 16 to 249 mg kg^{-1} Cd, 1,740 to 18,400 mg kg^{-1} Zn (Huston, 1999), and 4,670 to 20,700 mg kg^{-1} Pb (McCulley et al., 1993). Organic carbon in the tailings averaged 1.06%. Effluent from the local municipal wastewater treatment plant is scheduled to be diverted into the wetland in the near future. This will maintain a constant water depth over the exposed tailings. This was done to limit wildlife exposure to the tailings. Within 1 yr prior to sample collection for this study, the wetland had been excavated to accommodate the treatment plant effluent. One to 2 m of surface material were removed. The excavation resulted in the removal of all organic matter that had accumulated since the tailings impoundment had closed. In addition, the excavation exposed pure mine tailings that had been buried for over 50 years.

The present study was conducted to determine the effectiveness of surface amendments of biosolids compost and wood ash, with and without SO_4, for restoring a plant cover and lowering the bioavailable metal concentrations in the tailings. The experiments were conducted in a controlled greenhouse environment with a constant water cover. The amendment cap was anticipated to reduce metal availability through two different mechanisms. On a basic level, application of amendments to the surface of the tailings would provide a physical barrier to the contaminants that would be conducive to plant growth. Secondly, there is the potential that a surface application of the amendment mixture could alter the mineral form and bioavailability of metals in the underlying tailings. This would reduce the availability of Pb for sediments that are ingested.

Amendments of biosolids compost and wood ash are expected to facilitate SO_4 reduction by organotrophic anaerobes (e.g., *Desulfomonas* and *Desulfovibrio*), potentially providing an environment where Pb and Zn are converted to less available forms such as galena (PbS) (solubility product constant, $K_{sp} = 10^{-27.5}$) and sphlalerite (ZnS) (Paul and Clark, 1996). The initial phase of anoxic conditions would involve dissolution of Fe and Mn oxides. This effect has been observed in a laboratory study with C and N added to anoxic sediment collected from the Coeur d'Alene river (LaForce et al., 1998). However, as E_h continues to decrease, sulfates would also expect to be reduced. If a portion of the metals in the system are associated with Fe or Mn oxides, these should come into solution as the reducing conditions are maintained. If the reducing conditions are maintained, the initial flux of metals into solution concomitant with dissolution of Fe oxides, should subsequently be reduced with the precipitation of metal sulfides.

The objectives of this research were to determine how various biosolids/ash and sulfate amendments affected (1) revegetation of tailings-impacted sediments, (2) bioavailability of sediment Pb and (3) molecular –scale speciation of Pb. Different, complementary techniques were used to assess changes in Pb bioavailability and speciation induced by the treatments, and included PBET, SEM:AVS, sediment E_h and pH measures, pore water Pb concentrations, and EXAFS spectroscopy. While *in vivo* tests are an absolute measure of metal bioavailability to a given organism, several surrogate laboratory procedures have been developed. These include the physiologically - based extraction technique (PBET) which was developed to estimate the bioavailable portion of soil Pb to humans (Ruby et al., 1999) and the ratio of acid volatile sulfide to simultaneously extracted metals (AVS:SEM), which has been related to the toxicity of metals to aquatic organisms (Allen et al., 1993; DiToro et al., 1992). The PBET extraction is conducted at an acidic pH, with a high ratio of solution to soil. The exposure pathway for waterfowl involves ingestion of much higher rates of sediment in combination with foodstuffs. This would alter gastric pH as well as the potential for Pb adsorption. However, this extraction is the closest to a standard method for predicting Pb availability through direct ingestion of soils or sediments.

The underlying concept in AVS:SEM analysis is that reactive sulfides are capable of forming stable precipitates with metals in sediments that have a very low solubility, thus controlling their bioavailability (Lee et al., 2000). While neither of these *in vitro* methods were developed to mimic the behavior of waterfowl, observed reductions using these techniques may reflect lower metal bioavailabilityfor other organisms. It may also be possible to evaluate changes in bioavailability using techniques that document an actual change in the mineralogy of the contaminants to less soluble species. Mineral forms that are stable under equilibrium conditions may be predicted through the use of E_h – pH diagrams (Lindsay, 1979). Metal sulfide minerals can also be detected using spectroscopic techniques (Sayers and Bunker, 1988;Hesterberg et al., 1996; Wang et al., 1995).

To summarize, the goals of the study were (1)to determine if a surface amendment application of compost + wood ash, with or without supplemental SO4, could provide a fertile barrier to limit access to mine tailings in an anaerobic environment;(2) if surface amendment application could alter the bioavailability of Pb in the underlying tailings as measured through in vitro procedures and (3) if there would be an associated change in the mineral form of Pb.

Materials and Methods

Experimental Design and Treatments. This study was conducted at the University of Washington Center for Urban Horticulture greenhouse in Seattle, WA from May through

December of 1999. Sediment samples for the study were collected in two areas, north plot (NP) and south plot (SP), within the West Page Swamp in northern Idaho in March 1999. For each sample collection area, multiple cores were collected and combined. Samples were stored in a cold room at 2ºC prior to the study initiation. There was no standing water at the time the samples were collected. No effort was made to initiate anaerobic conditions after sample collection and before experimental setup. The two sediment sources corresponded to two experimental blocks, NP block and SP block, with a minimum of 2 replicates per block.

Four treatments were tested including a (1) Control, (2) Compost + ash, (3) Compost + ash + low SO_4 and (4) compost + ash + high SO_4. For the control treatment, pots were filled to a depth of 20 cm with tailings(control). For all other treatments, pots were filled to 8 cm with tailings and covered with 12 cm of biosolids compost and wood ash amendment (compost). The amendment mixture that served as the base for all treatments was made by combining biosolids compost and wood ash at a ratio of 3:1 compost: ash by volume. Biosolids compost was obtained from the City of Coeur d'Alene Wastewater Division Compost Facility located in Coeur d'Alene, ID. This material was characterized by a pH of 6.0 and a C/N ratio of 20:1 (220 g C kg^{-1} and 12 g N kg^{-1}). Wood ash was obtained from Avista Utilities, a wood-fired electricity generating facility in northeastern WA. The ash was characterized by a pH of 10.3 and a C:N ratio of 200:1 (186 g C kg^{-1} and 1 g N kg^{-1}). Elemental concentrations of the amendment mixtures and the sediment are reported in Table 1.

In addition to the compost mixture, 30 g of K_2SO_4 was added to each pot in the low SO_4 treatment and 120 g of K_2SO_4 of was added to each pot in the high SO_4 treatment. These amendments correspond to the following dry weight application rates: 300 t ha^{-1} compost, 80t ha^{-1} wood ash, 16 t ha^{-1} K_2SO_4 (low SO_4addition), and 64 t ha^{-1} K_2SO_4 (high SO_4addition). The

K_2SO_4 additions were determined according to calculations designed to provide (1) the total amount of SO_4 required to precipitate 100% of the sediment Fe, Pb and Zn as monosulfides if all SO_4 was reduced to S^{2-} (compost + high SO_4), (2) the amount of SO_4required to precipitate 25% of the Fe, Pb and Zn as sulfides (compost + low SO_4) and (3) no additional SO_4 (compost and control treatments). For the experimental units used in this study, each amended unit contained 5 kg tailings (dry weight) and 2.8 kg amendment (dry weight) and each control unit contained 12.5 kg dry tailings.

Amendment materials were combined in a large plastic container, and saturated with H_2O, then the H_2O was decanted to reduce salinity. This was done in order to better replicate the conditions at West Page Swamp, where moving fresh water is able to flush soluble salts out of the system. Electrical conductivity (EC) of the amendment mixture was measured using an automatic conductivity bridge and cell (YSI model 31 conductivity bridge) to ensure that its soluble salt concentration was reduced to within the range typically found in soils (0 to 4 dS m^{-1}; Brady and Weil, 1996). The mixture was then divided among three containers. Potassium sulfate (K_2SO_4) was mixed thoroughly into two of the containers at the low and high rates. It was not possible to remove excess salts from the sulfate treatments as this would have removed a portion of the sulfate amendment.

Plugs of two obligate wetland plant species native to the Coeur d’Alene River Basin, arrowhead [*Sagittaria latifolia* (L.)] and cattail [*Typha latifolia* (L.)], were grown in 3.6 L closed bottom polyethylene pots (approximately 24 cm high and 14 cm in diameter) containing tailings or tailings covered with each amendment. An illustration of the experimental pots and water and sediment sampling areas within the pot is presented in figure 1. Arrowhead and cattail were selected due to their importance as food and nesting material for wetland birds and small mammals (Stevens and Vanbianchi, 1993). Plant material was obtained from Wildlife Habitat Institute in Princeton, ID and stored in a cold room at 2ºC until planting. Arrowhead plants were planted as dormant rhizomes and cattail plants were planted as 16 cm^3 plugs with approximately 15 cm of shoot growth. Half of the control and compost treated pots contained two arrowhead plugs per pot. The remaining half contained two cattail rhizomes per pot. All of the compost + low SO_4 and compost + high SO_4 treated pots contained one arrowhead rhizome and two cattail plugs. In all pots, both species were planted within the top 16 cm of each pot.

The SP sediment was used in half of the control treatments, half of the compost treatments, and all of the compost + SO_4treatments. The NP sediment was used in half of the control treatments and half of the compost treatments only. There were a total of 3 replicates for each of the SO_4 treatments and 8 replicates for the control and compost treatments. Of the 8 pots in the control and compost treatments, 4 contained N tailings and 4 contained S tailings.A total of 4 pots of each treatment were planted with cattail (2 N sediment + 2 S sediment) and 4 with Sagitaria.

The pots were submerged in 19 L containers of water in order to provide a 5 cm water cover over the top of each substrate. These containers were arranged in a completely randomized design. Water was added as necessary throughout the duration of the experiment to maintain a constant water level. Porous ceramic water samplers (2.2 cm outside diameter, 6.4 cm long) attached to plastic tubes (2.2 cm outside diameter, 30 cm long) obtained from Soil Moistureâ were installed in four pots, one of each treatment (control, compost, compost + low SO_4, and compost + high SO_4), at three depths: 12 cm (high), 7.5 cm (middle) and 4 cm (low) from the bottom of the pot. To facilitate comparisons, all pots selected for water samplers contained SP sediment. In those pots containing a layer of amendment, the high sampler was located within the amendment layer, the low sampler was located within the tailings layer, and the middle sampler was located just beneath the interface between the amendment and tailings layers (figure1).

