Zinc Speciation in Smelter-Contaminated Soils Using Micro-XAFS and XRF Spectroscopies

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Introduction

As a result of ore processing and aerial deposition of metal-bearing phases, topsoils in the vicinity of smelters contain elevated levels of toxic metals such as Cd, Cu, Ni, Pb, and Zn. Once introduced into a soil environment, metal-bearing phases may undergo changes in speciation relative to their original form as a result of weathering processes, with the degree of solid phase dissolution being a function of the mineral solubility and environmental conditions.

Indirect approaches such as extraction-based techniques expedite the metal speciation process but may transform chemical forms. Bulk analytical techniques (i.e., XRD) provide more direct identification of species relative to extraction approaches, but these techniques may overlook minor species or noncrystalline entities. Extended x-ray absorption fine structure (EXAFS) spectroscopy has enabled researchers to estimate the chemical environment of metals in soils, be they major components of a solid phase or trace components associated with the bulk phase (i.e., adsorbed).[1] Moreover, spatially resolved micro(μ)-EXAFS and synchrotron μ-x-ray fluorescence spectroscopy (μ-SXRF) can interrogate a sample on a micron scale (2-10 μm), providing metal speciation and elemental associations on a scale nearing the most reactive surfaces in soils, a feature that bulk EXAFS does not offer.

Methods and Materials

For 82 years, 2,000 acres of land on the north-facing slope of Blue Mountain have been contaminated from the emissions of the nearby Palmerton Zn smelting plant. Organic-matter-rich surface soils (0-5 cm) and subsoils (5-10 cm) were collected from the slope and characterized using bulk techniques (extraction, XRD, EM-EDX) followed by synchrotron-based studies. The μ-SXRF and μ-EXAFS studies were performed on resin-embedded soil thin sections at GSECARS beamline 13-ID-C at the Advanced Photon Source. Elemental maps for Fe, Mn, and Zn were generated over a 300 μm^2 area using μ-SXRF, and Zn K-edge μ-XAFS spectra were collected on areas of interest. The beam was focused down to approximately 5 μm, and samples were set at an angle of 45° to the incident beam; fluorescence x-rays were detected using a 9-element Ge solid-state detector.

Results and Discussion

Micro-SXRF elemental maps for Mn, Zn, and Fe from the subsurface soil are presented in Fig. 1. Surface maps indicated that Zn was primarily associated with Fe in discrete phases (data not shown). Based on these maps, we observed regions where Zn was associated with Mn (spot 3), Fe (spot 2), and neither Fe or Mn (spot 1). The μ-EXAFS results for both surface and subsurface samples are presented in Fig. 2. For the surface soil, Zn was found in tetrahedral coordination and fits (using both a nonlinear combination of reference spectra approach and a nonlinear, least-square individual shell fitting approach) confirm that Zn is predominately found as aerially deposited $ZnFe_2O_4$ (franklinite) particles, a byproduct of smelting ZnS containing trace amounts of Fe. The Zn speciation in the subsurface sample varied considerably from the surface sample and was heterogeneous within the subsurface sample itself, with Zn found primarily as adsorption complexes to Al and Mn oxides. Spot 1 from the SXRF map (Fig. 1) was determined to be Zn bound to an Al (hydr)oxide phase as an inner-sphere complex, based on Zn-Al distances and the split in the first oscillation of the chi spectrum (indicated by arrows in left panel of Fig. 2), which can be attributed to Zn being bound to lighter elements (i.e., Al).[2] Spot 3 was attributed to Zn bound to Mn oxide; based on Zn-Mn bond distances, it was determined to be an inner-sphere complex. Moreover, Zn was present in octahedral coordination in spot 1 and in tetrahedral coordination in spot 3. For spot 2, Fe could not be fit in the second shell, despite the association of Zn with Fe in the SXRF map, indicating that an elemental association does not necessarily indicate a chemical bond.

The results from this synchrotron-based, micro-spectroscopic study demonstrate the variability of Zn in contaminated soils both between surface and subsurface samples and within a sample over a small area. Bulk EXAFS spectroscopy performed on the subsurface sample provided an average of Zn speciation over a much larger area, and these results were useful to interpret those spectra.

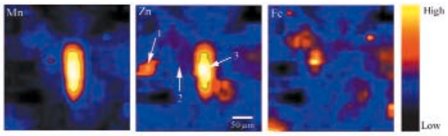

FIG. 1. Micro-SXRF elemental maps for Mn, Zn, and Fe in subsurface soil, with arrows indicating regions where Zn K-edge μ-EXAFS were collected (surface maps not presented). Yellow regions have relatively more metal than black regions.

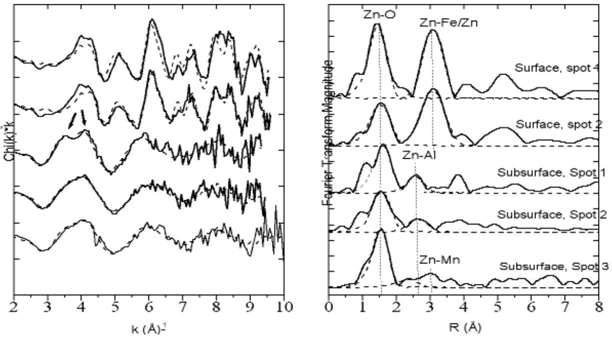

FIG. 2. Zn μ-XAFS chi spectra and fits (dashed lines) from linear combinations of reference spectra (left panel) and corresponding Fourier transforms and fit results from nonlinear shell fitting (right panel) for surface and subsurface soil samples.

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