

The Tri-State Mining Region USA: Twenty years of trace element research

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Abstract

Lead and Zn were mined extensively in the Tri-State Mining Region for over 100 years leaving a multitude of environmental issues. Large areas are void of vegetative cover, communities have been impacted by smelter emissions, and vast quantities of mine wastes and soils enriched with Pb, Zn, and Cd remain. Phytostabilization, soil amendments, and sub-aqueous disposal of mine wastes have been proposed as remediation approaches and the purpose of this paper is to present a synopsis of key research projects in support of such activities. Long-term viability of vegetative cover for phytostabilization is a significant concern and soil microbial ecology likely plays a role in the success or failure of this approach. Our results indicate that very high levels of compost (>200 Mg/ha) are needed to sustain soil microbial enzyme activities over time, which will facilitate long-term viability of vegetation. Phosphorus additions to soils induce the formation of Pb phosphate minerals, reducing bioavailability, and the source of P and time influence the reaction products. The conversion of metals to sulfide forms is slow under reducing conditions in the absence of added C. When in sulfides form, metal solubility and mobility should be greatly reduced.

Key Words

Zinc, cadmium, lead, mining, nonferrous, heavy metals.

Introduction

The Tri-State Mining Region is comprised of portions of the states of Kansas, Missouri, and Oklahoma in the central United States. Lead and Zn were mined extensively from the mid 1800's until the early 1950's, and smelted until the early 1970's. A variety of environmental issues remain including Pb-contaminated soils in a number of communities, highly contaminated abandoned smelter sites, large quantities of mine wastes, and thousands of hectares of land with little or no vegetation. A lack of vegetative cover can be attributed to poor soil chemical, physical, and biological properties that adversely impact the establishment or maintenance of vegetation. One particularly challenging aspect of phytostabilization is long-term viability of the vegetation. Soil amendments allow rapid growth of vegetation shortly after application, often in areas completely void of vegetation previously, but the vegetation slowly declines and can be completely gone within three to five years. Some investigators have proposed using very high application rates of organic amendments (>200 Mg/ha) to help establish a viable soil ecosystem. The use of P to reduce Pb bioavailability in contaminated soils has been proposed as an alternative to soil excavation and replacement. Early work has demonstrated the treatments are effective in reducing Pb uptake by rats with relative bioavailability (as compared to Pb acetate) reduced from 0.34 in unamended soil to 0.24 in the same soil amended with rock phosphate. What isn't known is the nature of the mineralogical changes in Pb induced by various P sources and how they may change over time. Subaqueous disposal of mine wastes involves collecting mine wastes present in large piles and placing it into mine voids. This removes the waste from the surface and fills numerous mine voids, facilitating remediation. Shallow groundwater is already negatively impacted by metals. It is assumed that metals in the mine wastes will be converted to insoluble sulfide forms in the anaerobic environment and, therefore, that subaqueous disposal will not increase existing groundwater concerns. The low C content of the mine wastes and aquifer may inhibit microbial activity and the conversion of metals to sulfide forms.

Materials and methods

Phytostabilization

Two field studies were established in areas highly contaminated in Pb and Zn. Of particular interest here are the contaminated control (C), low compost (LC, 45 Mg/ha), and high compost (HC, 269 Mg/ha) treatments. Soil samples were taken approximately one week after application to establish a Time 0 and switch grass (*Panicum virgatum*) was sown into each plot. Soil samples were again taken after 157, 371, 553, 729, and 1157 d. Soil enzyme activities (β -glucosidase, alkaline, and arylsulfatase) were assayed within 2 weeks after

sampling on field-moist samples and are reported on a dry-weight basis. Changes to soil microbial community were assessed at 729 DAT by measuring the soil phospholipid fatty acid (PLFA) content. Immediately after sampling/sieving, approximately 20 g of moist material was frozen at -20 °C and lyophilized. The total lipids were extracted from the lyophilized material, the total lipid extract was separated into PLFA and waste lipids using silicic acid chromatography, the fatty acids were cleaved from the glycerol backbone by KOH saponification, and the harvested fatty acids were methylated to form fatty acid methyl esters. The nomenclature used to designate the identified fatty acids is the total number of carbon atoms and number of double bonds, followed by the position of the double bond from the methyl end of the molecule.