Analysis of Soil Pore Water. Water samples were collected from the ceramic water samplers once a week using a 2 mm tube attached to a syringe. Although interactions between metal ions and the ceramic cups may occur, the relative concentration of Pb in the measured solution facilitates valuable comparisons. Samples were acidified with concentrated HCl and stored at 2ºC prior to analysis by flame atomic absorption spectrometry (Perkin-Elmer 5100 Atomic Absorption Spectrometer) to estimate pore water Pb concentrations.

Redox Potential and pH Measurements. Reduction-oxidation (i.e., redox) potential (E_h) was measured three times per week using an Orion 520A pH/mV/ORP/temperature meter with an Orion 96-78 redox platinum electrode. This same meter with an Orion model 91-07 platinum electrode was used to measure pH once per week. All measurements were taken in the top 2 cm of the substrate. Reported E_h values are relative to a standard hydrogen electrode.

Analysis of Plant Biomass. Aboveground, living plant tissue was harvested when plants exhibited toxicity symptoms (e.g., chlorosis, senescing leaves, etc.). Plants growing in control sediment were harvested from 38 d-59 d. All plants growing in compost -treated sediment were harvested after 94 d. Following harvest, plant tissues were washed in a mild sodium lauryl sulfate solution, rinsed in deionized water, and dried at 70ºC. Dried samples were weighed and ashed at 480ºC in a muffle furnace for 16 h, then digested in concentrated HNO_3 and dissolved in 3 *M* HCl. Extracts were diluted to 25 ml using 0.1 *M* HCl, and subsequently analyzed by inductively coupled argon plasma emission spectroscopy (ICP; Thermo Jarrel Ash ICAP-AES model 61E) to determine metal concentrations. For quality control, National Institute of

Standards and Technology (NIST) standards were routinely integrated into plant and soil analyses.

Analysis of Sediment. One half of the pots for each treatment were dismantled after 99 d. The remaining pots were maintained for a total of 207 d. This was done in order to compare changes in contaminant availability over time. At the time that the pots were dismantled, soil samples were collected from each of the respective levels: sediment, interface, and amendment. Interface samples were collected from the area just beneath the junction of the sediment and amendment layers. For each pot, samples from each layer were subdivided. Half of each sample was air dried and sieved. The remaining portion was kept wet and stored in a cold room at 2ºC. Total metal concentrations were determined for the dry <2 mm and <250 µm soil fractions by aqua regia digestion (McGrath and Cunliffe, 1985) followed by analysis by ICP).

PBET Analysis. The PBET extraction was conducted with a pH 2.5 solution for 1 h at 39ºC using <250 µm dry soil a 1:100 soil to solution ratio with a 0.4 M glycine solution (Brown et al., 2003;Ruby et al., 1999; Ruby et al;2001). J. Drexler at the University of Colorado at Boulder, Department of Geological Sciences, performed the PBET analysis for samples collected after 99 d. Sample analysis for samples collected at 207 d using the same method at pH 2.2, was conducted at the University of Washington. There was no difference in results as a function of extractant pH or time, so results have been averaged over both extraction times. In addition, the PBET procedure was conducted using moist samples collected after 207 d. Percent moisture was calculated for the samples and extractable Pb was adjusted accordingly.

AVS:SEM Analysis. AVS:SEM Analysis was conducted by Savannah Laboratories in Savannah, GA. In preparation for shipping, wet sediment was placed in 60 ml glass vials sealed with septa lids. Samples were packed in an ice chest with dry ice and shipped overnight.

Samples were collected at plant harvest. A minimum of 4 samples for the bottom and interface depth of the control and compost samples were analyzed. However, because we wanted to maintain the experiment, only 1 sample at each depth for both the low S and high S treatments were analyzed. For analysis, 10 g samples were placed in a vessel that had been purged with N_2. Twenty mLs of 6N HCl were added. Sulfur, volatilized as H_2S was trapped in a scrubber containing NaOH. The scrubber solution was then analyzed for total S colorimetrically. Simultaneously extracted metals in the sediment: HCl solutionwere analyzed by ICP after filtering.

X-ray Absorption Spectroscopy (XAS)

Sample Preparation and XAS Data Collection

Extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) analysis of Pb speciation was conducted on eight sediment samples at Beamline X-11A of the National Synchrotron Light Source at Brookhaven National Laboratory in Upton, NY. To facilitate comparisons, all samples were collected from pots containing SP sediment. These included one replicate of each treatment from pots dismantled after 99 d (all from the interface level), and one of each treatment from pots dismantled after 207 d (all from the interface level). Wet sediments were passed through a 500 μm stainless steel sieve and placed in high density polyethylene scintillation vials. To prevent desiccation, individual vials were wrapped in moist paper towels and placed in glass jars. The jars were subsequently purged with N_2 gas and sealed with Teflon ribbon-lined lids in order to exclude O_2. Samples were packed in an ice chest with dry ice and shipped overnight for XAS preparation. Upon receipt, samples were mounted under an Ar atmosphere in special acrylic sample holders, covered with Kapton tape (CHR Industries), and placed in cold (3˚C) storage until XAS data were collected.

XAS data were collected on moist sediment samples at ambient temperature across the lead L_{III} absorption. Sample data were collected in transmission mode using ionization chamber detectors. A metallic Pb foil placed between two detectors behind each sediment sample was used as a reference to correct for any energy shifts due to beamline optics. At least two EXAFS spectra collected on samples and standards were ensemble averaged (one spectrum was collected for the 99-d control sample).

EXAFS Data Analysis

Data processing was done using the computer program MacXAFS (Bouldin et al., 1995). EXAFS spectra were baseline corrected using a linear function between –200 and –50 eV relative energy, where the edge energy (E_0) was taken as the maximum in the first derivative spectrum and occurred between 13,055 and 13,058 eV. EXAFS background normalization was done across a relative energy range between about 13 and 550 eV (wavevector, k = 1.9 to 12.4 $Å^{-1}$) using a cubic spline function with five equally-spaced knots (Sayers and Bunker, 1988). An exception was the compost-treated sediment sample, for which five knots were placed near the nodes of the EXAFS oscillations to better remove low-frequency background oscillations as indicated by a false peak in the fourier-transformed spectrum (radial structure function – RSF) at a radial distance ≤1.2 Å. RSFs were produced by fourier transformation of k^3 weighted (w=3) chi [$\chi(k)$] data over a wavevector range between 2.4 and 10.5 $Å^{-1}$, with the exact endpoints for a given spectrum chosen at nodes ($\chi = 0$) in the EXAFS spectrum (Mansour and Melendres, 1998). No windowing functions were used in EXAFS transformations.

Multi-shell EXAFS fitting analysis was done using a combination of theoretical standards and physical standards following the general approach described by Hesterberg et al. (1997).Up to three shells (Pb-O, Pb-S, and Pb-Pb) were fit simultaneously. The mineralogical purity of the physical standards was verified using x-ray diffraction analysis. To determine bonding parameters (radial distance, coordination numbers, and Debye-Waller factors – $\Delta\sigma^2$); amplitude, phase shift, and theoretical EXAFS calculations were done using the University of Washington FEFF computer programs (Rehr et al., 1992). Theoretical EXAFS spectra for first-shell Pb-S or Pb-O coordination and higher-shell Pb-Pb coordination were generated using structural parameters for PbS (galena) and α-PbO (litharge), which have uniform first-shell coordination distances (Moller et al., 1989; Manceau et al., 1996). These spectra were used in fitting analysis to determine average bonding parameters for Pb species in the sediment samples. Amplitude reduction factors (S_o^2) for Pb-S coordination ($S_o^2 = 0.83$) and Pb-Pb coordination (($S_o^2 = 0.94$) were obtained by fitting the measured spectrum for PbS (galena) with their respective theoretical EXAFS spectra (Hesterberg et al., 1997), and taking the ratio of the fitted coordination numbers to the known crystallographic values of 6 (Pb-S) and 12 (Pb-Pb), respectively (Moller et al., 1989). The amplitude reduction factor of 0.83 determined for Pb-S bonding was also used to correct coordination numbers for Pb-O bonding because fitting of the β-PbO standard yielded a reduction factor (0.47) that was considered to be unrealistically low. The amplitude reduction factor is deemed to be more a function of electronic effects on the central Pb atom than on the coordinating atoms (Sayers and Bunker, 1988). Furthermore, Pb L_{III}-EXAFS spectroscopy can underestimate the total number of oxygen neighbors, particularly for Pb species having a high degree of anharmonic static disorder (multiple Pb-O bond lengths) as is typical of oxygen-bonded Pb(II) (Manceau et al., 1996).

EXAFS fitting analysis was done only on sediment samples collected at 99 days because data from the 209-d sampling showed a monochromator glitch across the wavevector range k =

7.3 to 8.0 Å^{-1} that could not be reliably removed. Spectra for the four 99-d samples were fit in r-space over a k-range between 2.5 and 10.1 Å^{-1} and a radial distance range between 0.9 and 4.7 Å. The exact k-range is shown by the fits to the chi spectra in Fig. 1 (discussed below), and the exact r range for fitting depended on the positions of peaks in the RSFs (Hesterberg et al., 1997). Simultaneous three-shell fitting (Pb-O, Pb-S, Pb-Pb) was tried on all samples, and the Pb-O shell was eliminated when fitting yielded a negative Pb-O coordination number. In two cases where an initial fitting analysis yielded a slightly negative $\Delta\sigma^2$ (Debye-Waller factor), suggesting better structural order than the theoretical standard with $\Delta\sigma^2 = 0$ Å^2, $\Delta\sigma^2$ was fixed at a low value (0.0001) to complete the fitting analysis. The energy shift (ΔE) was constrained in the fitting to be equivalent for all shells, so that the number of fitted parameters was always less than the number of independent points (Fendorf, 1999).

XANES Data Analysis

To determine whether we could detect changes in the speciation of sediment Pb between samples collected at 99 and 207-d, lead K-XANES data were analyzed. XAS data that had been baseline corrected were normalized to an edge step of 1 at 13,175 eV. To more quantitatively estimate differences in Pb speciation between samples, we performed non-linear least squares fitting (linear combination fitting) analyses on the XANES data as described in Hutchison et al. (2001). The fitting analysis was done using XANES data for four minerals standards – PbS (galena), PbO (massicot), $PbCO_3$ (cerrusite), and $PbSO_4$ (anglesite). Only fits that included the PbS were considered valid, because EXAFS data indicated the presence of PbS in all sediment samples. Only binary combinations of the standards yielding the best goodness of fit (lowest χ^2 value) are reported to avoid an excess number of fitted parameters. Three energy ranges were used in the fitting (13,030 to 13,130 eV, 13,030 to 13,090 eV, and 13,030 to 13,075 eV), and the results were averaged.

