 ![ESRF logo] ESRF	**Experiment title:** **Copper and zinc speciation in soil after long term spreading of pig slurry: original combination of XAS spectroscopy and density fractionation**	**Experiment number**: **30-02-1098**
Beamline: BM30B	**Date of experiment**: from: 11 December 2015 to 16 December 2015	**Date of report**: 13/02/17 *Received at ESRF:*
Shifts: 15	**Local contact(s):** Isabelle Kieffer (email: isabelle.kieffer@esrf.fr)	

Names and affiliations of applicants (* indicates experimentalists):

Dr Samuel LEGROS[1]*, Thiago FORMENTINI[2]*, Clément LEVARD[3]*, Maureen LE BARS[1,3]*, Gabrielle DUBLET[3]*, Dr Emmanuel DOELSCH[1]*

1. CIRAD, UPR 78 Recyclage et risque, avenue Agropolis, TA B01/78, 34398 Montpellier 04, FRANCE.
2. Federal University of Paraná (UFPR), PO Box 19011, 81531-990, Curitiba - PR, Brazil.
3. Géosciences de l'environnement – CEREGE Europole Méditerranéen de l'Arbois BP 80 13545 Aix en Provence Cedex 04, France.

Report

Aims of the experiment and scientific background

Spreading livestock manure as fertilizer on farmlands is a widespread practice. It represents the major source of heavy metal(loid)s (HM) input in agricultural soils. Since zinc (Zn) and copper (Cu) are present at high concentrations in manure, it poses special environmental concerns related to phytotoxicity, groundwater contamination, and introduction in the food chain. Therefore, investigations on the fate and behavior of manure-borne Zn and Cu, when it enters the soil environment, are necessary to predict the environmental effects. Nevertheless, long-term field studies assessing Zn and Cu speciation in the organic waste matrix, as well as within the soil after manure application, are lacking.

This study was designed to fill this scientific gap. We assessed the Zn and Cu speciation in pig slurry and soil samples from a field experiment installed in Campos Novos, Brazil, at the demonstrative field of the Cooperativa Regional Agropecuária de Campos Novos (Copercampos). The experiment lasted 11 years and treatments consisted of a control soil (no pig slurry application) and an amended soil (200 m^3 ha^{-1} year^{-1} of pig slurry). The soil 0-5 cm depth was sampled at the end of the 11th year of experimentation.

Moreover, we used soil density fractionation, a physical separation technique, to reduce the bulk matrix heterogeneity and complexity. We aimed at verifying the feasibility of a PCA-based approach to identify the most likely number of Cu and Zn species in complex matrices such as soils.

Experiment

The Experiment was conducted on beamline FAME (from 11/12/2015 to 16/12/2015) with a Si (220) monochromator. The spectra were recorded in fluorescence mode using a 30-elements solid-state Ge detector (Canberra) for the least concentrated samples and measured in transmission mode with a diode for Zn (or Cu) rich samples. All the references and samples were recorded at Helium temperature with a cryostat in order to avoid beam damage.

Thirteen samples were analyzed at the K edges of Cu and Zn: 2 bulk soil samples, 10 soil density fractions (5 fractions for a control soil and 5 fractions for an amended soil) and a pig slurry sample. Moreover, several synthesized ZnS nanoparticles with different particle sizes were analyzed.

