Zinc speciation in contaminated soils in relation to soil type

OLIVIER JACQUAT, ANDREAS VOEGELIN
AND RUBEN KRETZSCHMAR

Institute of Terrestrial Ecology, ETH Zurich, Switzerland
(jacquat@env.ethz.ch, voegelin@env.ethz.ch,
kretzschmar@env.ethz.ch)

The formation of surface precipitates is an important retention and sequestration mechanism of trace metals in soils. Laboratory studies have demonstrated that zinc may be incorporated into layered mineral structures such as layered double hydroxides (LDH) and phyllosilicates. Recent studies confirmed the formation of such mineral phases in contaminated soils. The formation of these precipitates depends on the availability of Al and Si from the weathering of primary minerals. Zn may also be incorporated into the gibbsite-like sheets of lithiophorite or Al-hydroxy interlayered minerals (HIM). At present, a general understanding of the influence of geochemical soil properties on the type of the resulting Zn bearing phases and their stability is still lacking.

In this study, the speciation and reactivity of Zn is investigated in a wide variety of soils developed from fluvioglacial sediments, sandstone, limestone, granite and gneiss under different climatic conditions. Contaminated soils were sampled across Switzerland undernieth Zn-coated towers of power transmission lines. The speciation of Zn in the soil matrix is studied by bulk Zn K-edge XAFS spectroscopy of soils, clay fractions, and Ca exchanged samples together with μ–EXAFS spectroscopy on a selected set of soils. Principal component analysis (PCA) is applied to a large set of sample spectra (~40 soils) to constrain the number of reference spectra required to describe the data. An extensive set of reference spectra for Zn in mineral structures, organic Zn complexes, and Zn adsorbed to inorganic and organic substrates is subsequently evaluated by target testing (TT) to determine the most suitable reference spectra. The contributions of those reference spectra to the individual experimental spectra are then determined by linear combination fitting (LCF).

First results indicate that Zn layered species are accounting for a significant fraction of the total Zn. The data suggest that Zn-LDH and Zn-phyllosilicates dominate over Zn-HIM and Zn-lithiophorite. The speciation of Zn as determined by PCA-LCF is related to the soil properties (pH, organic matter, soil mineralogy, iron (hydr)oxides, carbonates) and to the reactivity of Zn as determined by single and sequential batch extractions.

Natural speciation of Mn, Ni and Zn at the micrometer scale in a clayey paddy soil using X-ray fluorescence, absorption, and diffraction

ALAIN MANCEAU[1], MICHEL SCHLEGEL[2], SOPHIE RIHS[3]
AND MATTHEW A. MARCUS[4]

[1]LGIT-Maison des Géosciences, Univ. J. Fourier, BP53, 38000 Grenoble, France (manceau@ujf-grenoble.fr)
[2]DEN/DPC/SCP, CEA Saclay, BP 11, 91191 Gif sur Yvette, France (schlegel@azurite.cea.fr)
[3]Lab. de Géochimie, Université Louis Pasteur, 1 rue Blessig, 67084 Strasbourg, France (rihs@illite.u-strasbg.fr)
[4]Advanced Light Source, LBNL, One Cyclotron Road, Berkeley, California 94720, USA (MAMarcus@lbl.gov)

The natural speciation of Mn (0.19 g/kg), Ni (46 mg/kg) and Zn (42 mg/kg) in the argillic horizon of an Ultisol from a paddy soil in Taiwan was investigated by advanced X-ray synchrotron techniques. Microchemical associations were imaged by X-ray microfluorescence, host minerals were identified by standard and micrometer-resolved X-ray diffraction, and the local coordination environment of Mn, Ni, and Zn was probed using EXAFS spectroscopy on powdered samples, and polarized EXAFS spectroscopy on a highly textured self-supporting clay film from the <2 μm fraction of the soil. Manganese was concentrated in Fe-Mn soft mottles as turbostratic hexagonal birnessite and lithiophorite having Mn^{3+}/Mn^{4+} atomic ratios of about 20 % and 50 %, respectively. Ni (r = 0.70 Å) substitutes for Mn (r(Mn^{4+}) = 0.54 Å, r(Mn^{3+}) = 0.65 Å) in the manganese layer in the natural lithiophorite. In contrast, Zn (r = 0.74 Å) fills vacant sites in the gibbsitic layer of natural lithiophorite, in a similar manner as lithium (r = 0.74 Å) in synthetic lithiophorite. The partitioning of Ni and Zn between the two layers is a result of the general preference of Ni, whose size is intermediate between those of Mn^{3+} and Li^+, for slightly smaller sites. In contrast with nickel, which is detected only where there is lithiophorite, the Zn-lithiophorite association found in Fe-Mn mottles is not representative of the bulk soil. The combined use of X-ray diffraction, and powder and polarized EXAFS spectroscopy revealed that Zn is predominantly bound to hydroxy-Al interlayers sandwiched between 2:1 vermiculite layers in the fine soil matrix. The incorporation of Zn in the gibbsitic layer of both lithiophorite and vermiculite helps increase the stability of these minerals by providing positive charge to balance the negative charge from the 2:1 phyllosilicate layer and the $[(Mn^{4+}_{0.68}Mn^{3+}_{0.32})O_2]^{0.32-}$ layer of lithiophorite. This binding environment for zinc is probably the main mechanism by which zinc is sequestered in acidic to near-neutral aluminium-rich clayey soils.