Data Analysis. Data were statistically analyzed using SPSS version 10.0. Sediment elemental concentrations were compared using a t-test. Plant tissue Fe and Pb data was log transformed prior to statistical analysis in order to obtain normally distributed data. For ease of interpretation, non-transformed values are presented. Plant tissue and PBET data were tested for treatment and block effects using ANOVA followed by multiple comparison testing using the Waller-Duncan t-test. A significance level of $p<0.05$ was selected for determination of statistical significances. Since no statistical difference was found between PBET samples collected on two different sampling dates (d 99 and d 207), these values were combined for each depth of each treatment.

Field Application of Amendment. After samples had been collected from the West Page Swamp, the swamp itself was amended with compost and wood ash. Amendments were added to the surface of the swamp in October, 1998 and September, 2000. Compost and wood ash were mixed with a front -end loader in the same proportions as used in the greenhouse study. The amendment was applied using an aero-spread in 1998 and with a blower truck in 2000. A road was constructed through the swamp from woody waste from local log yards to facilitate amendment application. Volunteer plant species were allowed to revegetate the swamp. Plant data from the actual swamp restoration is also presented. Samples were collected from the excavated portion of the swamp prior to the amendment application in 1998 and from the amended portion of the swamp in 2000. For the control, 2 plants were sampled and 14 plants from 5 different portions of the treated areas of the swamp were sampled in 2000. .

Results and Discussion

Soil E_h Soil redox potential (E_h) values are shown in Figure 2. E_h was consistently highest in the control treatments, with measurements range between 100 and 400 mV for the duration of the study. Sulfide reducing (<-160mV) conditions (Bohn et al., 1985) were generally reached in the compost + low SO_4treatment by 20 d, and compost + high SO_4treatment after 8 d. E_h values in these treatments remained below -160 for the duration of the experiment. Compost (no SO_4) treatments produced the greatest redox fluctuations. E_h readings in these pots were initially similar to those in the compost + SO_4, treatments. Starting on 27 d, however, E_h in the compost treatments increased to > -160 mV while E_h in the treatments with SO_4 additions remained highly reducing.

Observed differences in redox potential among the various treatments may be related to plant growth. Rhizomes and plugs placed in the compost + low $SO_4$and compost + high SO_4 treatments experienced mortality immediately after planting. In contrast, plants in compost treatments experienced vigorous growth for the duration of the study. The more oxidizing conditions observed in the compost alone treatments during the later portion of the study may be related to root growth in the sediment layer. When the study was broken down, oxidized areas were observed alongside root tissue. The greatest increase in E_h coincides with the period following the harvest of aboveground plant tissue (94 d). As Patrick et al. (1996) pointed out, redox readings taken in or near decaying root tissue can differ significantly from those taken in bulk soil. Although there will be increased O_2 demand near decomposing roots, decayed roots can provide space for O_2 diffusion, thereby facilitating a net increase in redox potential. For this study, facilitated diffusion through the tailings where plant roots had been may explain the observed increase in redox.

Soil pH. Soil pH values are shown in Figure 3. Average sediment pH in control pots ranged from 6 to 7 for the duration of the study, while all other treatments exhibited pH >7. The compost + low SO_4 and compost + high SO_4 pots had the highest average pH readings; which ranged between pH 8 and 9. Average pH in the compost pots was initially in this same range, but began to decrease after approximately 28 d to pH <8 where it remained for the rest of the study.

Average E_h and pH values from the greenhouse study for selected dates (at one to two week intervals, when the two measurements were made in close proximity) beginning 8 d after planting were plotted on an E_h-pH diagram for Pb speciation. An E_h-pH diagram that includes the observations from this study is presented in figure 4. The majority of data points corresponding to the compost + SO_4 treatments fell within the area where galena (PbS) is predicted to be the dominant species. The compost - amended treatments fell primarily into the portion of the area where anglesite ($PbSO_4$) and cerrusite ($PbCO_3$) were predicted with some points lying in the area where galena would be thermodynamically predicted. Points corresponding to the control treatments all fell within the area where anglesite is the dominant solid phase. This information suggests that conditions were especially favorable for the formation of Pb sulfide minerals in the compost + SO_4 treatments.

Pore Water Lead Concentrations. Dissolved Pb concentrations were consistently ≤ 1.5 mg L^{-1} in the pore water collected from the tailings level of all treatments, including the control (Table 2). Concentrations were below 1 mg L^{-1} for all treatments excluding the control across all sampling times for the interface depth. At this depth, Pb in the control treatment ranged from

0.07 to 3.5 mg L^{-1}. Concentrations in the control were low until week 3 and then decreased after week 11. At the surface sampling depth, all compost treatments had pore water Pb < 1 mg L^{-1} for the duration of the study. Pore water Pb in the SO_4 treatments was generally stable across the experiment. These treatments had higher dissolved Pb than the compost alone treatment for the first 11 weeks of the study. The higher Pb concentration is probably due to the high ionic strength (indicated by EC) which would tend to increase soluble complexes of Pb^{2+} and decrease activity coefficients. After this point, concentrations in the compost treatment showed greater variability. This variability may be related to plant growth and root decomposition following harvest which occurred during week 13.At this depth, the control treatment Pb was below 0.5 mg L^{-1} until week 3 and then increased to an average value of 1.15 mg L^{-1} for the next 8 weeks. Concentrations subsequently decreased to < 0.5 mg L^{-1} for the duration of the study. It should be noted that the average dissolved Pb concentrations for all treatments at all depths in this study are well above the limit set for drinking water in the United States (0.015 mg L^{-1}).

Plant Growth. Plants grown in control tailings were generally characterized by stunted and chlorotic growth, and plants were harvested early in the study. Arrowhead and cattail plants grown in tailings amended with compost showedvigorous growth. Plants grown in compost-treated sediment were harvested after 94 d when some of their leaves had senesced. The plants were root bound at this time**.** Roots had grown throughout the containers and were directly against the walls of the pots.

All of the plants in the compost + low SO_4 and compost + high SO_4 treatments died almost immediately following planting. Salt toxicity as a result of the high rates of SO_4 addition was the likely cause of their demise. Average EC readings of the compost + low SO_4 and compost + high SO_4treatments were 17 and 41 dS m^{-1}, respectively. The average EC readings of the control and compost treatments, in contrast, were 1.0 and 0.6 dS m^{-1}, respectively.

In the amended portion of the wetland, volunteer plant species had completely colonized the treated areas within 1 year after application. The most likely seed source was an adjacent undisturbed wetland. Wind blown seed and seed from bird droppings were the probable sources of plant material. Vigorous growth has been maintained as was evidenced in a site visit in 10/2002.

Elemental Concentrations in Aboveground Plant Tissue. Mean elemental concentrations in aboveground plant tissue are shown in table 3. The compost amendment was sufficient to alleviate the phytotoxic conditions in the unamended sediment. Concentrations of Cd, Pb and Zn in plants grown in this treatment were significantly ($p<0.05$) reduced over those grown in the control sediment. Arrowhead and cattail plants in the control pots averaged 50 and 13 mg Cd kg^{-1} while treated plants averaged 3 and 4 mg Cd kg^{-1}, respectively. Zinc concentrations in control plant tissue (900 mg kg^{-1} to 1600 mg kg^{-1}) exceeded the phytotoxicity threshold (>400 mg kg^{-1}; Knezek and Ellis, 1980); concentrations in compost-treated plants (100 mg kg^{-1} to 300 mg kg^{-1}), in contrast, were below phytotoxic range. Lead concentrations were reduced from 80 to 300 mg kg^{-1} in control plants to 1 to 2 mg Pb kg^{-1} in treated plants. The observations in the wetland itself, mirrored those in the greenhouse study. Plant tissue Zn was reduced from 1000 mg kg^{-1} in the unamended wetland to an average value of 115 mg kg^{-1} in the years following amendment addition. These data suggest that consumption of aboveground plant tissue grown in compost-treated, metal contaminated sediments would result in lower food chain transfer of these elements.

AVS: SEM Analysis.

The ratio of acid volatile sulfide to simultaneously extractable metals, generally expressed as AVS:SEM, has been used as a measure of the potential toxicity of metal-contaminated sediments(Allen et al., 1993). When this ratio is below 1, metals are thought to be potentially bioavailable because they tend to be toxic to aquatic organisms (DiToro et al, 1992). Although all of the metals to sulfide ratios measured in this study were less than 1, a comparison of the ratios for the different treatments is useful for assessing their relative potential metal toxicities.

At both the interface and bottom sampling depths, total SEM for all treatments were similar averaging 78.7± 0.9 μmol g-1. For both SO_4 treatments, there was no detectable AVS at the bottom depth. AVS in both the control and compost alone treatments at this depth averaged 1± 0.33 μmol g^{-1}. For all treatments, the ratio of AVS:SEM clearly indicated potentially toxic conditions (Figure 5). At the interface depth however, there were significant increases in AVS as a result of amendment addition. AVS increased in the control treatment to 2± 0.5 μmol g^{-1}. This increase may have been the result of increased microbial activity closer to the surface. In the compost alone treatment, AVS also increased to 4± 1.5 μmol g^{-1}. The most significant increases in AVS were observed in the compost + SO_4treatments. This is expected, due to the higher concentrations of sulfur in these treatments. AVS increased to 8 μmol g^{-1} in the low SO_4 treatment and to 25 μmol g^{-1} in the high SO_4 treatment. It should be noted that E_h (measured about 12 cm above the samples collected for AVS:SEM was highly reducing in both sulfur treatments at the time the samples were collected (99 d). E_h in the control measured 122 mV with E_h in the compost equal to –66 mV. For the low SO_4 treatment E_h measured –235 mV and was –245 in the high SO_4 treatment. The observed increase in AVS make sense both because of increased SO_4 concentration as well as increased microbial activity as evidenced by the increased electron activity. Although this data suggests a decrease in toxicity as measured by AVS:SEM primarily in the treatments that contained SO_4, the implications for waterfowl that ingest sediment directly are not clear.

