	Experiment title: Copper and zinc speciation in soil after long term spreading of pig slurry	Experiment number: 30-02-1075
Beamline: BM30B	Date of experiment: from: 07 May 2014 to: 13 May 2014	Date of report: 01/09/14
Shifts: 18	Local contact(s): Isabelle Kieffer (email: isabelle.kieffer@esrf.fr)	*Received at ESRF:*

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Report:

Pig slurry spreading in crop fields can partially replace chemical fertilization and is common practice. However, Cu and Zn can occur in high quantities in pig slurry. The first environmental impact following pig slurry spreading is a significant increase of Cu and Zn concentrations in soil. Then, Cu and Zn bioavailability could induce toxicity to plants and Cu and Zn leaching could induce toxicity to water resources. Nevertheless, the Cu and Zn speciation in the soil after pig slurry spreading is still not well described. Most of the studies used short term soil/slurry incubation and chemical extractions. Chemical extraction presents strong shortcomings: it is strongly method dependent and its selectivity is weak. We recently demonstrated the interest of X-ray absorption spectroscopy to decipher Zn and Cu speciation in pig slurry.

Therefore, the objective of this study was to evaluate how "long-term" intensive applications of pig slurry affect Cu and Zn speciation of a soil by using XAS. We studied soil samples from a long term (12 years) field experiments installed in Brazil.

The main challenge of the proposed experiment concerns the quantitative speciation of trace elements within a complex matrix (soil amended with pig slurry) and the reliable detection of the EXAFS resulting from a mixture of species.

Experiment was conducted on beam line FAME (from 07/05/2014 to 13/05/2014) 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.

For this study, it was fundamental to register spectra (XANES and EXAFS) Zn and Cu model compounds which are representatives of tropical soils and organic wastes. The library of Zn and Cu model compounds consisted in selected minerals and synthetic compounds. It included Cu or Zn mineral that could precipitate in pig slurry (e.g. covelite (CuS) or sphalerite (ZnS)), Cu or Zn complexed to different type of organic matter (e.g. Zn acetate or Cu methionine), and Cu or Zn sorbed on minerals observed in the studied soil (e.g. Cu sorbed on goethite or Zn sorbed on kaolinite). In the last two types of reference compounds the Zn and Cu concentrations were low in order to be as close as possible of the environmental conditions.

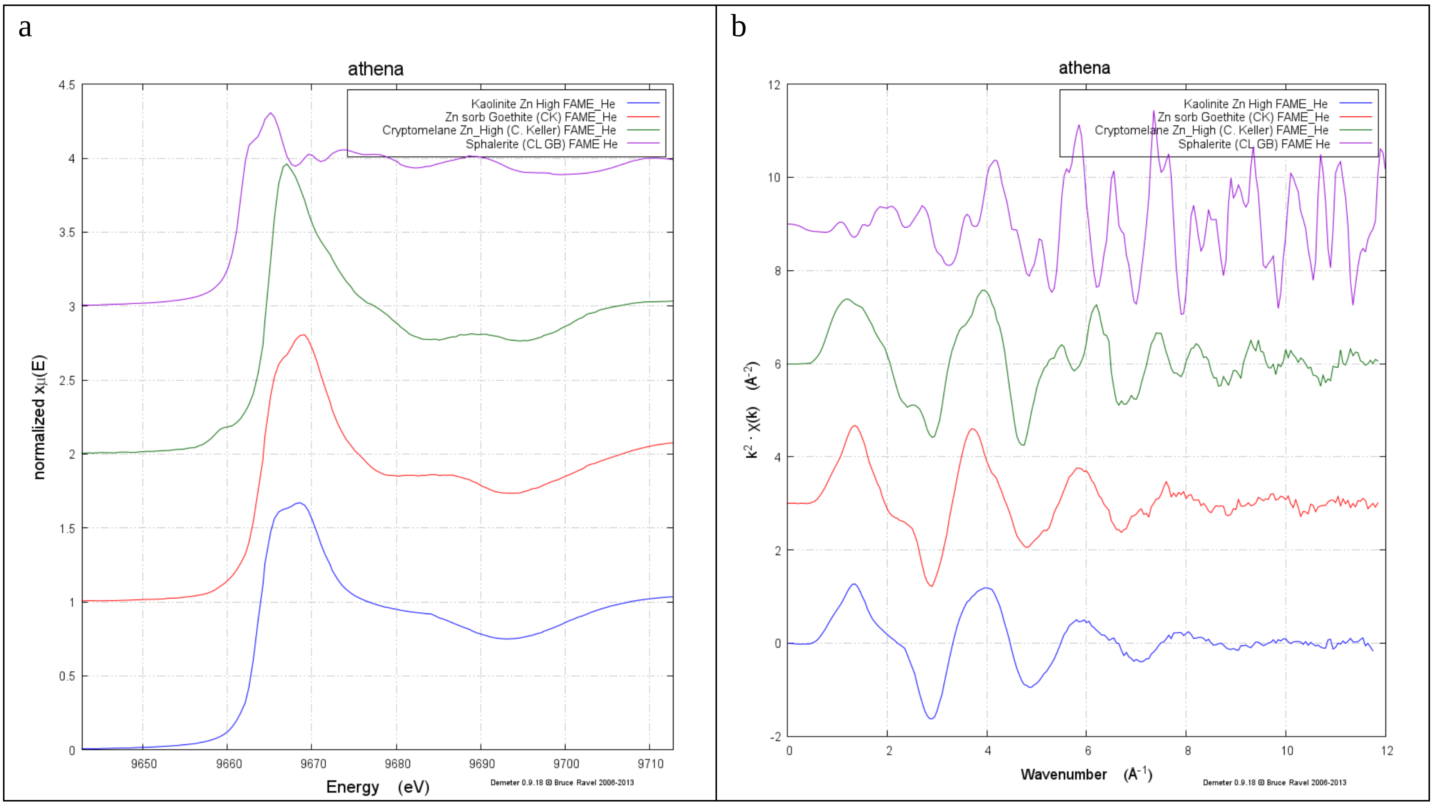

Figure 1: a) XANES and b) EXAFS ($k^2\chi(k)$) spectra of Zn model compounds.

