XAS analysis of Copper in a soil matrix (II)

S.M. Kristiansen[1], M.W. Murphy[2], M.T. Nielsen[1], S. Gomes[3], M. Amorim[3], and J.J. Scott-Fordsmand[4]

[1]Depart of Earth Sciences, Aarhus University, Høegh-Guldbergs Gade 2, DK-8000 Aarhus, Denmark
[2]HASYLAB, DESY, Notkestraße 85, 22607 Hamburg, Germany
[3]Department of Biology & CESAM, University of Aveiro, Aveiro, Portugal
[4]Bioscience, Aarhus University, Vejlsøvej 25, DK-8600 Silkeborg, Denmark

The aim of this study was to analyse and describe the actual speciation and bonding of copper (Cu) in soils contaminated with either $CuNO_3$-salts or Copper-nanoparticles. The distribution of Cu in soil has tremendous economical importance and the fate of Cu has attracted considerable attention in international research [1], but with no knowledge in the area of nano-materials. Previous studies show differences in toxicity between the two forms (Cu-salts and Cu-nanomaterial), which suggest that there probably is a difference in their state. However, as mentioned the nature of the bonding and the processes by which the copper and copper-nanoparticles are available, taken up by, and handled by soil organisms remain unclear. The present study was an attempt to enlighten this using both Danish field contaminated soil and amendments of Cu-nanoparticles to uncontaminated soil from the same site.

We analysed a number soil samples, both Cu-contaminated in the field and nano-material contaminated using the beamline-C and -X1 at DORIS (Hasylab, DESY) for XANES and EXAFS spectra collection, using a Si (111) crystal pair monochromator for the Cu energy range with a resolution $\Delta E/E$ of $< 10^{-4}$ (<1 eV). Appropriate Cu reference compounds were used. Data was subsequently analysed using the SixPACK software package [2].

We expected to find differences in the speciation and bonding of copper in accordance to different exposure treatments ($CuCl_2$-salt versus Cu-nano). The first preliminary spectra revealed differences in their oxidations states, and bonding. The copper is generally in oxidation state zero for the nano-form and two for the Cu-salt (Fig. 1). These XAS analyses were compliment with additional wet chemical and mineralogical analysis to obtain a fuller picture of the Cu status in the natural contaminated soil. Fractionation and activity of Cu and a range of biological toxicity studies were also applied. The combined results have shown in general that soils contaminated by Cu-nanoparticle and Cu-salts are bound similar in the soil although some interesting differences were observed. The results has been presented at international workshops [3,4] and are recently submitted to a peer-reviewed journal [5].

References

[1] Scott-Fordsmand et al 2000. Importance of Contamination History for Understanding Toxicity of Copper to Earthworm Eisenia fetica (Oligochaeta: Annelida), using Neutral-Red Retention Assay. Environmental Toxicology and Chemistry, 19: 1774-1780.

[2] SixPACK (Sam's interface for XAS analysis package. Powered by IFEFFIT by Matt Neville, University of Chicago.

[3] Nielsen, MT, Scott-Fordsmand, J, Murphy, MW, Kristiansen, SM (2011). Speciation of Copper in polluted and non-polluted soil from a Danish site – Synchrotron-based X-ray Absorption Spectroscopy evidence. Novel technologies, modeling and macroscopic impacts, Proceeding of the Microsoil II conference, June. 14–15, 2011. Dundee, Scotland. Abstract. s. 38-39.

[4] Gomes, SIl, Amorim, MJB, Nielsen, MT, Kristiansen, SM Soares, AMVM, Scott-Fordsmand, JJ (2011). Effects of copper on Enchytraeus crypticus (Oligochatea): comparison of exposure to Cu-NP, Cu-salt and historical contamination, including in depth characterisation. Society of Environmental Toxicology and Chemistry Conference, May, Italy. Abstract.

[5] Gomes, SIL, Murphy, M, Nielsen, MT, Kristiansen, SM, Amorim, MJB & Scott-Fordsmand, JJ (submitted). Toxicity of copper nanoparticles in Enchytraeus crypticus (Oligochaeta): comparison with Cu-salt and historically field Cu-contamination. NanoLetters.