PBET. There was no statistical difference between PBET results for samples collected after 99 d versus those collected after 207 d, consequently, data from these two sampling periods were averaged. Percent reduction in bioavailable Pb (relative to the respective control sediment) are presented in Table 4. These values were obtained by comparing the PBET extractable Pb from the control and the treated soils in reference to the total Pb in the 250 μm sediment fraction . As measured by the PBET extraction, a higher percent of the total Pb in the SP sediment was bioavailable than in the NP sediment. As a result, despite differences in total Pb, estimated bioavailability was similar between these two blocks. Aside from this block effect, no statistical differences were detected among the pots within the sediment level. Differences among treatments were, however, observed within the sediment, interface and amendment levels of the pots.

For extractions run on the dried samples, Pb bioavailability was significantly reduced at the interface level in the low $SO_4$and high SO_4 treatments by 24% and 34%, respectively. PBET extractable Pb in the compost and ash alone treatment at this level was similar to the control. At the bottom depth, both SO_4 treatments reduced the PBET fraction of Pb by approximately 30%. In contrast, the compost alone treatment increased PBET Pb at this depth by 13% over the control. It is likely that the observed increase in PBET-Pb in the compost alone treatment was related to root growth and improved oxygen flow at this depth.

The protocol for this extraction calls for materials to be air - dried. It was initially developed to measure Pb availability in aerobic soil systems with a human endpoint. As the primary concern in this case is for waterfowl that ingest the reduced sediment, it may be appropriate to carry out this extraction using wet materials. For wet samples, the observed decrease in bioavailability was more pronounced. The high SO_4 treatment showed a 41 and 24% reduction in bioavailability at the interface and bottom levels respectively. In addition, the compost alone amendment reduced bioavailability in the NP sediment by 18% over the control. There were not sufficient wet tailings to run the PBET procedure for the low SO_4 for all experimental units. However, for the single samples that were extracted, this treatment showed a 70% and 35% reduction in bioavailability at the interface and bottom depths. These data suggest that the addition of a compost layer to tailings may result in reduced sediment Pb bioavailability, and supplementary SO_4 decreases bioavailability even further.

The PBET extraction was also carried out on the amended portion of the columns. Here, total concentrations of Pb were significantly lower than the Pb in the sediment. In addition, a smaller fraction of total Pb was bioavailable . All of the treatments were effective at this level with reductions in bioavailability over the control ranging from 42 - 50% in the compost alone treatment to 76-80% in the compost + SO_4 treatments. We found that the percent of available Pb in the tailings located in the bottom and interface levels was between 44 and 63%, whereas tailings in amendment level was about 96 and 99% or almost all available. In sediment or tailings that contain very high concentrations of Pb, the location of the sediment within the soil profile may be very important both in terms of accessibility and availability. In addition, the compost amendment may serve as an effective barrier to the contaminated sediment.

X-ray Absorption Spectroscopy

EXAFS Results

Figure 6 shows experimental lead L_{III}-EXAFS spectra (chi data) overlaid with model fits for interface level pot samples collected after 99 d and two mineral standards. The model fits represent the multi-shell, EXAFS fitting results shown in Table 5. Radial structure functions derived from fourier transformation of the k-space data are shown in Fig. 7. A comparison of EXAFS results for samples with those for the PbS (galena) standard indicates that Pb-sulfide was present in all four sediment samples. This result is particularly evident from the correspondence of the EXAFS oscillations between the sediment samples and galena in Fig. 6, and the high-magnitude peak at about 2.4 Å (uncorrected for phase shift) in Fig. 7. Fitting analysis (Table 5) yielded an average Pb-S bond length between 2.85 and 2.91 Å for sediment samples, which was comparable to the Pb-S bond length determined for galena (2.92 Å). The discrepancy between these results and the published Pb-S bond length of 2.97 Å for galena (Moller et al., 1989) is consistent with underestimation of Pb(II) coordination distances by ambient temperature EXAFS analysis (Manceau et al., 1996). Higher-shell Pb-Pb distances for all sediment samples (4.12 to 4.17 Å) also corresponded (within 0.08 Å) with Pb-Pb interatomic distances of galena, which was about 0.6 Å greater than the Pb-Pb distance determined for β-PbO (Table 5).

EXAFS fitting results for the control and compost-treated samples also showed the presence of Pb-O bonding, with bond lengths of 2.34 to 2.45 Å (Table 5). For reference, the nearest-neighbor, Pb-O bond lengths for some mineral and adsorbed forms of Pb(II) are as follows: $PbCO_3$ (2.69 Å), $PbSO_4$ (2.67 Å), $Pb_5(PO_4)_3OH$ (2.42 Å), α-PbO (2.31 Å), β-PbO (2.24 Å), Pb(II) adsorbed on γ-Al_2O_3 (2.23 to 2.30 Å) (Manceau et al., 1996; Ryan et al., 2001; Strawn et al., 1998; Chisholm-Brause et al., 1990). Because the interatomic distance determined by

EXAFS analysis represents an average of distances for all Pb species in the sediment samples, one cannot distinguish based on fitting parameters alone whether one or multiple species with the given average bond length is dominant. Because we lacked ambient-temperature EXAFS data for a wide variety of mineral and adsorbed Pb standards, no attempt was made to quantify Pb speciation through linear combination fitting of the EXAFS data. The main trend shown by our EXAFS data for the 99-d samples was a greater proportion of total Pb occurring as Pb-sulfide in the compost+ash+SO_4 amended samples compared with the control and compost+ash only amended samples. This trend indicates that supplementary SO_4 amendment promoted the formation of Pb-sulfide in the sediments. The lower E_h and higher pH measurements for these two samples indicated that conditions were thermodynamically favorable for sulfate reduction and Pb-sulfide formation (Fig. 4). The occurrence of PbS in the control sample suggests that Pb-sulfide (a main source of mineral Pb) was present in the original mine tailings and remained unaltered from its original state in the sediment (Tonkin et al., 2002).

XANES Results

To evaluate whether any detectable changes in Pb speciation of sediments from the potting study occurred over time, we compared lead L_{III}-XANES results between samples taken at 99 and 207 days. Results showed detectable changes in Pb speciation between samples for the same treatment taken at different time periods (Fig. 8). In comparing possible oxygen-bonded and sulfur-bonded mineral species of Pb, XANES data for the standards used in this study showed that $PbSO_4$ and $PbCO_3$ had a more distinct white-line (WL) peak at 13,065 eV than PbS. The WL peak of β-PbO was uniquely shifted to a greater energy. The shapes and intensities of the WL peaks for the spectra for the sediment samples were intermediate between those of the oxygen bonded Pb species (particularly $PbCO_3$ and $PbSO_4$) and PbS. Compared with the SO_4-

amended samples (“low SO_4” and “high SO_4 treatments), the XANES spectra for the control and compost samples exhibited a more distinct WL peak that was more characteristic of spectra for $PbCO_3$ and $PbSO_4$ than PbS.

Results of linear combination fitting analysis to more quantitatively analyze the signficance of differences in the XANES spectra are shown in Table 6. Ideally, such analyses would best be accomplished by fitting with combinations of a large number of possible Pb species. We included only mineral standards that were representative of stable phases predicted by thermodynamics (Fig. 4) or included in the EXAFS analyses. Nevertheless, results in Table 6 should be viewed as indicating trends, not as a a full quantitative assessment of the species present. Nevertheless, the XANES fitting results showed several notable trends. First, the proportion of the Pb-sulfide standard spectrum in the fit was always greater in samples that had been amended with supplementary SO_4 (“low sulfate” and “high sulfate”) than in the “control” and “compost” samples (Table 6). The proportion of PbS found by XANES fitting was not sensitive (within 10 mol%) to whether $PbSO_4$, $PbCO_3$, or both of these standards were included in binary or ternary fits. proportions of the PbS standard. Trends in the XANES data were consistent with EXAFS results showing a combination of first-shell Pb-O and Pb-S bonding in the “control” and “compost” samples, with only Pb-S bonding detected in the “low sulfate” and “high sulfate” samples (Table 5). The fact that we did not detect Pb-O bonding in the SO_4-treated samples using ambient-temperature EXAFS analysis may be attributable to an underestimation of Pb-O bonding due to non-uniform Pb-O bond lengths (Manceau et al., 1996). XANES fitting results in Table 6 also indicated that samples collected after 207 d contained a greater proportion of total Pb as Pb-sulfide than samples collected after 99 d of incubation. Based on data for these two sampling periods in the potting study, Pb-sulfide apparently formed over time for all treatments, forming to a greater extent in the SO_4-treated sediments. Finally, the XANES fitting results for the samples collected at 207 d after exposure to the low-SO_4 and high-SO_4 treatments showed an equal or better fit with a combination of PbS and $PbSO_4$ standards as with a combination of PbS and $PbCO_3$ standards. This result suggests that some Pb-sulfate formed in the sediment samples that received supplementary SO_4. Overall, the XANES and EXAFS results indicated that some of the added sulfate in the potting study was reduced to sulfide, causing part of the sediment Pb contained in oxygen-bonded species (perhaps $PbCO_3$) to be converted to Pb-sulfide.

Discussion

Vigorous plant growth and reduced metal concentrations observed in the aboveground tissue of arrowhead and cattail plants grown in compost-and-wood-ash-amended sediment in the greenhouse and the field are evidence that this treatment is be sufficient to restore a plant cover to the tailings-impacted wetland area that was the basis of this study. In addition, metal concentrations in plant tissue were below those related to negative effects for wildlife, suggesting that consumption of plants grown on amended tailings would not pose an unacceptable risk (Larison et al., 2000). This was true for both plants grown in a controlled environment as well as for plants collected from the actual restored wetland (table 3). For treatments receiving supplementary additions of sulfate, the levels of added sulfate were apparently too high, and resulted in plant demise due to high salinity (or perhaps sulfide toxicity). In a field situation, the rate of sulfate addition would need to be adjusted to avoid negative effects on plant growth.

EXAFS and XANES analyses indicated that a portion of the Pb in all treatments was present as PbS. However, the surface application of compost + ash + sulfate (at each of two levels) was especially effective in promoting an increase in the proportion of total Pb bound as

Pb-sulfide in the underlying sediment, apparently through sulfate reduction. These observations were in accord with the pH and E_h measurements that indicated that PbS would be stable in these treatments. For the compost and ash treatments, it is not clear if increased redox potential and the reduced rate of PbS formation is an artifact of the pot study or represents what is actually occurring in the field. It is likely that the plant roots grew into the contaminanted sediment because of the small size of the pots. In the field, root growth may be limited to the amended horizon. If this is the case, it is likely that reducing conditions would persist in the underlying tailings as they did in the 40 d – 90 d portion of the greenhouse study.

