



Experiment title: Copper and zinc speciation in soil after long term spreading of pig slurry		Experiment number: EV-131
Beamline: BM30B	Date of experiment: from: 22 April 2015 to 28 April 2015	Date of report: 13/02/17
Shifts: 15	Local contact(s): Isabelle Kieffer (email: isabelle.kieffer@esrf.fr)	<i>Received at ESRF:</i>

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Report

Aims of the experiment and scientific background

Pig slurry has fertilizing properties and spreading it on crop fields can partially replace chemical fertilization. However, pig slurry presents high concentration of heavy metals, especially copper (Cu) and zinc (Zn), which may induce significant increase of Cu and Zn concentrations in amended soils. These heavy metals are then released in the environment and could be toxic to animals and plants or cause contamination of water resources by leaching. Therefore, the environmentally safe use of organic amendments (e.g. pig slurry) requires adequate control of the potential pollutants (e.g. Cu and Zn).

The objective of this study was to evaluate how long-term intensive applications of pig slurry affect Cu and Zn speciation within a soil. We investigated the evolution of Cu and Zn speciation in the soil after pig slurry spreading in samples from a long-term field experiment. The experimental field was 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 ($200 \text{ m}^3 \text{ ha}^{-1} \text{ year}^{-1}$ of pig slurry). The soil 0-5 cm depth was sampled at the end of the 11th year of experimentation.

Experiment

The main challenge of this experiment concerned the quantitative speciation of Cu and Zn within a complex matrix (pig slurry and slurry-amended soil) and the reliable detection of the EXAFS resulting from a mixture of species.

The experiment was conducted on beamline FAME (from 22/04/2015 to 28/04/2015) 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.

Samples were analyzed at the K edges of Cu and Zn: 2 bulk soil samples (control and amended soils at the 0-5 cm depth), and the pig slurry. The Cu and Zn concentrations in the samples ranged from 74 to 207 mg kg⁻¹. Numerous XAS scans per sample were necessary in order to obtain a good signal-to-noise ratio. A

screening of the 5 density fractions was also performed even though a good signal to noise ratio could not be obtained for all of them during this experiment.

Moreover, several Cu- and Zn-containing minerals and synthetic compounds had their EXAFS spectra recorded as reference materials. It included minerals that could precipitate in pig slurry [e.g. covelite (CuS) and sphalerite (ZnS)], Cu or Zn complexed to different types of organic matter (e.g. Cu-acetate and Zn-malate), and Cu or Zn sorbed on minerals previously observed in the studied soil (e.g. Cu sorbed on goethite or Zn sorbed on kaolinite).

Results

We recorded and compared the k^2 -weighted Cu and Zn K-edge EXAFS and Fourier transform (FT) spectra of the bulk soil samples (control and amended) and the pig slurry. Results are summarized in Figure 1 and Figure 2 (adapted from Formentinini, 2016^[1] and Formentinini et al., 2017^[2]).

The Cu K-edge EXAFS spectra of the control (CT) and amended (PS200) soils presented a distinct shoulder in the left side of the first oscillation, at 3.45 \AA^{-1} (vertical dashed line, Figure 1a), as well as a deep in the second oscillation, at 6.1 \AA^{-1} . These two well-defined spectral features were also present in both the Cu-kaolinite and Cu-vermiculite references.

The Cu K-edge EXAFS spectrum of the pig slurry sample may be distinguished by its second EXAFS oscillation, centered at 5.85 \AA^{-1} (vertical dashed line, Figure 1a), which was also present in the Cu₂S reference. Moreover, analysis of the R-space spectra showed that Cu nearest neighboring atom was S, as indicated by the FT peak representing the Cu first coordination shell at 1.85 \AA (not phase-shifted, vertical dashed line, Figure 1a).

LCF indicated that Cu in the control soil (CT) was associated to the clay minerals kaolinite (60%) and vermiculite (40%). Cu speciation within the amended soil (PS200) was composed of 69% Cu-kaolinite and 31% Cu-vermiculite (Figure 1b). Comparison between the Cu speciation before (CT) and after (PS200) the PS amendments indicated that 90.3% of the exogenous Cu was associated to kaolinite within the amended soil. Cu speciation in the pig slurry was 85% Cu₂S and 15% CuCl.