Results

Firstly, we analyzed references that could have precipitated in pig slurry, i.e. ZnS nanoparticles of different particle sizes: 2.5 nm, 4.7 nm and 5.9 nm. We had hypothesized that Zn in the pig slurry could consist of nano-sized ZnS, which would explain the low stability of ZnS within oxic and complex environments such as the studied soil. Figure 1 shows the k^2-weighted Zn K-edge EXAFS and Fourier transform (FT) spectra of ZnS of different particle sizes compared to Zn spectrum of the pig slurry. These results were published in the Environmental Pollution journal (Formentini et al., 2017 [1]).
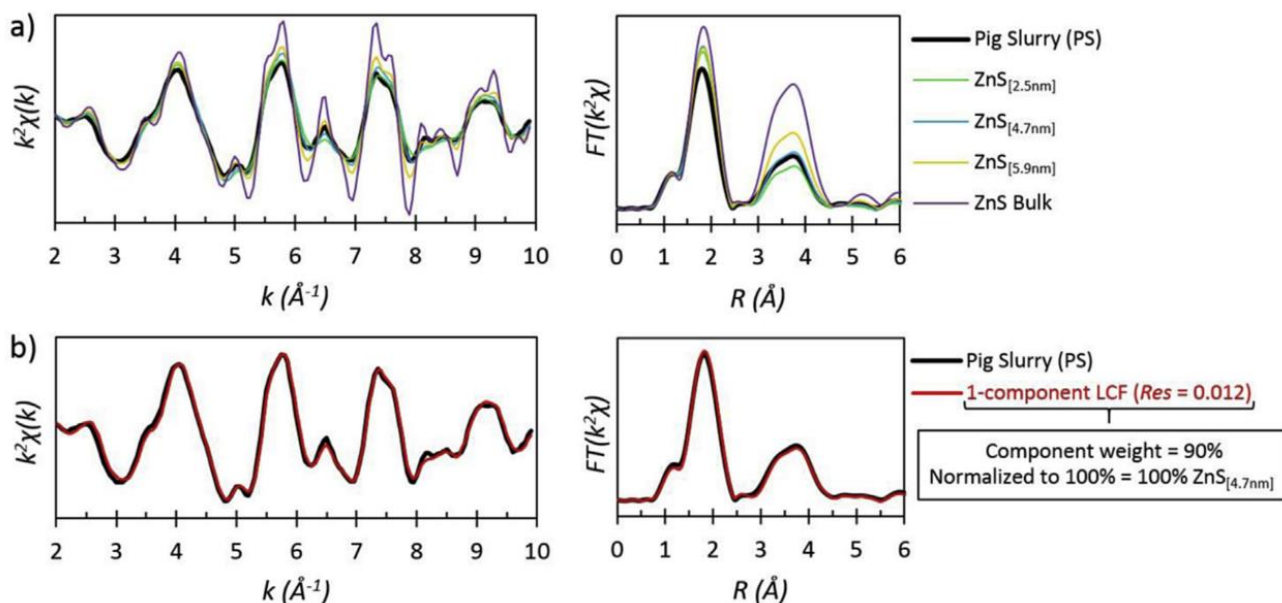

Figure 1 – (a) k^2-Weighted Zn K-edge EXAFS and Fourier transform (FT) spectra of the pig slurry, as compared to bulk and nano-sized ZnS; (b) 1-component LCF for the PS sample (adapted from Formentini et al., 2017[1]).

In bulk ZnS, the FT peak at 1.9 Å (not phase shifted, Figure 1a) indicated that the first Zn coordination shell was consisted of four S atoms located 2.34 Å from the central atom. The FT peak centered at 3.7 Å originated from the Zn-Zn interaction in the second coordination shell, with a bonding distance of 3.87 Å and a coordination number of 12. Moreover, the second peak at 3.7 Å may have received a contribution from the Zn-S interaction in the third coordination shell. The lower amplitude, sharpness (EXAFS) and intensity (FT) in spectra of the synthesized nano-ZnS references and the PS sample (compared to the bulk ZnS) may have been due to the greater proportion of under-coordinated Zn atoms located at the particle surfaces, causing a decrease in the average number of Zn neighbors. This was confirmed in the second FT peak (centered at 3.7 Å) in Figure 1a, in which the peak intensity declines with the ZnS particle-size.

The spectral features of the pig slurry sample and the ZnS[4.7nm] reference presented the most pronounced similarity, both in the EXAFS and FT. This was confirmed by the LCF procedure. The best LCF for the PS sample was nearly perfectly adjusted to the sample spectra and was achieved by using only one component: ZnS[4.7nm] (Figure 1b). This was the highest proportion of ZnS ever reported in organic waste.

Although EXAFS analysis may not be conclusive on particle-size determination, it may be assumed that the ZnS phase detected in the pig slurry had a relatively disordered structure compared to the bulk ZnS. We put forward the hypothesis that these ZnS particles were nano-sized, which was also the first literature report of its kind for a pig slurry matrix.