Changes in Pb speciation induced by sediment amendments should directly affect the environmental impacts of sediment Pb. Previous *in vivo* studies indicated that the bioavailability of Pb to swine (a surrogate for humans) is directly affected by the mineral form of Pb present in the soil(Ruby et al., 1994; Ruby et al., 1996). Furthermore, the portion of total Pb that was bioavailable in PbS (galena) was less bioavailable Pb than in other Pb minerals, including $PbSO_4$ (anglesite) and $PbCO_3$ (cerrusite). Thus, an increase in Pb-sulfide as a proportion of total Pb in the sediment is expected to decrease the bioavailability of Pb from ingested sediment. Indeed, our results from indirect chemical (in-vitro) assessments (PBET - Pb and AVS:SEM ratio) indicated that the compost + ash + SO_4 treatments (and compost + ash alone) should decrease bioavailable Pb, particularly at the sediment/cap interface level (Table 4, Fig. 5). It should be noted, however, that each of the bioavailability procedures used was developed to predict changes in toxicity for very different exposure pathways. The PBET extract was designed to mimic the human gastric system. The AVS:SEM procedure was developed to predict toxicity to benthic organisms, such as clams and aquatic worms, whose feeding habits and digestive systems differ substantially from vertebrates. While the results of this assay may not relate directly to vertebrates other than humans, indications of decreasing Pb bioavailability to other organisms may nonetheless be pertinent. In addition, plant tissue data (Table 3) indicated that a compost + ash treatment decreased the amount of Pb taken up by wetland plants. It should also be noted that these mineral shifts and reductions in in vitro assays were achieved only when the treatments had a consistent water cap. Results would be expected to differ with a fluctuating water table and similar reductions would not be expected.

Conclusions

In conclusion, this potting study indicated that the risk of Pb poisoning to waterfowl from sediments at the West Page swamp could be reduced by amendments of compost + ash (with or without supplementary sulfate addition). This risk reduction may be achieved by one or a combination of several mechanisms: (1) an overlying cap of a compost + ash amendment would serve as a physical barrier to diminish ingestion of contaminated sediment by waterfowl; (2) the amendments chemically alter Pb in the tailings at the amendment/sediment interface such that a greater proportion of the Pb is bound as Pb-sulfide, which results suggest would be less bioavailable if the sediment were ingested; and (3) a compost + ash treatment without supplementary sulfate allowed vigorous plant growth, probably by providing a more favorable rooting medium for the plants. Furthermore, the Pb content of the plant tissue was diminished in the compost + ash amended sediment compared with a control treatment, which would reduce Pb exposure via ingestion of plant tissue.

Field observations since this potting study confirm the effectiveness of the compost + wood ash treatment. In the portion of the West Page Swamp that was treated with a surface application of compost and ash in 1998, volunteer plants restored a lush cover to the area by 1999, and this cover persists at present. Plant tissue data shows concentrations of Pb, Cd, and Zn comparable to what was observed in the greenhouse (Table 3). Continued monitoring of the swamp indicates that wildlife have returned to the area (personal communication with Mark Sprenger, US EPA Environmental Response Team).

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Figure Captions

Figure 1. A diagram of the experimental units used for the study. The diagram shows the depth of the tailings, the compost amendment and the water cover. It also shows the amendment, interface and tailings sampling points.

Figure 2. Sediment E_h potential values averaged over all replicates of the North and South plot sediments for each sampling period for the greenhouse study. Measurements were taken in the top 2 cm of substrate.

Figure 3. Sediment pH values for the greenhouse study. Measurements were taken in the top 2 cm of substrate. Data points represent the means of all replicates averaged over North and South plot sediment for each sampling date.

Figure 4. Eh and pH data from the control, compost, Compost + low SO_4 and compost +high SO_4 treatments plotted on an Eh-pH diagram for a range of Pb minerals. This diagram does not take into account changes in stability based on variable sulfur concentrations.

Figure 5. Acid volatile sulfide: simultaneously extractable metals from the tailings at the interface and bottom level (99 d) from amended and control treatments in the green house study. Different letters above bars indicate significantly different values using the Duncan Waller means separation procedure ($p < 0.05$).

Figure 6. Stacked, normalized k^3-weighted L_{III}-EXAFS spectra (chi data) for lead in sediment samples taken after 99 days of incubation with various treatments, and mineral standards. Experimental spectra (solid lines) are overlaid with spectral fits (dashed lines) based on the fitting parameters reported in Table 5.

Figure 7. Stacked radial structure function (RSF) magnitudes derived by fourier transformation of k^3-weighted, lead L_{III}-EXAFS spectra shown in Fig. 6. Radial distances are not corrected for phase shift, and therefore, do not reflect actual interatomic distances.

Figure 8. Stacked, normalized L_{III}-XANES spectra for for lead in sediment samples and standards. Sediment samples were collected at 99 days (solid line) or 207 days (dashed line) for each treatment. Data for standards are represented as solid lines for $PbCO_3$ and $PbSO_4$, and dashed lines for PbS and PbO.

Table 1. Select elemental concentrations in <2 mm sediment samples collected from north and south areas of West Page Swamp in northern Idaho and for the compost and ash amendment used in the study. Values followed by the same letter for each element are not significantly different ($p<0.05$).

Tailings and amendment	Ca	Cd	Cu	Fe	K	Mg	Mn	P	Pb	Zn
	——————				mg kg^{-1} ——————					
North plot (NP)	3200 b	70 b	240 a	119000 a	1200 b	5500 a	12500 b	1120 b	10000 b	13000 a
South plot (SP)	2700 c	200 a	190 b	112000 b	1100 b*	5200 b	11800 a	1110 b	12000 a	13000 a
Compost + Ash	47000 a	3 c	200 b	9000 c	5200 a	5600 a	1500 c	23000 a	300 c	750 b

Table 2. Average pore water Pb concentrations by depth within pot, averaged over all sampling times (mean±SE).

Treatment	Sediment Level	Interface Level	Amendment Level
	¾¾¾¾¾¾¾¾¾¾¾¾	mg Pb L^{-1}	¾¾¾¾¾¾¾¾¾¾¾¾¾¾
Control	0.7 ± 0.09	1.2 ± 0.28	0.8 ± 0.16
Compost	0.2 ± 0.05	0.2 ± 0.07	0.2 ± 0.07
Compost + low SO_4	0.3 ± 0.02	0.3 ± 0.02	0.3 ± 0.02
Compost + high SO_4	0.7 ± 0.07	0.6 ± 0.05	0.5 ± 0.05

Table 3. Mean elemental concentrations in aboveground tissue of arrowhead (*Sagittaria latifolia* (L.) and cattail plants (*Typha latifolia* (L.) grown in control and compost-treated tailings in the greenhouse study and in the control and compost amended West Page Swamp. Values within the same column and species followed by the same letter are not significantly different ($p<0.05$).

Species and Treatment	Ca	Cd	Cu	Fe	K	Mg	Mn	P	Pb	Zn
	¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾ mg kg^{-1}¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾¾									
Arrowhead										
Control	3 900 b	50 a	20 a	220 a	36 000 a	2 200 a	830 a	7 000 a	300 a	1 600 a
Compost	8 000 a	3 b	7 b	30 b	30 000 a	1 000 b	250 b	3 000 b	1 b	300 b
Cattail										
Greenhouse										
Control	12 000 a	13 a	9 a	200 a	27 000 a	3 300 a	1 300 a	3 100 a	80 a	900 a
Compost	7 000 b	4 b	4 b	20 b	26 000 a	1 400 b	700 a	2 000 b	2 b	100 b
Wetland										
Control -1998	8 000 a	5.3 a	10 a	140 a	1 300 a	2 700 a	4 400 a	800 a	120 a	1000 a
Compost - 2000	10 200 a	0.4 b	7.6 a	110 a	15 700 b	1 180 b	2 500 a	1900 b	5 b	115 b

Table 4. Physiologically -based extraction technique (PBET) data from greenhouse study indicating percent reduction in Pb bioavailability in <250 μm soil fraction at the sediment, interface, and amendment levels. Means are averages of samples collected after 99 d and 207 d for dry samples and 207 d for wet samples. Values within the same column and at the same sampling depth that are followed by the same letter are not significantly different ($p<0.05$). NP and SP refer to North and South sediments.

Level	Sediment Source	Treatment	%Reduction in Pb Bioavailability	% Reduction in Pb Bioavailability
Bottom			DRY	WET
	NP	Compost	-13 a	0 a
	SP	Compost	0 b	0 a
	SP	Compost + low SO_4	30 c	
	SP	Compost + high SO_4	29 c	24 b
Interface				
	NP	Compost	2 a	18 b
	SP	Compost	-6 a	0 a
	SP	Compost + low SO_4	24 b	
	SP	Compost + high SO_4	34 b	41 c
Amendment				
	NP	Compost	42 a	
	SP	Compost	50 a	
	SP	Compost + low SO_4	81 b	
	SP	Compost + high SO_4	76 b	

Table 5. Lead L_{III}-EXAFS fitting results for sediment samples collected after 99 d of incubation with various treatments, and selected standards.†

Sample Treatment	Coord-ination	Radial Distance (Å)	Coordination number (N)¥	Debye-Waller factor $-\Delta\sigma^2$ ($Å^{-1}$)	En sh ΔE
Control	Pb-O	2.34 (±0.05)	0.3 (±0.2)	0.0001‡	8
	Pb-S	2.85 (±0.03)	2 (±1)	0.009 (±0.006)	
	Pb-Pb	4.12 (±0.08)	4 (±7)	0.018 (±0.017)	
Compost	Pb-O	2.45 (±0.06)	2 (±2)	0.021 (±0.018)	8
	Pb-S	2.88 (±0.02)	1.0 (±0.2)	0.0001‡	
	Pb-Pb	4.16 (±0.05)	2 (±4)	0.009 (±0.014)	
Low sulfate	Pb-S	2.90 (±0.02)	3 (±1)	0.013 (±0.004)	3
	Pb-Pb	4.17 (±0.04)	8 (±6)	0.021 (±0.008)	
High sulfate	Pb-S	2.91 (±0.03)	4.3 (±1)	0.018 (±0.005)	3
	Pb-Pb	4.17 (±0.04)	5.7 (±5)	0.016 (±0.008)	
β-PbO (yellow)	Pb-O	2.18 (±0.02)	1.1 (±0.4)	0.003 (±0.003)	1
	Pb-Pb	3.49 (±0.02)	2.1 (±2)	0.009 (±0.005)	
PbS (galena)	Pb-S	2.92 (±0.02)	6 (±2)	0.018 (±0.004)	2
	Pb-Pb	4.18 (±0.03)	12 (±8)	0.022 (±0.007)	

† Estimated errors on fitting parameters were computed by the MacXAFS program (Bouldin et al., 1995).