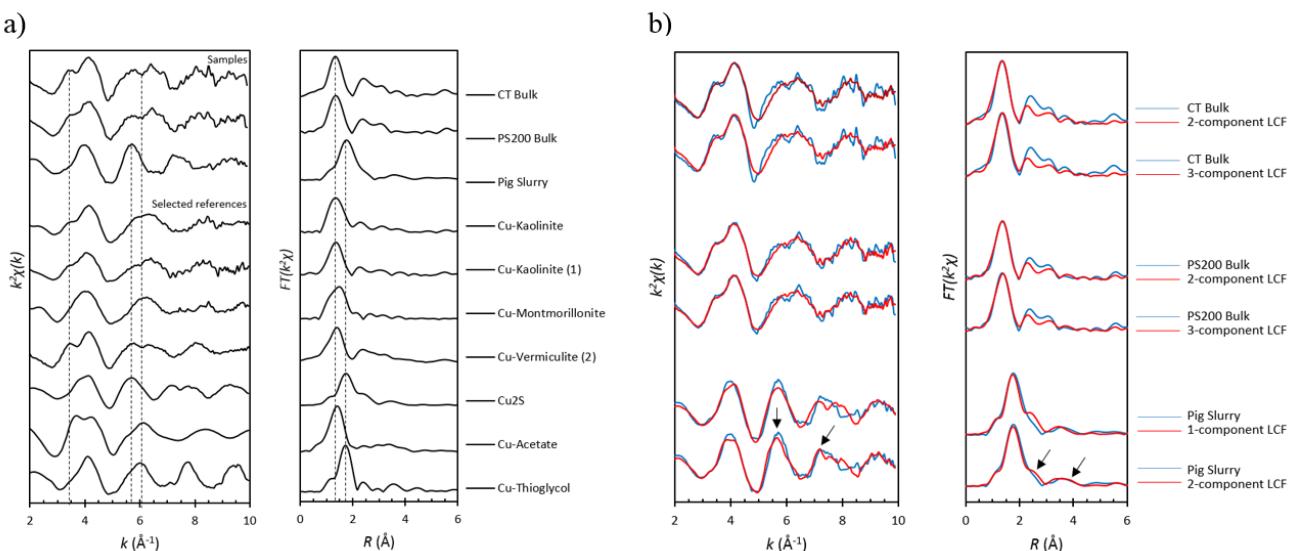


Figure 1 – (a) k^2 -Weighted Cu K-edge EXAFS and Fourier transform (FT) spectra of control soil (CT), amended soil (PS200) and pig slurry samples as compared to Cu-containing or Cu sorbed on selected mineral and organic references; (b) k^2 -weighted Cu K-edge EXAFS and FT spectra of samples (blue) superposed by the best LCF fits for each sample (red). (adapted from Formentinini, 2016^[1]).

The Zn K-edge EXAFS spectra of the bulk soil samples (CT and PS200) showed a distinct splitting in the first oscillation, at 3.75 \AA^{-1} (vertical dashed line, Figure 2a). The same splitting was also found in the references containing Zn sorbed on phyllosilicates: Zn-kaolinite and Zn-HIM (hydroxy-interlayered mineral). This splitting suggests that Zn in Zn-HIM was octahedrally coordinated and mainly incorporated in the dioctahedral vacancies of gibbsite layers, with 6 Al atoms in the second coordination shell, as reflected by the FT peak at 2.75 \AA (not phase-shifted, vertical dashed line, Figure 2a). This molecular arrangement was

also reflected by the FT peak at 5.5 Å (vertical dashed line, Figure 2a), originated from multiple scattering along the 6 collinear Zn–Al-Al axes.

In contrast, Zn uptake into the kaolinite reference might have occurred partly due to incorporation into vacant dioctahedral sites and partly due to substitution for Al. In the latter, the number of Al atoms in the second shell is reduced to 3. This was phenomenological reflected by the lower amplitude of FT peaks at 2.75 Å and 5.5 Å, as compared to the corresponding peaks in the Zn-HIM reference.

The Zn EXAFS spectra of Zn-kaolinite presented a shoulder in the left side of the second oscillation, at 5.2 Å⁻¹ (vertical dashed line, Figure 2a), which was absent in the Zn-HIM reference. This curvature was also observed in the spectra of bulk soil samples, being more pronounced in the CT sample. In addition, the FT peak at 5.5 Å slightly shifted to a shorter distance in the Zn-HIM reference, as opposed to Zn-kaolinite and the soil samples. Therefore, Zn-kaolinite presented characteristics more in agreement with the soil samples than Zn-HIM.

