0034 - Investigation of copper and zinc speciation in pig slurry by a multitechnique approach

Samuel Legros¹, <u>Emmanuel Doelsch</u>¹, Perrine Chaurand², Jerome Rose², Armand Masion², Daniel Borschneck², Olivier Proux³, Jean-Louis Hazemann⁴, Valérie Briois⁵, Jean-Henry Ferrasse⁶, Hervé Saint Macary¹, Jean-Yves Bottero²

¹CIRAD, UPR Recyclage et risque, Montpellier, France, ²CEREGE, CNRS, Université Aix Marseille, IRD, CdF, Europôle Méditerranéen de l'Arbois, Aix-en-Provence, France, ³CNRS, OSUG, St Martin d'Hères, France, ⁴CNRS, Institut Néel, Grenoble, France, ⁵Synchrotron SOLEIL, Gif-sur-Yvette, France, ⁶MSNM-GP UMR 6181 CNRS Université Paul Cézanne, Aix-en-Provence, France

Copper (Cu) and Zinc (Zn) occurs in high quantity in pig slurry since they are used as essential micronutrients at high concentrations in animal feeds despite the low Cu and Zn assimilation by pigs. Cu and Zn accumulation was therefore measured in soil surface layers that had been amended with pig slurry, while also determining the phytotoxicity as well as the extent of groundwater quality degradation. Better prediction of the mobility and bioavailability of Cu and Zn from pig slurry spreading can be achieved by determining the speciation of this element in addition to its total concentration.

The aim of this study was to present a multitechnique approach to investigate Cu and Zn speciation in pig slurry. Size fractionation was first carried out to account for the complexity of pig slurry. Then X-ray diffraction (XRD), scanning electron microscopy, coupled with energy dispersive spectrometer (SEM-EDS), Micro X-ray fluorescence spectroscopy (µXRF) and extended X-ray absorption fine structure (EXAFS) or X-ray absorption near-edge structure spectroscopy (XANES) analyses were combined to assess Cu and Zn speciation.

The present study demonstrated that only 0.2% of total Cu or Zn present in pig slurry was bound to particles with a size less than 0.45 μ m, while 75% of total Cu and Zn was bound to particles in the 0.45–20 μ m size range. μ XRF highlighted the colocalisation of Cu and sulfur (S). In addition, geochemical modelling demonstrated that physical chemical conditions within pig slurry lagoon are compatible with the precipitation of chalcocite (Cu2S). Finally, XANES shows that Cu speciation in raw pig slurry and size fractions is described by Cu2S and that its oxidation state is Cu(I). These Cu speciation in pig slurry may be the main reason for the observed Cu accumulation at the the soil surface. Zn speciation revealed three patterns 49% Zn bound to organic matter, 37% amorphous Zn hydroxide, and 14% sphalerite. The detected presence of sphalerite, or Zn sulphide, was unexpected and is reported for the first time. These three Zn forms seemed to be soluble in neutral or weakly acid soil systems, so the long-term impact of pig slurry spreading could lead to Zn leaching.