Goodness of fit (reduced χ^2) values are adjusted for the number of degrees of freedom in the fitting analysis (Sayers, 2000).

‡ Parameter fixed during fitting.

¥ Coordination numbers were adjusted by an amplitude reduction factor (S_0^2 – Sayers and Bunker, 1988) of 0.83 (Pb-O and Pb-S) or 0.94 (Pb-Pb) to yield structural parameters consistent with crystallographic data for galena (R_{Pb-S} = 2.97 Å, N = 6; R_{Pb-Pb} = 4.20 Å, N = 12 - Moller et al., 1989).

Table 6. Lead L_{III}-XANES fitting results showing the relative proportions (mole percentages) of PbS, $PbCO_3$, and $PbSO_4$ standards yielding the best fits to the soil XANES data in binary (or ternary) linear combination fitting†.

Treatment	PbS	$PbCO_3$	$PbSO_4$	Goodness of fit (χ^2)
	--------------------mol% of total Pb		--------------------	
control – 99 d	35 ± 3	66 ± 3		0.0048
control – 207 d	49 ± 2	51 ± 2		0.0025
compost – 99 d	33 ± 2	67 ± 2		0.0042
compost – 207 d	40 ± 1	60 ± 2		0.0024
low sulfate – 99 d	62 ± 2	38 ± 2		0.0013
low sulfate – 207 d‡	87 ± 1 (88.3 ± 0.4)	13 ± 1	 (11.0 ± 0.3)	0.0025 (0.0026)
high sulfate – 99 d	62 ± 2	38 ± 2		0.0015
high sulfate – 207 d	80.0 ± 0.8		20.0 ± 0.4	0.0053

† Mole percentages reported represent means ± standard deviations of results for three fitting ranges of the XANES spectra: 13,030 to 13,130 eV; 13,030 to 13,090 eV; and 13,030 to 13,075 eV. The χ^2 parameter is the mean for the three fitting results.

‡ Fitting using standards of PbS + $PbCO_3$ versus PbS + $PbSO_4$ yielded nearly equivalent goodness of fit, with each standard combination giving a better fit in different portions of the sample spectrum.

Figure 1.

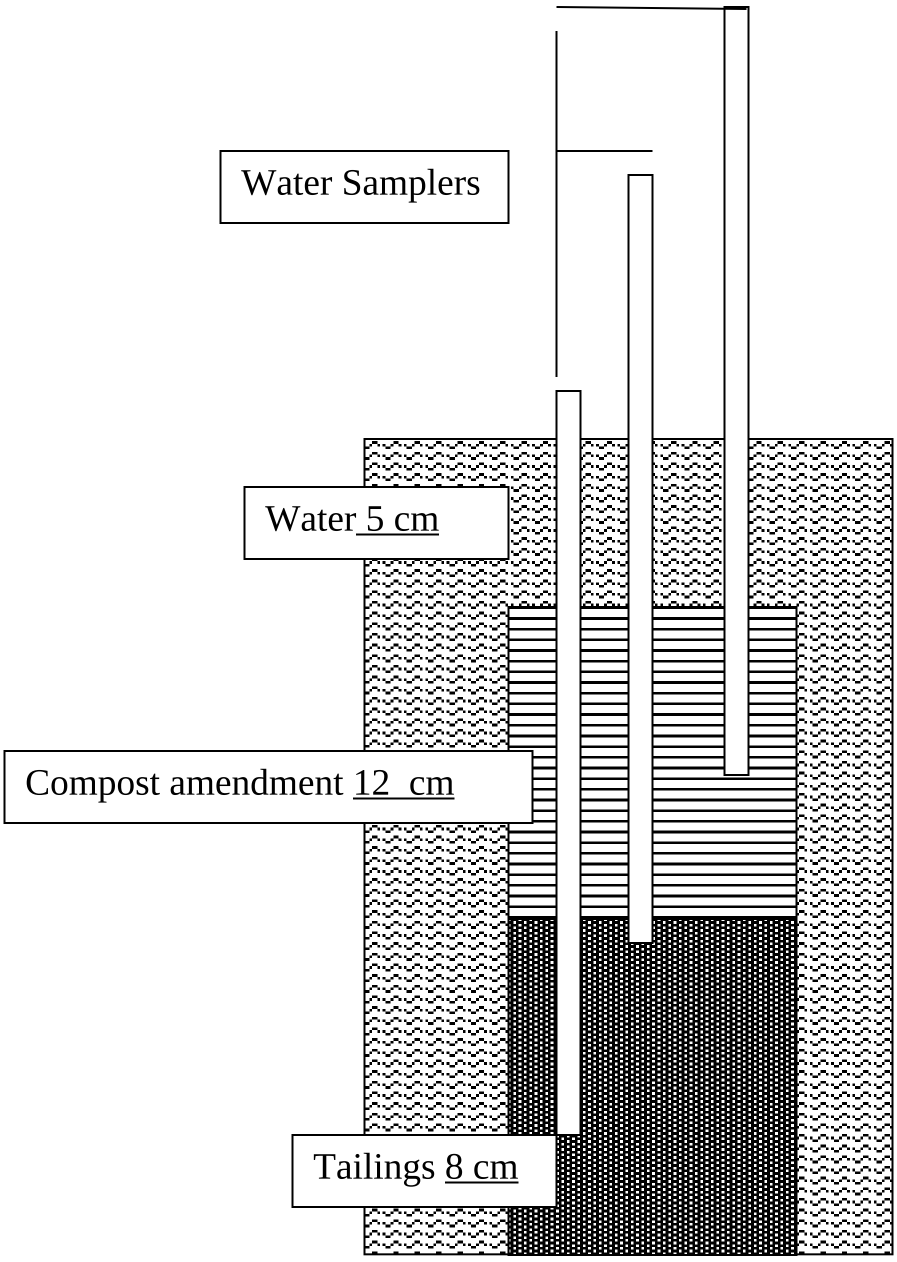

Water Samplers
Water 5 cm
Compost amendment 12 cm
Tailings 8 cm

Figure 2.

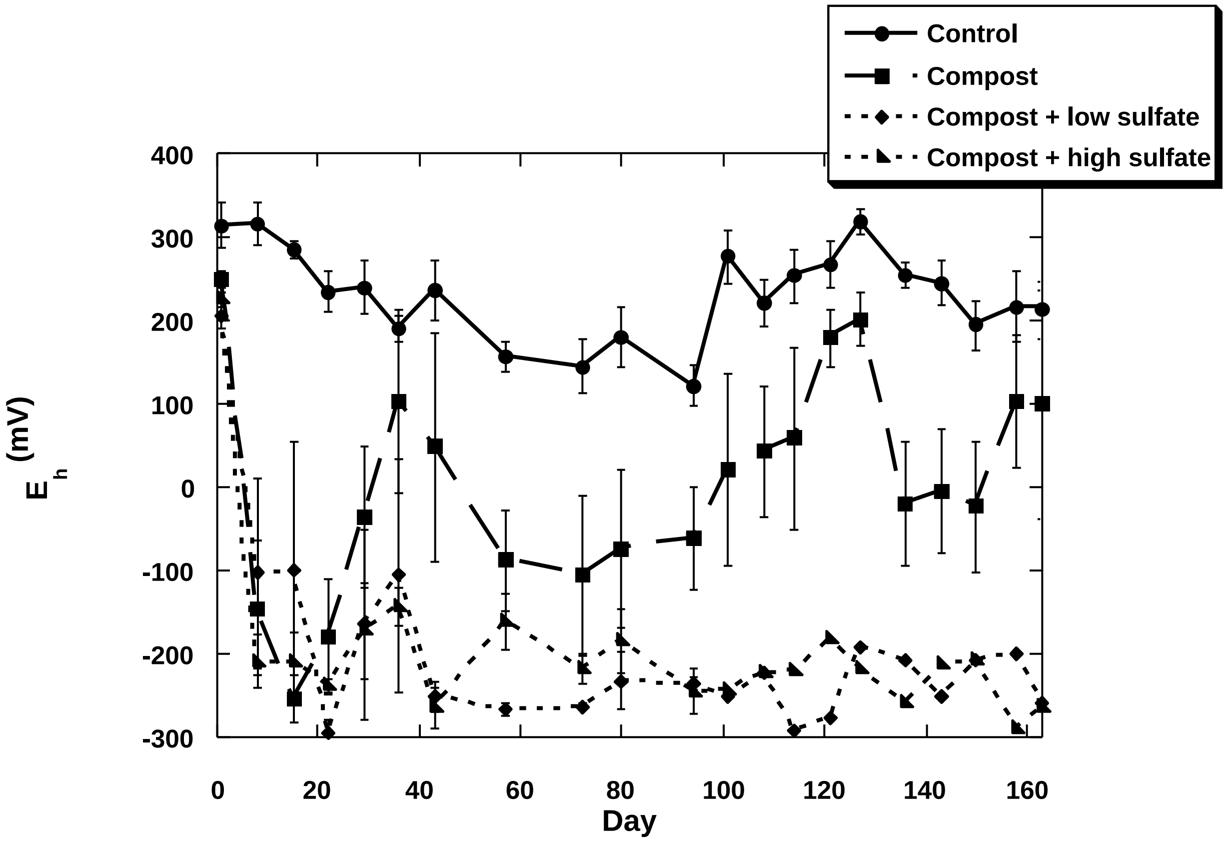
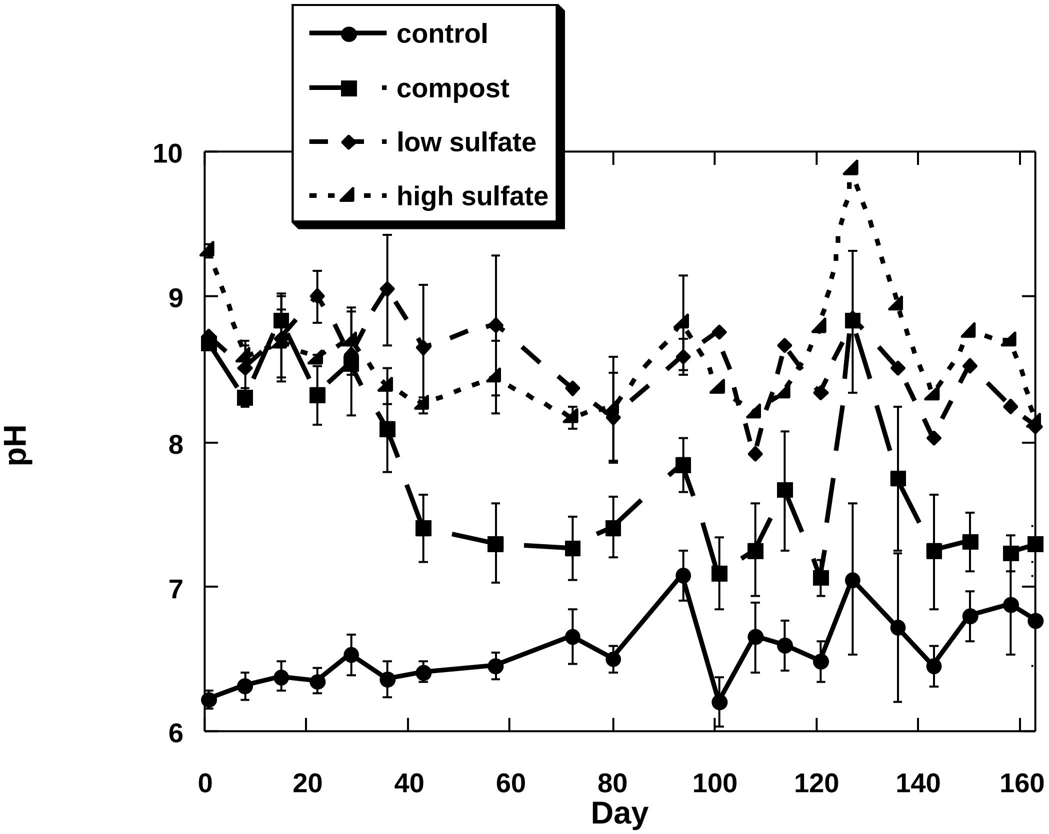

