Natural Attenuation of Copper in Soils

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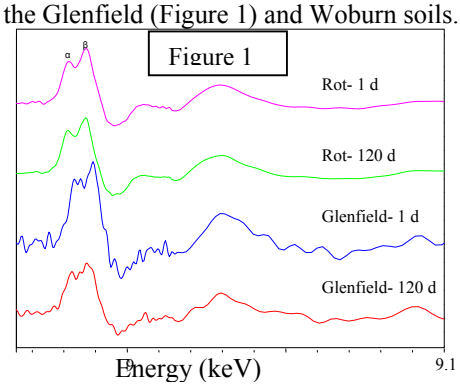
The term "natural attenuation" describes the process by which the availability and/or toxicity of Cu added to soils decreases with time. This process, which is commonly observed for several elements, is sometimes also termed "aging" or "fixation". Using isotopic dilution techniques we have demonstrated that the labile pool of Cu in soils decreases with time (Ma et al., 2006). In a previous experiment at the ANBF at the Photon Factory in Tsukuba, Japan our group found that even as short as one day after addition of Cu to the materials, there was a significant decrease in lability of Cu in goethite and montmorillonite and for all of the materials, there was no significant change in either the Cu lability or the EXAFS spectra between 1 and 180 days. This contrasts with results from soils indicating that the natural attenuation of Cu occurs much faster in mineral pure phases than in soils. The main objective of this experiment was to provide a mechanistic explanation regarding the observed differences in ageing between pure mineral phases and whole soils.

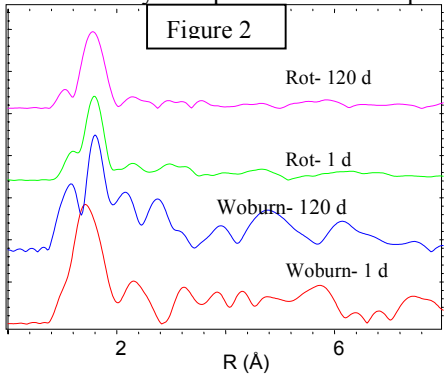
Samples used for this study were OECD "artificial soil" (10 % sphagnum peat, 20 % kaolin, 70 % sand and Ca carbonate to bring pH to 6.0±0.05, OECD Guideline, 1984), and three different natural soils with contrasting characteristics. Those were Woburn (neutral), Rot (alkaline calcareous), and Glenfield (acidic). Samples were spiked with Cu as $Cu(NO)_3$ to levels that would result in a solution concentration of $10^{-4/5}$M and those were 1000, 1500, 1800, and 350 mg/kg for OECD, Woburn, Rot, and Glenfield, respectively. Soils were incubated at field capacity moisture content for 120, 60, 30, 7, and 1 day at constant temperature (23±0.2 ºC). In parallel, Cu spiked minerals, mixtures of minerals and charcoal, humic acid (HA) coated-minerals and their mixtures were incubated in 1:10 solid: 0.01 M $Ca(NO_3)_2$ for 120, 60, 30, 7, and 1 day at pH 6.5±0.05 to use as comparisons for soil data.

For each sample triplicate XAS scans were collected which covered the range from 200 eV below to 860 eV above the absorption edge. XANES and EXAFS data analysis was done using WinXAS 3.1. The K^3-weighted Fourier back transformed EXAFS spectra were further analysed in a two step procedure (principal component analysis (PCA) and EXAFS least squares fitting) using the Labview software at beamline 10.3.2 at the ALS.

Both the pre-edge peak (due to $1s \rightarrow 3d$ transitions) and the shoulder structure (due to $1s \rightarrow 4\,p$ transitions) were evident in the first derivative of XANES spectra of all the soil samples as shown in Figure 1. It can be concluded that the binding structure of Cu in soil samples is tetragonally-distorted octahedral. No apparent changes were observed for Rot soil between 1 and 120 days while some changes to the ratio of α and β splitting was evident for both the Glenfield (Figure 1) and Woburn soils.



The radial structure functions (RSFs) of the 1 and 120 day samples of the soil samples showed a first major peak which is due to the Cu-O bond at about 1.5 Å (Figure 2). There were obvious visual changes in the RSFs of Woburn soil with time. The PCA analysis gave good spectral fits for the Woburn soil change from 79% Cu citrate for 1 day samples to ~100% of 180 days incubated Cu adsorbed goethite for Woburn 120 days sample. In contrast good spectral fit for Rot soil was independent from the incubation time and was about 90% similar to 180 days incubated Cu adsorbed montmorillonite. These observations might be an indicative of time dependent divalent metal cation attenuation that can occur in neutral soils in comparison to rapid attenuation of Cu in alkaline soil systems. Cu EXAFS data obtained at 17C1 wiggler beamline suggest that there are differences in Cu attenuation and effects of aging among the studied soils. Further these differences appeared to be in agreement with results obtained by isotope dilution techniques.



References

Ma Y, E. Lombi E., I.W. Oliver, L. Solana, M.J. McLaughlin. 2006. Long-term Aging of Copper Added to Soils: II. Modeling of Isotopic Exchangeability as a Function of Soil pH and Time. (submitted).