Secondly, we recorded the XAS spectra for a control and a pig-slurry-amended soil, as well as for the five corresponding density fractions of each soil: d<1.9, 1.9<d<2.25, 2.25<d<2.5, 2.5<d<2.7, and d>2.7 g cm^{-3}. Figure 2 shows the Cu and Zn k-edge EXAFS spectra for the soil amended with pig slurry and its five

fractions. The total concentration of Cu and Zn was rather low regarding the sensitivity of synchrotron X-ray beamlines. Nevertheless, the signal-to-noise ratio was high enough to make possible the data extraction and interpretation.
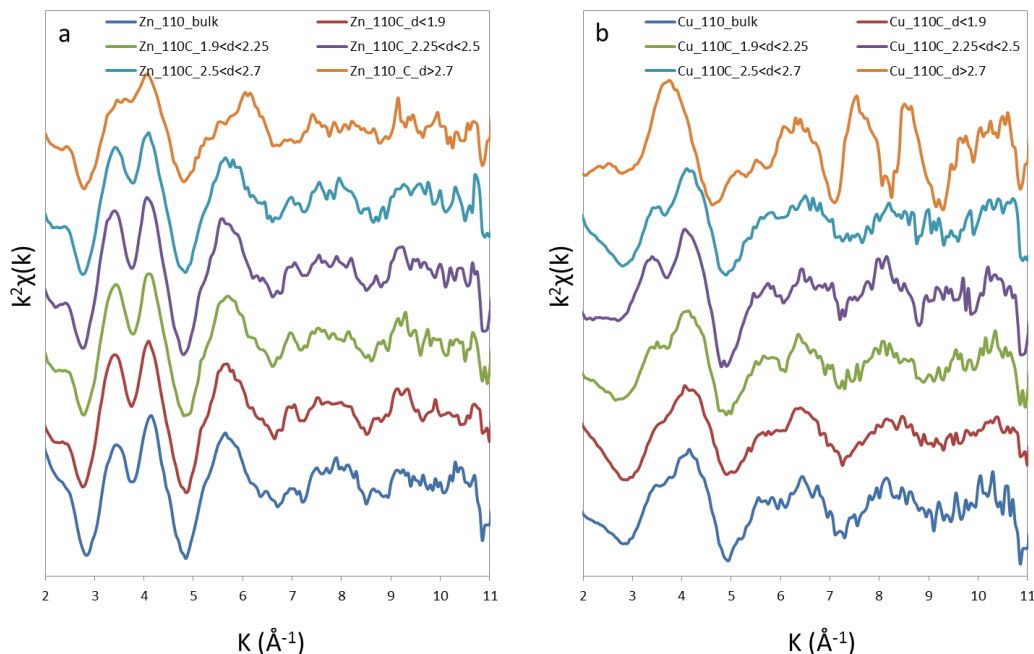

Figure 2 – (a) Zn and (b) Cu k^2-weighted K-edge EXAFS of the amended soil and density fractions (0-5 cm depth).

Since the EXAFS spectrum of the sample is a weighted sum of the spectra of all isolated species present, the speciation of Cu and Zn will be obtained by linear combination fits (LCF) of this spectrum using reference spectra. This approach is well stablished in the literature. Nevertheless, the number of reference spectra needed to fit the unknown sample will be determined by principal component analysis (PCA). The PCA approach is better accomplished when the number of species present in a set of samples is smaller than the number of sample spectra, and when the species composition of these samples varies. These requirements may be fulfilled by the density fractionation, which reduces the bulk matrix heterogeneity and complexity. Relevant reference compounds will be identified via target transformation and the SPOIL function in a large collection of organic Cu or Zn minerals and species. Data treatment is ongoing.

References

1.   Formentini, T. A.; Legros, S.; Fernandes, C. V. S.; Pinheiro, A.; Le Bars, M.; Levard, C.; Mallmann, F. J. K.; da Veiga, M.; Doelsch, E., Radical change of Zn speciation in pig slurry amended soil: Key role of nano-sized sulfide particles. *Environmental Pollution* **2017**.