LCF showed that 70% of the Zn in the control soil was associated to kaolinite (Figure 2b). The remaining 30% speciation was composed of Zn-Fe-oxide. Zinc speciation within the amended soil was composed of Zn-kaolinite (54%) and Zn-Fe-oxide (27%), which had been detected also in the control soil, plus Zn-OM (19%), which was absent in the control soil (Figure 2). Comparison between the Zn speciation in the control and in the amended soils resulted in the following contribution to the assimilation of exogenous Zn: 35.8% Zn-kaolinite, 24.5% Zn-Fe-oxide and 39.6% Zn-OM.

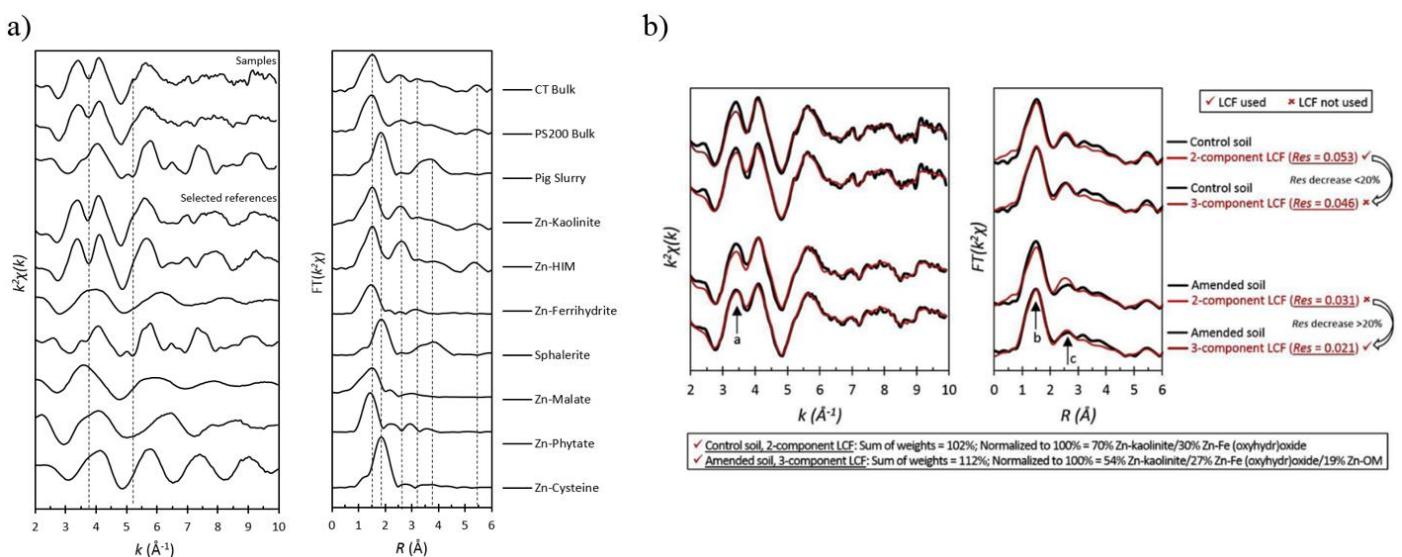


Figure 2 – k^2 -Weighted Zn K-edge EXAFS and Fourier transform (FT) spectra of control soil (CT), amended soil (PS200) and pig slurry samples as compared to Zn-containing or Zn sorbed on selected mineral and organic references; (b) k^2 -weighted Zn K-edge EXAFS and FT spectra of samples (black) superposed by the best LCF fits for each sample (red). (adapted from Formentini, 2016 and Formentini et al., 2017).

Zn speciation in the pig slurry was 100% composed of ZnS. It was very surprising that neither ZnS nor Cu₂S were detected within the amended soil, although pig slurry was the only source responsible for a nearly two-fold increase in Cu and Zn concentrations within the amended soil.

The first results obtained on the density fractions confirm this observation and it is important to further investigate the Cu and Zn speciation in these fractions. More time is needed to improve the signal to noise ratio of the fractions XAS spectrum. . Besides, we 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. This hypothesis needs also more investigations.

References

1. Formentini, T. A. *Macroscopic, microscopic and molecular scale interactions affecting Copper and Zinc transfer within a clayey hapludox soil subject to long-term pig slurry application*. PhD thesis, Federal University of Paraná, Curitiba, 131 pp., 2016.
2. 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* 222, 495-503, 2017.