



	Experiment title: Long-term fate of Zn in contaminated soils in relation to soil type	Experiment number: 01-01-673
Beamline: BM01B	Date of experiment: from: 27-OCT-04 to: 01-NOV-04	Date of report: 23-2-05
Shifts: 12	Local contact(s): Denis Testamale	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Andreas VOEGELIN* Prof. Dr. Ruben KRETZSCHMAR Dr. Maarten NACHTEGAAL* Olivier JACQUAT*		

Report:

Introduction:

Zinc is an essential nutrient for all organisms but may reach phytotoxic levels in contaminated soils, thereby reducing soil fertility and crop yield. The mobility and bioavailability of Zn strongly depend on its chemical speciation. When released into soils, Zn may adsorb to clay minerals, oxides, carbonates, and to soil organic matter. Zn may also sequester into newly forming precipitates of layered double hydroxide (LDH) or phyllosilicate type or into the gibbsite-like sheets of lithiophorite or Al-hydroxy interlayered clay minerals (HIM). Recent studies demonstrate the formation of those different types of layered species under field conditions¹⁻⁴. However, the quantitative link between key soil properties such as pH and mineralogy and the type and stability of layered Zn species forming is not yet established. The objectives of this project therefore are 1) to characterize the speciation and availability of Zn in a wide range of contaminated soils and 2) to determine the relation between Zn speciation and reactivity and key soil properties.

Materials and Method:

About 60 contaminated soils were sampled below the Zn-coated towers of power transmission lines across Switzerland. The samples cover a wide range of soils developed from different substrates (alluvial and fluvioglacial sediments, sandstone, limestone, gneiss, granite) with pH values from 4.0 to 7.7. The Zn concentrations range from 250 to 30000 mg/kg. Exchangeable zinc (1 g of soil extracted with 50 mL of 10 mM CaCl₂) accounts for <1 to 44 % of the total Zn. The speciation of Zn in soil samples is studied by X-ray absorption fine structure (XAFS) spectroscopy at the Zn K-edge (9659 eV). Soil samples prepared as powders or pellets are measured at room temperature in fluorescence and/or transmission mode. Reference spectra were recorded in transmission mode. The experimental spectra are evaluated by principal component analysis (PCA) and linear combination fitting (LCF) using

an extensive set of reference spectra for Zn in mineral structures, organic Zn complexes, and Zn adsorbed to inorganic and organic substrates. Finally, the results from EXAFS analysis will be interpreted in relation to the properties of the respective soils and the reactivity of Zn.

Results:

So far 35 bulk soil spectra were collected at BM01B and other X-ray absorption spectroscopy beamlines (ANKA/XAS, NSLS/X11A). PCA on those spectra indicates that 6 components are sufficient to describe the major features of all experimental spectra. Target transform analysis (using the first 6 components from PCA) suggests that the reference spectra from various layered Zn-phases (Zn-LDH, Zn-phyllsilicate, Zn-HIM, and Zn-lithiophorite) are suitable to describe spectra from bulk soils. Zn-phytate and Zn sorbed to montmorillonite represent reference spectra for adsorbed Zn in tetrahedral and octahedral coordination, respectively. Preliminary LCF results using those reference spectra show that layered Zn species are quantitatively relevant in most of our soils accounting for up to 73% of the total Zn. The data suggest that Zn-lithiophorite and/or Zn-HIM are less abundant than Zn-LDH and/or Zn-phyllsilicate. The distinction between Zn-HIM and Zn-lithiophorite and between Zn-LDH and Zn-phyllsilicate is complicated by the similarity in their EXAFS signal due to the similar structure of their octahedral sheets. Small differences in these reference spectra are further weakened by the spectral contributions from adsorbed Zn species.

Conclusions and outlook:

Our results demonstrate the presence and quantitative relevance of various types of layered Zn species in soils. Similarities in the EXAFS spectra of different layered Zn phases causes some difficulties for quantitative Zn speciation. To overcome these and to improve the Zn speciation for our samples, we will follow three approaches: 1) Record bulk XAFS spectra on soil samples treated to remove adsorbed Zn (0.1 M BaCl₂), thereby providing better spectra for the residual Zn species allowing for a more accurate quantification. 2) Record polarized XAFS spectra on the oriented clay fraction of selected soils to distinguish layered species by the angular dependence of their XAFS signal. 3) Use micro-XRF and micro-EXAFS on representative soil thin sections to obtain information on element associations and local Zn speciation. Based on the data from this project, we will be able to constrain the soil properties and chemical conditions that lead to the formation of different types of layered Zn species in soils.

Acknowledgements:

We acknowledge the Swiss Norwegian Beamline at the European Synchrotron Radiation Facility for the provision of beamtime at the beamline BM01B and would like to thank Denise Testamale and Herman Emerich for their assistance. This project is funded by the Swiss National Fund (SNF) under the contract nr. 200021-10176/1.

References:

- [1] Voegelin, A. et al. (2002), *Env. Sci. Technol.*, 36, 3749-3754
- [2] Juillot F. et al. (2003), *Am. Miner.*, 88, 509-526
- [3] Manceau A. et al., (2004), *Geochim. Cosmochim. Acta*, 68, 2467-2483
- [4] Scheinost A. C. et al. (2002) *Env. Sci. Technol.*, 36, 5021-5028