Laboratory incubations of P-amended Pb-contaminated mine spoils

The material used in this study was collected from an abandoned Pb/Zn smelter. The material was brought to 25% gravimetric water content and placed into plastic containers. Phosphorus treatments (phosphate rock (PR) or phosphoric acid (PA)) were applied in a line across the container. Treatments were covered with additional moist contaminated soil, covered, incubated for 4 or 52 weeks, and air dried before impregnation two part (epoxy/hardener) resin. The hardened resin was then cut using a petrographic trim saw to expose the P treatments and surrounding waste material. At the Advanced Photon Source (APS), μ -XRF maps (typically 6000- by 3000- μ m) were collected for Pb near the point of P application. Pb points of interest (POI) were selected from each map to perform Pb μ -XANES (13,035 eV) to detect changes in Pb speciation as affected by P source, time, and distance from the point of application.

Subaqueous metal transformations of Pb- contaminated mine-spoils

Two contrasting metal-rich mine-spoil materials were used for this study. Oxygen-free feed solution was used to submerge these materials. Organic C (OC as sodium lactate) was added tri weekly to support growth of microorganisms. Samples with and without added OC were incubated for 1 and 2; 11 and 10 months in an anaerobic glove box chamber in a sequential manner. Solution samples were analyzed periodically for pH, Eh, and soluble constituents. Characterization and speciation of solids samples were performed using SEM-EDX analysis, μ -XRF maps and μ -XAS.

Results and discussion

Alkaline phosphatase activity is presented as a representative enzyme. Phosphatase activities were significantly increased by the HC treatment at all sample times (Figure 1) and remain relatively constant with time. PLFA analysis indicated that gram (+), gram (-), fungi, and total microbial biomass were significantly increased by compost additions at 729 d, but actinomycetes were unchanged relative to the control.

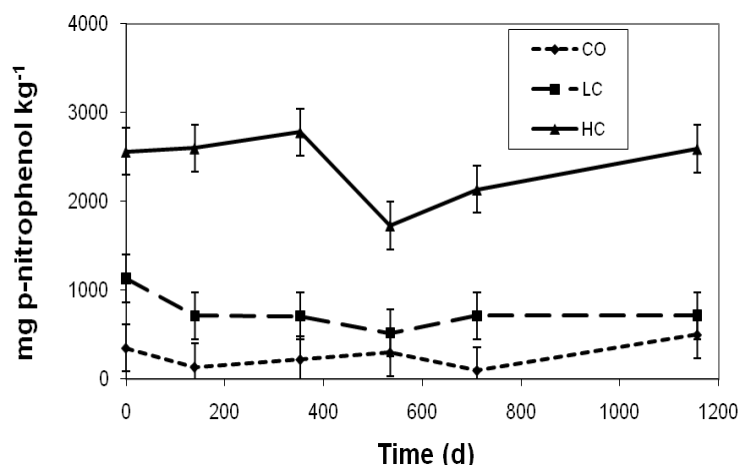


Figure 1. Alkaline phosphatase activity with time.

The Pb μ -XANES spectra for the untreated control samples indicated the presence of cerussite [PbCO₃], galena [PbS], anglesite [PbSO₄], magnetoplumbite [PbFe₆Mn₆O₁₉], and plumboferrite [Pb₂Mn_{0.2}Mg_{0.1}Fe_{10.6}O_{18.4}] as the dominant Pb mineral species, while no phosphate minerals were detected. Plumbogummite [PbAl₃(PO₄)₂(OH)₅·H₂O] was present at 4 wks for all P sources and at 52 weeks, plumbogummite and pyromorphite [Pb₅(PO₄)₃Cl] were found. Micro-XRD analysis was able to confirm results obtained with linear combination fitting.