Control
Compost
Compost + low sulfate
Compost + high sulfate
E_h (mV)
400
300
200
100
0
-100
-200
-300
0
20
40
60
80
100
120
140
160
Day

Figure 3


control
compost
low sulfate
high sulfate
pH
10
9
8
7
6
0
20
40
60
80
100
120
140
160
Day

1 Figure 4

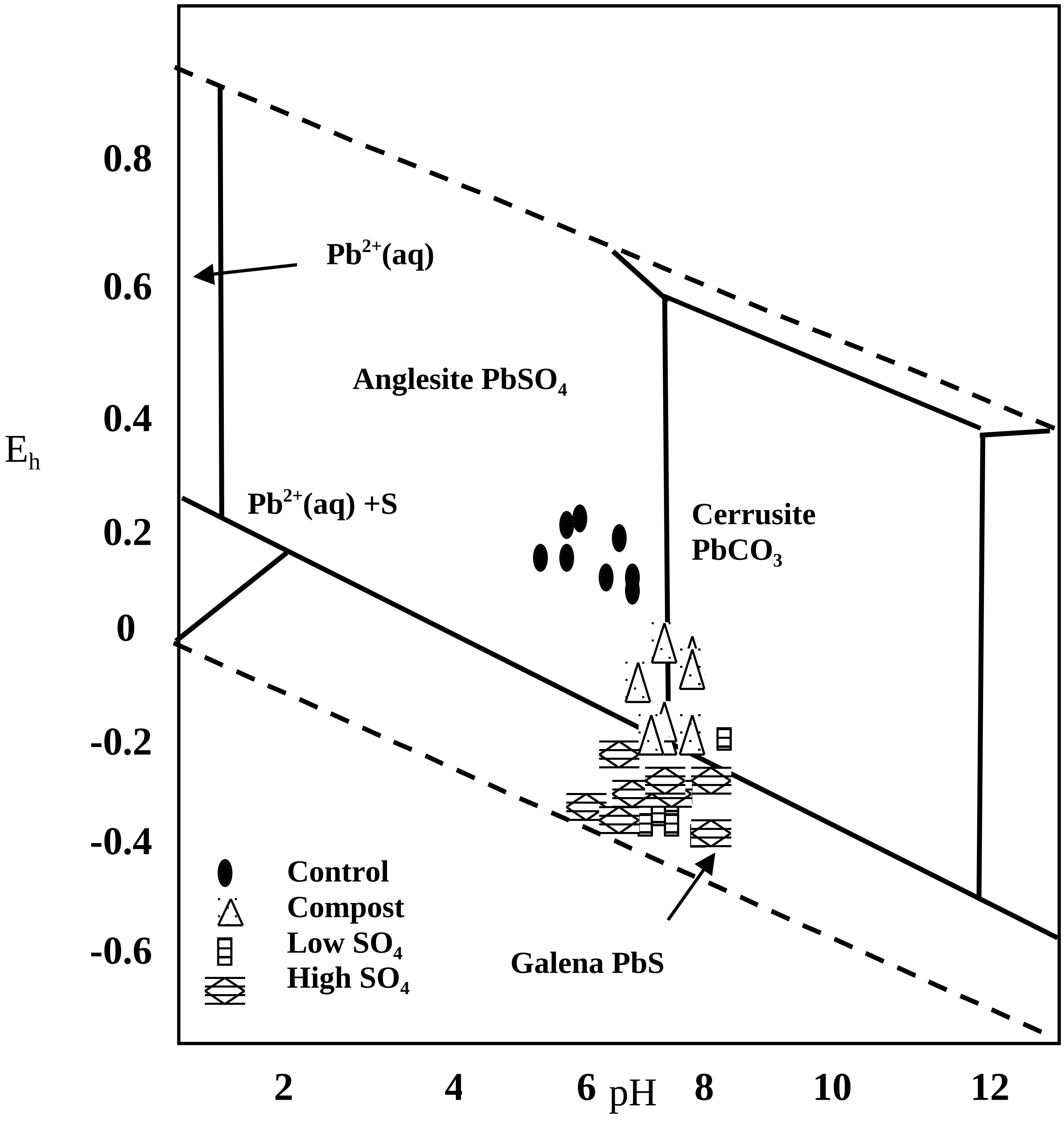
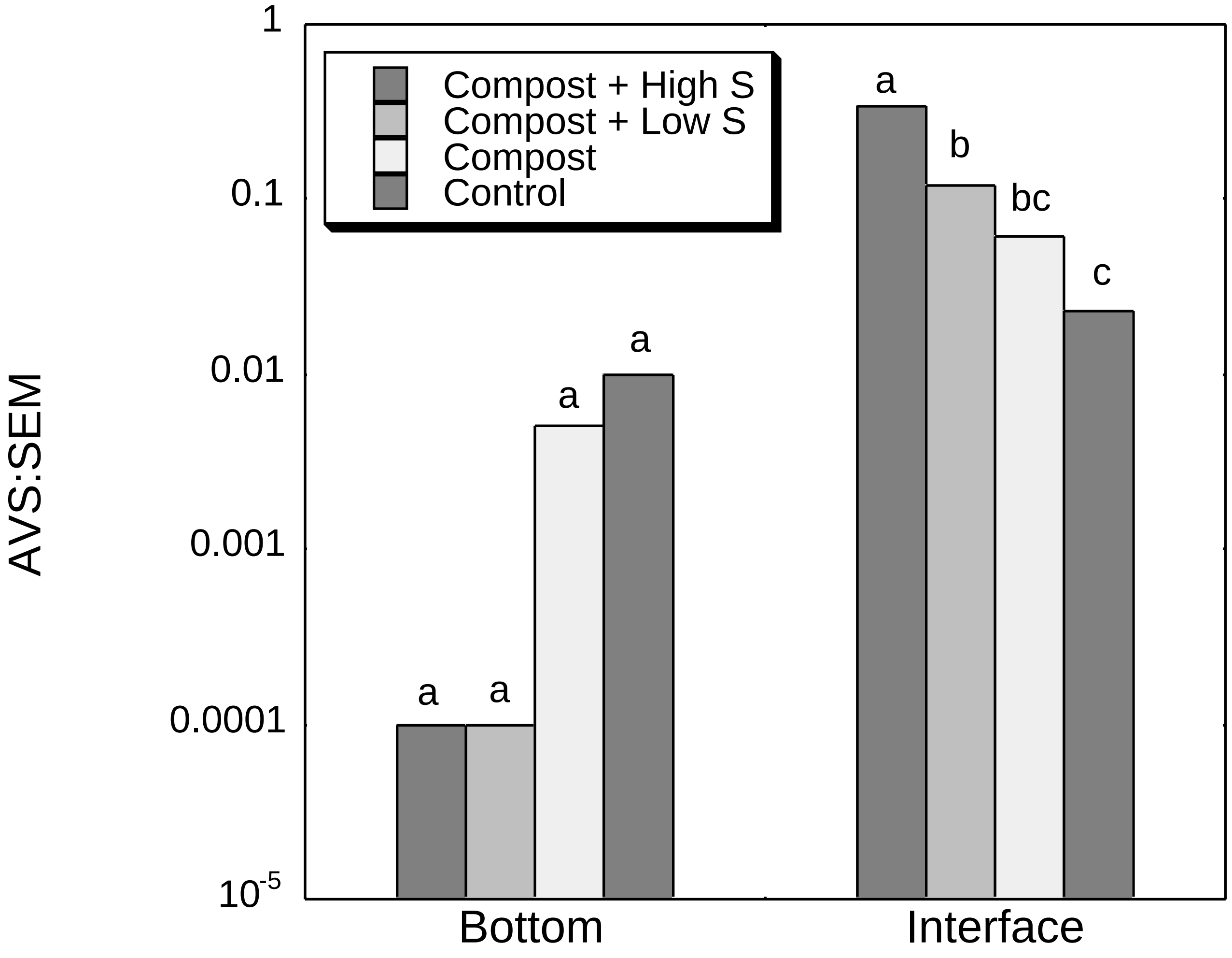
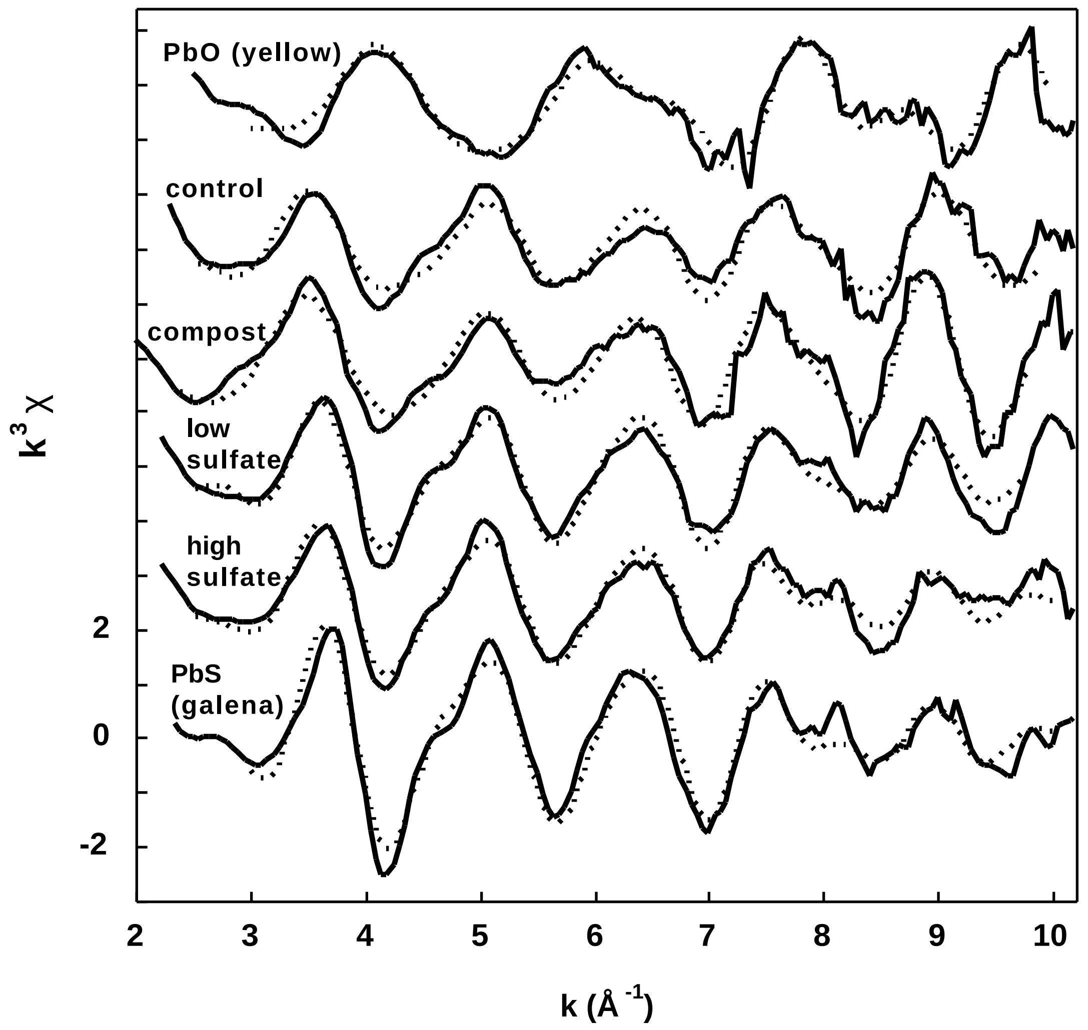

