Effect of fulvic acid fractionation on TME speciation/availability in soils

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Introduction

The evaluation of the ecotoxicological impact of trace metal elements (TME) in soils requires knowledge on relations existing between speciation and bioavailability of TME in soils, particularly in the presence of complex organic acids.
To address this issue, we studied both the competitive sorption of Cu, Zn and Pb and the molecular-scale sorptive fractionation behaviour of soil fulvic acids (FA) in ternary mineral-FA-metals systems by using batch method and ESI-FTMS. Kaolinite or hematite were used as model surfaces for simple soil clays or for Fe-rich minerals bearing ferrinol sites, respectively. The results obtained were used to interpret results on the desorption and bioavailability of metals in (peri-)urban soils in terms of metal speciation.

Results

MS data obtained on the model systems supported that competitive sorption of metals depends on the type of the organic compounds which are preferentially sorbed -amongst all FA constituents- on the mineral surface, and whose chemical identity differs depending on the mineral and the FA-to-mineral ratio (r) of the experiment. In the presence of FA, the sorption of Zn is favored (over Cu/Pb sorption) onto kaolinite due to preferential sorption (by H-bonding) of FA compounds of intermediate O/C ratios to which this metal tends to bind. In contrast, at low r, the sorption onto hematite of Lewis' strong acids like Pb and Cu is favored by formation of metallo-organic surface complexes involving the most acidic FA compounds adsorbing strongly at the surface. At high r, few of these molecules are sorbed (due to aqueous complexation of Fe released by dissolution) and Pb competes successfully against Cu for organic surface coordination.
Latter results compare well with the desorption/ bioavailability orders observed for metals in the (peri-)urban soils investigated (Zn>Cu>Pb); with soils richer in Fe-smectite clays showing lower Pb and Cu availability than the others, whatever the total TME content. All results suggest that Zn and Cu are bioavailable in the studied soil systems as Zn^{2+} ions and copper fulvate, respectively, whereas Pb is strongly sorbed with FA on smectites.