EXAFS study of metal sulphide stability in a contaminated soil

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Metal sulphides may reduce the toxicity of heavy-metal contaminated sediments (Di Toro et al., 1992), but the importance of metal sulphides for reducing impacts of heavy metals in soils is poorly understood. Seasonal variations in hydrology can cause soils to undergo redox changes that are conducive for oxidation of metal sulphides. We used synchrotron extended X-ray absorption fine structure (EXAFS) spectroscopy, to characterize the local molecular bonding of heavy metals (Hg, Cu, Pb, and Zn) in several poorly-drained soils and a groundwater aquifer. Because average first-shell, metal-sulphur bond lengths (r) are greater than metal-oxygen bond lengths, the proportion of metal bonded with sulphide could be estimated. Following is a summary of our past results: (1) Mercury sulphide (metacinnabar) was dominant in a soil sample from a contaminated floodplain in Tennessee, U.S. (Wang et al., in press); (2) zinc sulphide was dominant and lead sulphide was absent in a contaminated groundwater aquifer zone underlying a poorly-drained soil in the Piedmont region of North Carolina, U.S. (Hesterberg et al., 1997); and (3) copper-, zinc-, and lead-sulphides were found in deeper zones (47−101 cm) of a contaminated soil in the lower coastal plain of North Carolina (Sayers et al., 1998). These findings indicate that authigenic metal sulphides form in contaminated soil exposed to reducing conditions. In this study, we completed laboratory soil column experiments with supporting EXAFS analysis to investigate the stability of metal sulphides under changing redox and pH conditions.

Experimental approach

Soil samples were collected from four depth intervals (zones) in a contaminated soil on the Marine Corps Air Station, Cherry Point, NC and preserved. The soil samples contained 1000 to 1800 mg Cu/kg, 1600 to 4000 mg Pb/kg, and 4000 to 10000 mg Zn/kg determined by hot nitric acid extraction. The two shallower zones (0−23 cm and 23−47 cm) were more oxidized, as indicated by redox potential measurements and the absence of acid-volatile sulphides (AVS). The deeper zones (47−73 cm and 73−101 cm) were reduced and contained AVS at levels between 1425 and 1970 mg S^{2-}/kg. Separate subsamples of soil from different depths were used for column flow studies to determine the effects of exposure to oxidizing conditions (aerated, 0.01 M $CaCl_2$ solution) and pH on transformation (oxidation) of metal sulphides and concomitant dissolution of metals. The extent of metal sulphide oxidation during a column study was determined by comparing EXAFS spectra from the original soil samples and samples of the treated column.

Results and discussion

EXAFS analysis of the original soil samples showed that the shallower zones contained Cu(II), Pb(II), and Zn(II) primarily bonded with oxygen (see Fig. 1 for Cu data). Because oxygen is the most abundant element in soils, first-shell metal-oxygen bonding is dominant for many metal species. The presence of Cu-sulphide in the deeper soil samples is indicated by the greater radial distances of the highest amplitude (first-shell) peaks in the radial structure functions in Fig. 1. After flowing aerated, 0.05 M $CaCl_2$ solution through the columns for 32 days at pH 7.6, only minor changes in the EXAFS spectra were apparent, indicating that Cu-sulphide was not substantially oxidized. Similar results were found for lead and zinc, which had moderate amounts of metal-sulphur bonding in the original and treated soil samples. A reduction in AVS and an increase in dissolved SO_4 in column effluent samples indicated that other forms of sulphide were oxidized. Dissolved levels of Cu and Pb remained mostly below 1 μg Cu/L and 10 μg Pb/L, and dissolved Zn showed contrasting trends between samples from the shallow and deeper soil zones.

In a subsequent experiment, soil samples were acidified to pH $\leqslant$ 6.5 in the absence of oxygen, then exposed to aerated $CaCl_2$ solution for about 90 days. Although dissolved metal concentrations in the effluent solutions increased with decreasing pH, a
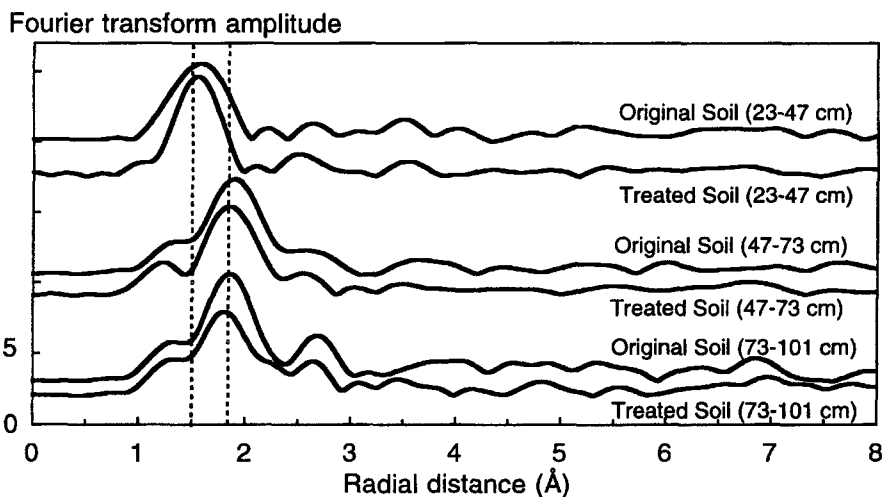
Fourier transform amplitude

FIG. 1. Radial structure functions (RSFs) derived from Fourier transforms of k^3-weighted Cu K-EXAFS spectra for samples taken at different depths in a soil profile (original soil), and for samples that were exposed to aerated electrolyte solution for 32 days (treated soil). All data are uncorrected for phase shift, so radial distances do not reflect actual bond lengths. The vertical eye guides correspond to positions of first-shell peaks (not shown) for tenorite (CuO; r_{Cu-O} = 1.95 Å) and covellite (CuS; r_{Cu-S} = 2.25 Å).

significant portion of Cu-sulphide in the deepest soil sample remained intact after the acidification and oxidation treatment.

References

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