In reaction vessels with no added OC, E_h remained stable around +250 mV (moderately reduced) from 42 to 98 d. Then within a week time (between 98 to 105 d) E_h dropped down to ~115 mV indicating a major shift in terminal electron acceptors. In contrast, in vessels with OC added E_h dropped down to ~+50 mV after 28 d, remained below 0 mV between 59 to 70 d, and then increased to +50 mV again by 112 d of submergence. The pH in these systems appeared to be unaffected by OC addition and stabilized around 7.6 after 42 d of submergence indicating that the level of OC in these systems are critical in determining redox changes. Recent SEM-EDXA analyses revealed more C in metal-rich particles examined (appeared more like precipitates in SE and BSE images) from systems in which OC was added (Figure 2). In contrast, S concentrations in metal rich particles were either non-detectable or very low. We suspect that high carbonate in these geological materials and microbial respiration might have caused increased levels of bicarbonate concentrations and the formation of metal carbonate solid solutions instead of sulfide solid solutions. This hypothesis will be verified using μ -XRF maps and μ -XAS at the APS in December 2009. Soluble Fe^{2+} concentrations in samples collected from systems with OC added were significantly higher ($23 \mu\text{mol/L}^1$) than the no-OC added samples ($\sim 4 \mu\text{mol/L}^1$) at 110 d of submergence. In contrast, soluble Mn, Pb and Zn concentrations in samples collected from systems with OC added were significantly lower than the no-OC added samples indicating major differences in transformation products of these two (with and without OC) systems.

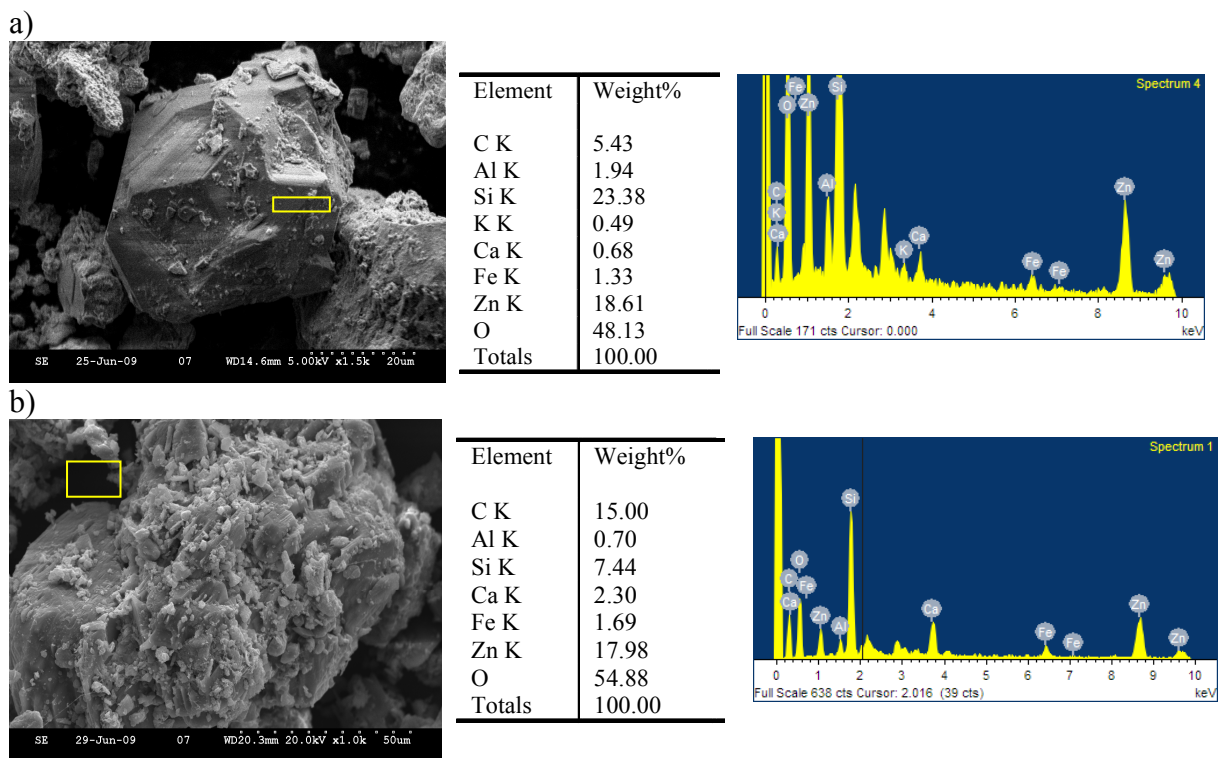


Figure 2. SEM image of original mine-spoil with a) no OC added and b) OC added, submerged for 110 days, and EDXA spectra of particle, located on the larger particle or separately, shown on the SEM image.