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## Stability of copper sulfide in a contaminated soil

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Because of their low solubility under reduced soil conditions, metal sulfides may decrease the toxicity of heavy-metal contaminants. Periodic variations in soil moisture may expose reduced soils to oxidizing conditions that are conducive to oxidative dissolution of metal sulfides. Using EXAFS spectroscopy, we determined the proportion of copper sulfide in soil samples before and after exposure to more oxidizing conditions for 35 days at pH 6.6 or 7.6. The samples were collected from the reduced zone (47 to 73 and 73 to 101 cm depth) of a contaminated soil and contained about 1,700 mg Cu/kg. In both the original and the treated soil samples, we detected only Cu-S bonding in the first shell, indicating that the soil samples were not oxidized to Cu-O bonding during the treatment.

**Keywords:** X-ray absorption, XAFS, environmental

### 1. Introduction

The mobility, bioavailability, and ecotoxicology of heavy metals in contaminated soils may be reduced by the formation of insoluble chemical species such as metal sulfides. If so, then naturally-occurring soil processes may reduce detrimental environmental impacts of heavy metal contaminants that are left in a soil without receiving specific remediation treatments. However, long-term changes in pH and redox potential (Eh) may affect the chemical speciation

and solubility of metals in soils, sediments, and groundwater aquifers. (Calmano et al. 1994) showed that when reduced sediments were exposed to oxygenated water, maximum concentrations of dissolved Pb, Cu, Zn, and Cd occurred during the transition from reduced to oxidizing conditions. The authors suggested that elevated levels of dissolved metals were due to oxidative dissolution of metal sulfides.

To evaluate changes in the content of soil metal sulfides during oxidation of soil samples at different pH values, we carried out a study using XAFS spectroscopy on reduced samples from a contaminated soil. The samples were exposed to aerated aqueous solutions at pH 6.6 and 7.6 to produce more oxidizing conditions. We present here the XAFS results at the Cu K-edge which were used for determining any differences in first-shell copper-sulfur bonding in the contaminated soil samples before and after oxidation.

### 2. Materials and methods

#### 2.1 Soil Samples and treatment

Soil samples were collected from the Marine Corps Air Station (MCAS) in Cherry Point, NC. The sampling site was adjacent to Slocum Creek, a tributary to the Neuse River in the eastern coastal plain of North Carolina. Between 1949 and 1955, the site was used as an incinerator area for hydrocarbon-based wastes and for disposal of municipal refuse. The disturbed soils have an alkaline pH, and are laden with metal parts and other debris. The soil samples were collected from four depth intervals within the soil profile, but only the reduced samples from 47 to 73 cm (zone 3) and 73 to 101 cm (zone 4) depths are discussed in detail here. The samples were sieved to < 4 mm and preserved at 3 °C under oxygen-free conditions by triple-sealing them in a container immersed in a dilute aqueous solution of Na-sulfide (Hansen, 1997). This storage method maintained a constant level of acid volatile sulfides for 200 days, and we found no evidence for an influx of sulfide from the Na-sulfide solution.

To determine the stability of metal sulfides, homogenized soil samples were packed into Teflon sleeves fitted with end caps. A sequence of 0.01 M CaCl<sub>2</sub> solutions were pumped through the columns at pH 7.6 and pH 6.6 respectively under saturated flow conditions: (i) oxygen-free solution;

(ii) HCl-acidified, oxygen-free solution to lower pH (pH 6.6 case only); (iii) solution aerated with normal atmosphere. As the column flow study at pH 7.6 progressed, Eh increased and dissolved  $\text{SO}_4$  was produced by sulfide oxidation (Hansen, 1997).

## 2.2 XAFS Analysis

XAFS analyses were performed at Beamline X-11A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory in Upton, NY. Both the original soil samples and samples exposed to the different redox and pH conditions in the soil columns were analyzed. Soil samples were mounted in polyacrylamide sample holders in a glovebox under an atmosphere of oxygen-scrubbed,  $\text{N}_2$  gas, and covered with a thin sheet of aluminized Mylar film and Kapton tape to minimize exposure to light and oxygen. XAFS data were collected in fluorescence mode using a solid-state, multielement detector. Standard data collection and analysis methods were used (Sayers and Bunker, 1988).

