

MICROSCALE ZN SPECIATION IN A SMELTER-CONTAMINATED SOIL USING MICRO-XAS AND XRF TECHNIQUES

Darryl R. Roberts¹, Andreas C. Scheinost², Geraldine Lamble³, and Donald L. Sparks¹

¹ *Department of Plant and Soil Sciences, University of Delaware, Newark, DE*

² *Institute of Terrestrial Ecology, Swiss Federal Institute of Technology Zurich, Switzerland*

³ *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California*

The historic smelting facility in Palmerton, PA has resulted in the introduction of Cd, Pb, and Zn emissions into the vicinity around the site. One area that has been severely impacted is the Blue Mountain operable unit. This area consists of 2,000 acres on the north slope of Blue Mountain. Revegetation efforts began in 1991 and currently half of the 2,000 acres is covered by grass. The other half of the mountain has limited vegetative growth so soil erosion continues to be of great concern. The heavy Zn deposits have resulted in Zn concentrations in the percentage range. Once on soil surfaces, metal-bearing smelter byproducts may undergo dissolution reactions followed by one of many pathways including reprecipitation into new solid phases, sorption to organic and inorganic soil constituents, colloid-facilitated transport, and uptake by plants and organisms. Determining the speciation and any metal-mineral transformations which occur as a result of natural processes in soils is necessary to employ the most effective remediation strategies and to predict the fate of metals in the environment. The purpose of this study was to employ advanced spectroscopic techniques to determine the speciation of Zn in the soils of Blue Mountain.

The application of spectroscopic techniques to study soils has enabled researchers to estimate the chemical environment of contaminants in soils without relying on sequential extraction methods. Standard X-ray absorption spectroscopy (XAS) probes an area of several square millimeters. Since the most reactive soil components have particle sizes in the micron range, the signal from such an area often may constitute the average of several contaminant species. In heterogeneous soil systems, however, variations in metal speciation may occur over much smaller areas. To accurately quantify the speciation of Zn in these soils, this study employed micro-XANES and micro-XRF spectroscopies on Zn-contaminated soils at beamline 10.3.2 at the Lawrence Berkeley National Lab Advanced Light Source (LBNL-ALS). Surface (< 5 cm) and subsurface (< 500 cm) soil samples were collected, air-dried, embedded in an acrylic resin (LR-White resin), and polished into 50 μm thin sections. Elemental maps were collected for Fe, Mn, and Zn over an area of 1 mm^2 with 5 μm steps. Using the generated map, XANES spectra were collected on "hot spots" (areas of highest metal concentration) 100 eV below the absorption edge to 500 eV beyond the absorption edge with increments varying from 0.05 to 10 eV. Spectra were collected on several Zn-bearing mineral phases and for Zn sorbed on reference oxides and clay minerals to aid in Zn speciation. In addition, samples were analyzed using bulk-XAFS and sequential extraction techniques in order to compare results using a variety of speciation methods.

Micro-XAS and XRF results from beamline 10.3.2 ALS indicated that in the organic-matter rich surface soil the Zn was present as discrete Zn-sulfide (sphalerite) and Zn-Fe/Mn oxide mineral phases (franklinite). This difference in Zn speciation in the surface soil occurred in an area of only a few hundred square microns, a difference that was not detected using standard XAS. In the subsurface soil, both the micro and bulk XAS revealed Zn to be predominately present as an adsorbed complex to a Mn oxide phase. This difference in Zn speciation in the surface and subsurface soils suggests weathering, transport and sorption processes have occurred. The results from this study show the utility of micro-focused spectroscopic studies relative to bulk-spectroscopic studies in determining contaminant speciation in soils.