Pb2+(aq)
0.8
0.6
Anglesite PbSO4
0.4
Eh
Pb2+(aq) +S
0.2
Cerrusite
PbCO3
0
-0.2
-0.4
-0.6
Control
Compost
Low SO4
High SO4
Galena PbS
2
4
6
pH
8
10
12

Figure 5



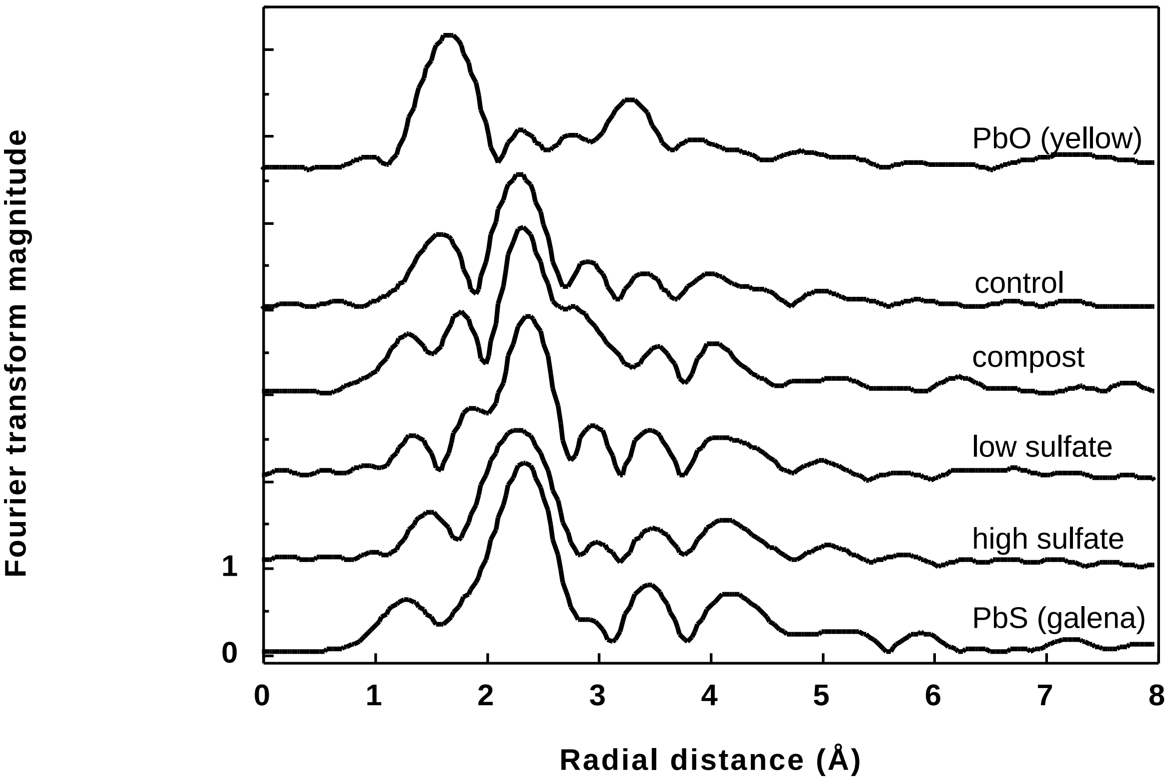
Compost + High S
Compost + Low S
Compost
Control
AVS:SEM
1
0.1
0.01
0.001
0.0001
10^{-5}
a
a
a
a
a
b
bc
c
Bottom
Interface

Figure 6


PbO (yellow)
control
compost
low sulfate
high sulfate
PbS (galena)
k$^3\chi$
2
0
-2
2
3
4
5
6
7
8
9
10
k (Å^{-1})

1

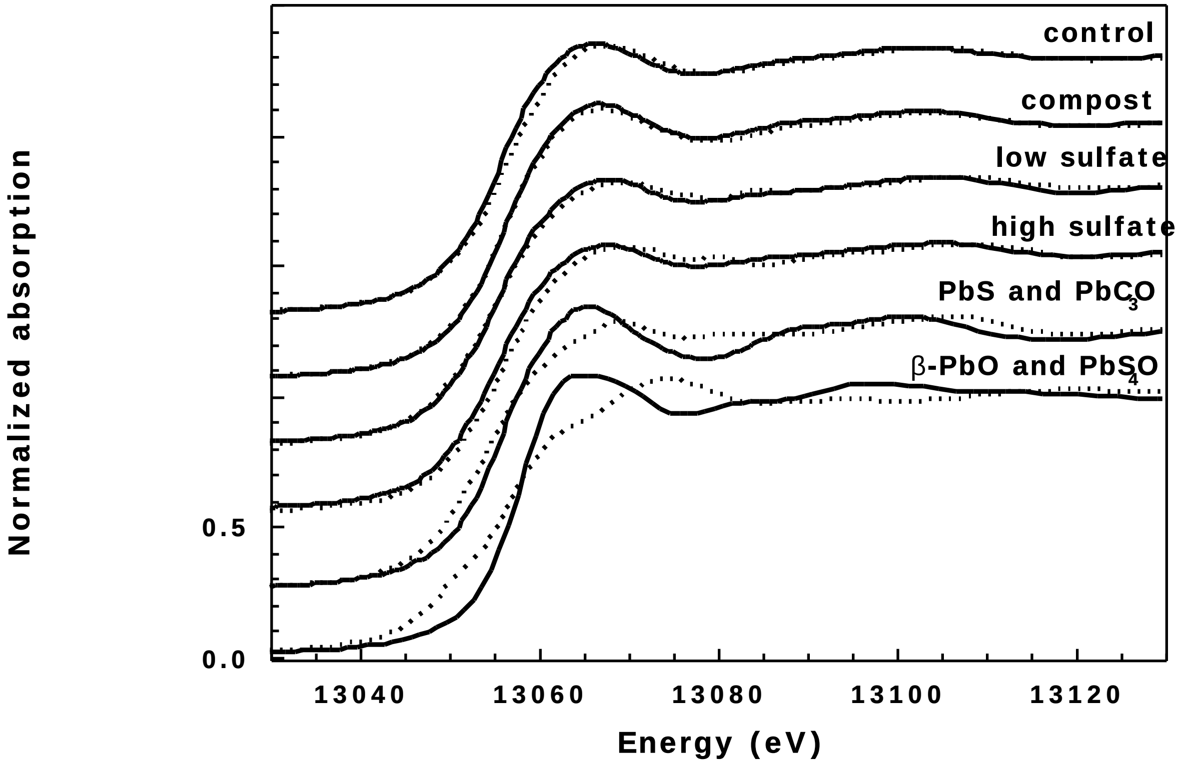
Figure 7



Fourier transform magnitude
1
0
0
1
2
3
4
5
6
7
8
Radial distance (Å)
PbO (yellow)
control
compost
low sulfate
high sulfate
PbS (galena)

1

Figure 8


control
compost
low sulfate
high sulfate
PbS and PbCO3
β-PbO and PbSO4
Normalized absorption
0.5
0.0
13040
13060
13080
13100
13120
Energy (eV)