| ESRF | **Experiment title:**<br>**Influence of field conditions on Cu and Zn speciation** | **Experiment number**:<br>30-02/1146 |
|---|---|---|
| **Beamline**:<br>BM30 | **Date of experiment**:<br>from: November 04th, 2020 to: November 10th, 2020 | **Date of report**: |
| **Shifts:**<br>12 | **Local contact(s)**:<br>Denis Testemale (e-mail: denis.testemale@esrf.fr) | *Received at ESRF:* |

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# Report

## Scientific background:

Cu and Zn are supplemented in the diets of livestock owing to their growth and antibiotic attributes. Due to the low body absorption, most of them are excreted in the manure. Soil accumulation of manure-borne Cu and Zn have been reported by several studies[1],[2],[3] and pose threats such as food-chain incorporation, groundwater contamination and phytotoxicity. The environmental fate and behavior of these heavy metals highly depend on their chemical speciation in the origin (i.e. manure, sludge, etc.) as well as on soil characteristics (texture, mineralogy, redox conditions, etc.). Studies assessing the transformations of Cu and Zn throughout organic livestock waste (OLW) recycling on agricultural soils, as well as the impact of such transformations on the long-term fate of heavy metals in the environment, are lacking.

Direct observation of ZnS in sewage sludge and pig slurry is as recent as 2014[4] and 2017[5], respectively. In the latter study[2], ZnS accounted for a 2-fold increase in the Zn concentration in the amended soil, but was not detected in this soil by Zn K-edge EXAFS. Indeed, Zn was bound to clay minerals, Fe (oxyhydr)oxides and organic matter in the amended soil. The nano size of the ZnS crystallites in the pig slurry favoured their oxidative dissolution and transformation after spreading on the soil, thus explaining its low stability in the long term.

Zinc sulphides may dominate the Zn speciation, most likely in the nano-size regime, in different types of OLW commonly used as soil amendments on farmlands. However, very little is known on the long-term environmental fate and behavior of such contaminants in real systems.

## Aims of the experiment:

We assessed the Cu and Zn speciation in OLW and soils from three long-term field experiments with OLW application into soils conducted in southern Brazil. The experiments were selected due to unique characteristics such as detailed monitoring history, different types and rates of OLW applied, long duration and different types of soils. The characteristics of the field experiments are described in Table 1.

We analyzed the samples with the highest contrast in Cu and Zn concentrations, i.e. a sample from uncontaminated soil (control soil - CS), from the soil that received the highest OLW application rate (amended soil - AS) and from the OLW that has been applied on the soil (organic livestock waste – OLW).

**Table 1 - Characteristics of long-term field experiments.**

| ID | Location | Type of soil | Type of OLW | Amendments Period | Application rate ($m^3 ha^{-1} year^{-1}$) |
|---|---|---|---|---|---|
| **FE1** | Santa Maria, RS | Sandy loam | Pig slurry | 2004-2016 | (Based on N rates) |
| **FE2** | Braço do Norte, SC | Sandy loam | Pig slurry and pig litter | 2003-2012 | 180 |
| **FE3** | Ponta Grossa, PR | Clay loam | Cattle manure | 2005-2019 | 180 |

## Experimental method:

The Experiment was conducted on beamline BM30 (from November 4th to November 10th, 2020) with a Si (220) monochromator. The spectra were recorded in fluorescence mode using a 23-elements solid-state Ge detector (Canberra) at Helium temperature with a cryostat in order to avoid beam damage. Twelve samples were analyzed at the K edges of Cu and Zn: 3 control soils (surface layers of each field experiment), 6 amended soils (two layers per soil) and 3 OLW (pig slurry - PS, pig litter - PL and cattle manure - CM).

## Preliminary results:

We highlight preliminary results for the Zn speciation in samples from experiment FE2 (Braço do Norte, SC). Figure 1a shows the comparisons of the Zn K-edge EXAFS spectra of control soil (BN_CS), amended soils with pig slurry (BN_AS_PS), pig slurry (PS) and the references of Zn sorbed on kaolinite and sphalerite (ZnS). Figure 1 (b) shows the comparisons of the Zn K-edge EXAFS spectra of control soil (BN_CS), amended soils with pig litter (BN_AS_PL), pig litter (PL) and the references of Zn sorbed on kaolinite and Zn sorbed on ferrihydrite.

The EXAFS spectra of the control soil sample showed a distinct splitting in the first oscillation, at 3.75 $Å^{-1}$. The same splitting was also found in the reference containing Zn sorbed on kaolinite. Zn-kaolinite may dominate the Zn speciation in the control soil sample. The EXAFS spectra for the control soil and amended soils with pig slurry (BN_AS_PS) presented similar shape. However, the splitting at 3.75 $Å^{-1}$ is less pronounced for the amended soils, indicating a smaller proportion of Zn-kaolinite in the amended soils. The EXAFS spectrum of pig slurry sample is distinct from the control and amended soils spectra, showing oscillation patterns similar with the sphalerite (ZnS) reference. This suggests that ZnS dominated the Zn speciation in the pig slurry, but this species underwent transformation after applied to the soil.