The quality of the data obtained with the reference compounds can be checked on Figure 1, taking the some Zn reference compounds as an example. These spectra were recorded with 2s by point and it clearly shows identifiable XANES pattern and EXAFS fine structure until 12 $Å^{-1}$.

Zn and Cu K-edge EXAFS spectra of the pig slurry and some soil samples are presented in Figure 2. At first it is worth noting that the total concentration of Zinc and Copper in the

selected soil from Brazil is quite high (around 100 mg.kg^{-1}) concerning the "average" content of Zn and Cu in non-contaminated soil, but quite low regarding the sensitivity of synchrotron X-ray beamlines.

Nevertheless, the signal/noise ratio is high enough to interpret the data, and the data treatment is ongoing. Since the EXAFS spectrum of the unknown sample is a weighted sum of all species spectra present, the atomic fraction of each metal species will be obtained by linear combination fits (LCF) of this spectrum to reference spectra. The minimum number of reference spectra needed to fit the unknown sample will be determined by principal component analysis (PCA). 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.

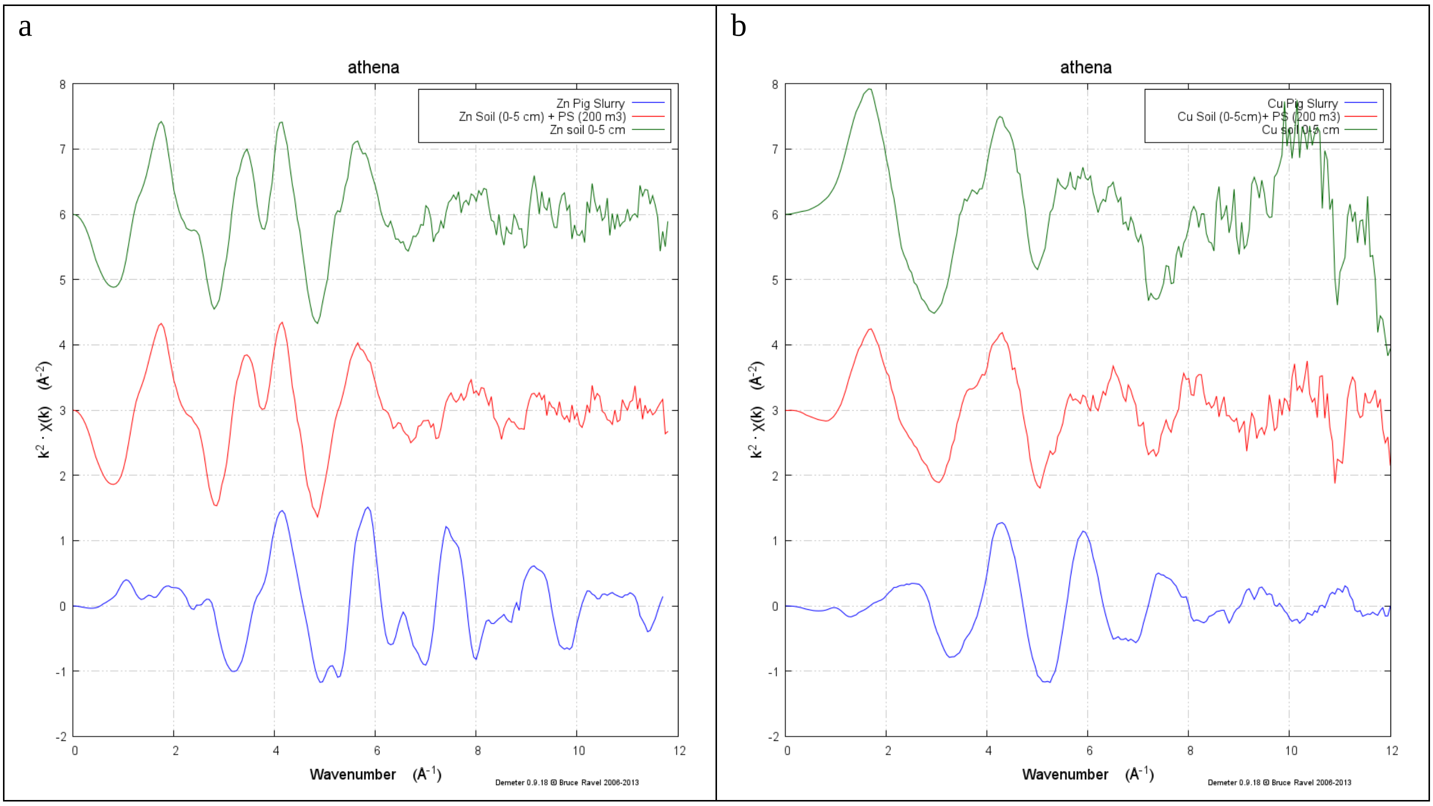

Figure 2: EXAFS ($k^2\chi(k)$) spectra of the pig slurry and soil samples a) at Zn edge and b) at Cu edge

The EXAFS results obteined in this study for quantitative Cu and Zn speciation in soil amended with pig slurry will be compared to selective sequential extractions already obtained on the same samples.