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XAFS Characterization of Copper Contamination in the Unsaturated and Saturated Zones of a Soil Profile

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Abstract. The fate of heavy-metal contaminants in the environment, and the design and success of remediation strategies at hazardous waste sites depend on the chemical speciation of the contaminants. The objective of this study was to determine the molecular-scale chemical form (species) of heavy metals in different zones of a contaminated soil having a shallow ground water table. Copper in the unsaturated surface horizon and the water-saturated and partially-saturated subsurface horizons of a disturbed soil from the lower eastern coastal plain of North Carolina was characterized using XAFS spectroscopy. Extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) data showed that the dominant form of Cu(II) bonding ranged from Cu-S in the deeper soil zones to Cu-O in the shallowest zone. The results suggest that the surface and subsurface horizons will respond differently to remediation treatments.

1. INTRODUCTION

Chemical speciation is one of the more important factors affecting the solubility, fate, and treatability of heavy-metal contaminants in the environment. XAFS spectroscopy has the potential for providing molecular-scale speciation of metals occurring at low concentrations in complex media such as soils. The objective of this study was to determine the chemical forms (species) of copper occurring at different depths in a contaminated soil in the lower eastern coastal plain of North Carolina, USA. Because the saturated zone of this soil is at ~1 m, redox potential was expected to play a significant role in metal speciation, particularly with regard to metal-sulfide formation. Previous research showed that XAFS is particularly useful for identifying metal sulfides in soils, because of the larger ionic radius of S^{2-} relative to O^{2-} [1].

2. MATERIALS AND METHODS

Soil samples were collected from three depth intervals at a metal-contaminated site on the Marine Corps Air Station in Cherry Point, North Carolina: 28-56 cm, 56-71 cm, and 71-86 cm. These intervals approximately represent an unsaturated zone of strong brown color (7.5YR 5/8), a black colored (7.5YR 2/0) zone that possibly experiences intermittent water saturation, and a black colored (7.5YR 2/0) water-saturated zone. The site is a disturbed area that was used for landfilling. Samples were sieved to <2-mm particle size to remove debris, freeze-dried, then crushed to pass a 125- μ m stainless-steel sieve. XAFS analyses were done at Beamline X-11A at the National Synchrotron Light Source, Brookhaven National Laboratory. Samples were analyzed in fluorescence mode at the Cu K-edge (8,979 eV) using a multielement detector. Data analyses were completed using CuO (tenorite, first-shell bond length - $r_{Cu-O} = 1.95$ Å) and CuS (covellite, $r_{Cu-S} = 2.25$ Å) as standards. Fourier transforms of EXAFS spectra were done over the wavevector range $k = 3.0$ - 10.2 Å⁻¹, and model fitting was done over the radial distance ranges $R = 0.8$ - 2.2 Å for the 28-56 cm sample and $R = 0.8$ - 2.5 Å for the two deeper samples.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show radial structure functions (RSFs) and XANES spectra for the soil samples and selected standards, including a sample of Cu bound with humic acid [2]. RSFs for the soil samples exhibit a broad 1st-shell peak that shifts from about 1.6 Å to 1.85 Å between the shallowest and deeper samples (Fig. 1). These radial distances approximately correspond with first-shell peaks for standards having Cu-O bonding [CuO and Cu bound to humic acid] and Cu-S bonding (CuS), and indicate that Cu(II) in the two deeper soil samples is predominantly Cu-S bonded (presumably CuS). Based on relative coordination numbers Cu-O and Cu-S bonding derived from EXAFS data fitting [1], the following percentages of Cu-S bonding were calculated for the soil samples: 36% (28-56 cm), 77% (56-71 cm), and 81% (71-86 cm). Based on the standard errors calculated for fitting parameters, we estimate that the accuracy of these data is $\pm 10\%$. XANES results (Fig. 2) show a high degree of similarity between spectra for Cu(II) in the two deeper soil samples and the CuS standard, while the shallowest soil sample was more similar to the oxygen-bonded standards. These results are consistent with the EXAFS data.

Figure 1: Radial structure functions for Cu(II) in soil samples from different depths and selected standards. Data are not corrected for phase shift; therefore, peaks do not represent exact bond lengths. Vertical lines are eye guides.

Figure 2: Stacked XANES spectra for Cu(II) in soil samples and selected standards.

The classical method for operationally speciating heavy metals in soils is by sequential chemical extractions. A sequential chemical extraction analysis was done on the soil samples using the following extractants: (i) 0.5 M KNO_3 , (ii) deionized water, (iii) 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, (iv) 0.5 M NaOH , and 4 M HNO_3 at 80 °C (3, 4). We found an increase in hot HNO_3 -extractable Cu between the shallowest zone ($71 \pm 4\%$ of total Cu) and the two deeper zones ($87 \pm 1\%$ and $89.7 \pm 0.7\%$). This extractant targets metal sulfides and other residual species. Because XAFS results indicated that there was only about 36% Cu-S bonding in the shallow zone, much of the HNO_3 -extractable Cu in this zone apparently occurs in some other residual fraction. The fact that CuS and oxygen-bonded Cu(II) should react differently to changing soil redox potential or pH conditions [5] illustrates the advantage of XAFS spectroscopy over chemical extractions for determining metal speciation and potential fate of metals in soils.

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