The EXAFS spectra of amended soils with pig litter (BN_AS_PL), on the other hand, presented shape similar to the pig litter that has been applied to the soil, indicating that species present in the PL sample persisted in the soil after the amendments. Thus, the fate of exogenous Zn within the contaminated soils was dependent on the Zn speciation in the source, i.e. pig slurry vs. pig litter.

These spectra, together with those from Santa Maria and Ponta Grossa, will be subjected to a least-square linear combination fitting (LCF) using a library of Cu/Zn model compounds to identify and quantify the Cu/Zn-bearing components in the samples. Data treatment is in progress.

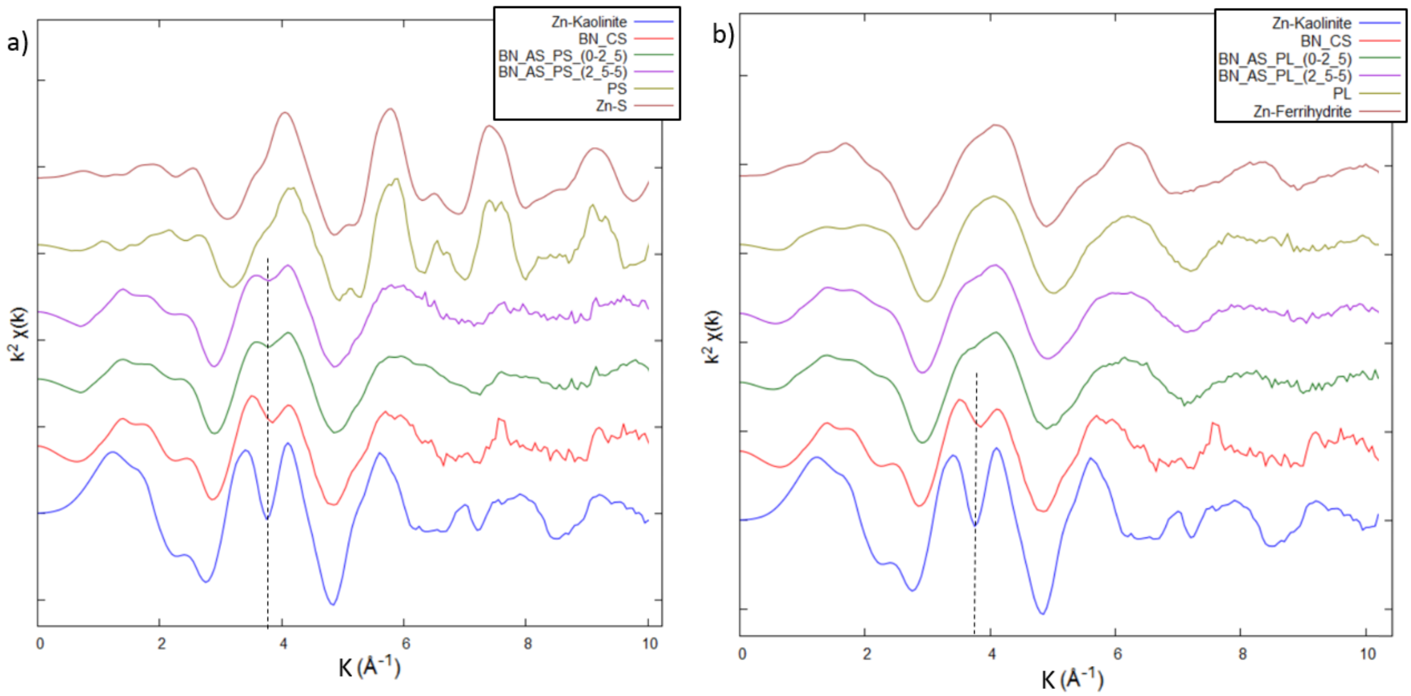


**Figure 1 - Zn K-edge EXAFS spectra from FE2 samples of control soil; a) amended soils with PS, pig slurry, Zn-kaolinite and ZnS references; b) amended soils with PL, pig litter, Zn-kaolinite and Zn-ferrihydrite references.**

## References:


[1] FORMENTINI, T.A. et al. *Sci Total Environ*, 536, 831-839, 2015.
[2] MALLMANN, F.J.K. et al. *Vadose Zone Journal*, 16, 2017.
[3] GRÄBER, I. et al. *Danish Journal of Geography*, 105, 15–22, 2005.
[4] KIM, B. et al. *Journal of Environmental Quality*. 43, 908–916, 2014.
[5] FORMENTINI, T.A. et al. *Environmental Pollution*, 222, 495–503, 2017.