## 3. Results and discussion

As reported earlier (Sayers et al., 1997), soil samples from depths < 47 cm were dominated by first shell Cu-O bonding. Figure 1 shows radial structure functions (uncorrected for phase shift) at the Cu K edge in samples from each of the two deeper soil zones before and after treatment in columns at pH 7.6 and pH 6.6. Also included in the figure are reference samples CuO (tenorite) and CuS (covellite). Table 1 shows first shell EXAFS fitting results for both the original and treated soil samples from different depths at pH 7.6 and pH 6.6. As we can see from the figure and fitting results, Cu-S bonding dominated in all samples (100% Cu-S for both zones). This result indicates that Cu occurred as some forms of Cu-sulfide in the original and treated soil samples. It was consistent with the initially low redox potential in these soil zones ( $E_h = 148 \pm 11$  and  $138 \pm 9$  mV for samples from 47 to 73 and 73 to 101 cm depths, respectively) compared with  $E_h \geq 400$  mV in shallower samples (Hansen, 1997). During the column flow study at pH 7.6,  $E_h$  initially decreased to a minimum of about 50 mV, then increased to 245 mV (47 to 73

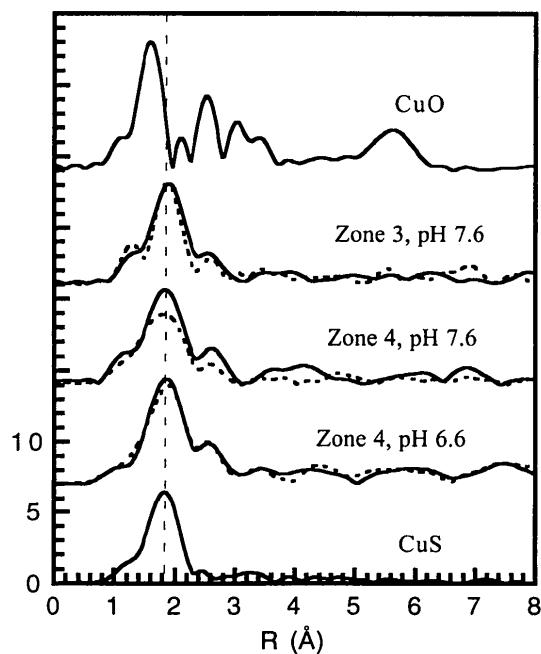
**Table 1**

First-shell Cu K-edge EXAFS fitting results for soil samples collected from different depths at MCAS - Cherry Point. Original soil represents samples that were not treated in the column, and column soil represents samples that were exposed to aerated solution at a given pH in the soil column. N is the coordination number. R is radial distance.  $\sigma$  is Debye-Waller factor.

Depth (cm)	Soil sample description	Bond type	N	R(Å)	$\sigma^2$ (Å <sup>2</sup> )
47-73	Original	Cu-S	$3.3 \pm 0.5$	$2.29 \pm 0.02$	$0.009 \pm 0.002$
	Treated	Cu-S	$3.2 \pm 0.5$	$2.29 \pm 0.02$	$0.009 \pm 0.002$
73-100	Original	Cu-S	$4.0 \pm 0.5$	$2.27 \pm 0.02$	$0.013 \pm 0.002$
	Treated	Cu-S	$3.4 \pm 0.5$	$2.27 \pm 0.02$	$0.011 \pm 0.002$
73-101	Original	Cu-S	$3.6 \pm 0.5$	$2.27 \pm 0.02$	$0.011 \pm 0.002$
	Treated	Cu-S	$3.9 \pm 0.5$	$2.27 \pm 0.02$	$0.011 \pm 0.002$

cm) or 295 mV (73 to 101 cm). On the other hand, during acidification of a soil sample to pH 6.6,  $E_h$  increased. After

## Fourier transform magnitude



**Figure 1**

Radial structure functions for Cu at K edge in original soil samples (solid line), samples collected from the soil columns (dash line) after the flow study of redox effects, and reference samples CuO (tenorite) and CuS (covellite).  $k^3$ -weighted Fourier transform is from  $k = 2.7$ - $11.5 \text{ \AA}^{-1}$ .

1300 pore volumes of oxidation treatment, Eh stabilized at 450 mV. As indicated in Table 1, there was no detectable Cu-O bonding in the treated samples, regardless of pH or soil depth. Therefore, under the redox conditions and duration of the oxidation treatment, Cu-S bonding remained stable.

#### 4. Conclusions

Consistent with soil redox conditions, XAFS analyses showed that Cu in the < 4-mm size fraction of the soil samples taken between 47 and 101 cm depths from MCAS-Cherry Point was predominantly bonded with sulfide. In terms of the data analysis on higher shells (not shown), it is possible that the soil contains a more than one copper sulfide structures, among them there may be some covellite (CuS). XAFS analysis of soil samples after an oxidation treatment at pH 7.6 or pH 6.6 showed no evidence for oxidation of Cu-sulfide in these samples. If there occurs some oxidation from Cu-S to Cu-O, say, on the surface of the minerals, it should be beyond XAS detection limit in terms of the current data quality in this study. On the other hand, in the same oxidation treatment experiment, other metal sulfides, such as Fe, Pb, Zn and Mn, were observed to be oxidized to different oxidation state levels, which were consistent with their thermodynamic stability. Therefore, we conclude that copper-sulfide was kinetically stable, even when the soil was exposed to oxygen.

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