Cu(II) speciation in multicomponent synthetic systems and natural soils

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Because of $CuSO_4$ fungicide spill (especially "Bordeaux mixture"), agricultural soils and especially vineyard soils exhibit Cu concentrations above recommended values ([Cu] > 300 $mg.kg^{-1}$). Though total trace metal content is useful to evaluate soil contamination, it gives insufficient information on the potential mobility of trace metals. A better understanding of the chemical behaviour of trace metals is of special interest as contamination of soils can cause groundwater and superficial water pollution. The environmental effects of trace metals are directly related to their chemical forms in soils (*i.e.* their geochemical partitioning). Trace metals can be associated with different soil components differing in their ability to retain or release metals: adsorbed on the surface of minerals (Fe- or Mn-oxides, clays, calcite), complexed with organic matter, present in the crystal lattice of primary (silicates) or secondary (carbonates, phosphates, sulphates, sulphides) minerals.

In this context, the aim of this work consists in performing structural analysis of Cu(II) binding in multicomponent systems with increasing complexity: from binary systems to synthetic soils reconstituted with seven components (calcite ($CaCO_3$), quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$), iron oxides (goethite and ferrihydrite), birnessite ($K_{4,6}Mn_{14}O_{27,9}$, 6 H_2O), and soil organic matter), and finally on natural soil samples. This original approach will help to understand the behaviour of copper in soils and to predict its fate in the environment.

During the 9-shifts session onto the C beamline, we obtained data on about 30 samples. Cu K-edge (8979 eV) XANES spectra were recorded on both set of samples (synthetic systems and natural soils) in order to identify the soil fractions involved in its retention. Data analyses were in progress using linear combination of the XANES spectra. Although many studies have already studied the Cu speciation in soils and single phase systems, few studies have addressed the molecular scale characteristics of Cu(II) binding in synthetic multicomponent systems, which are more representative of natural systems. The first results obtained (Figure 1) allow us to confirm the involvement of the organic matter into the copper retention together with ferrous oxides and in a less extent clay minerals.

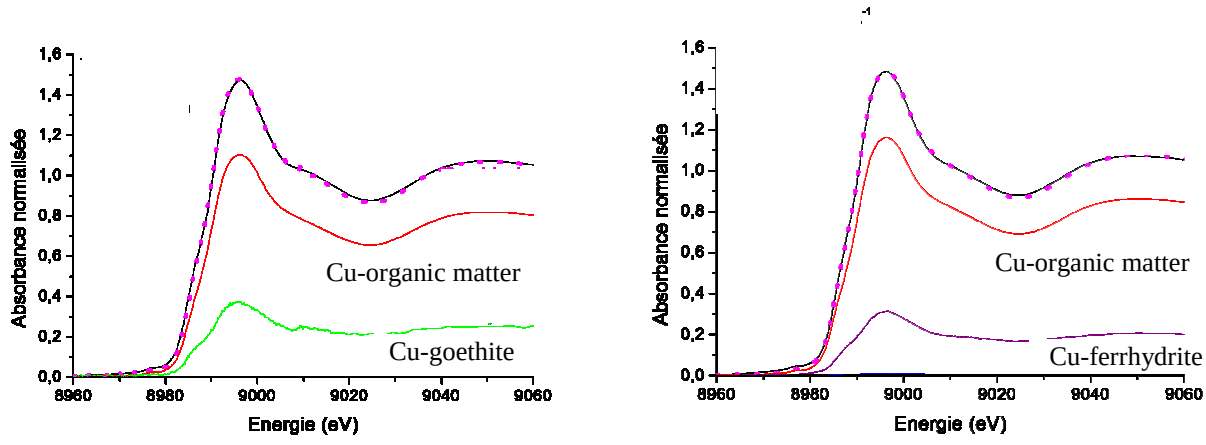

Figure 1: Example of experimental XANES spectra and the linear combination fitting results.

These results should help to understand the mechanisms of Cu retention in soils and to better constrain the geochemical modelling of Cu sorption onto mineral and organic surfaces. Moreover, the comparison of these results to those obtained from chemical extraction procedures already performed on vineyard soil samples should allow to test the efficiency of these procedures, which might then be refined.