	Experiment title: Zn speciation in wastes and organically amended soils: a comprehensive XAS study in three long-term field experiments.	**Experiment number**: EV 266
Beamline: BM30B	**Date of experiment**: from: 19 Oct 2017 to: 24 Oct 2017	**Date of report**: 23 Feb 2023
Shifts: 15	**Local contact(s)**: Mauro Rovezzi	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Thiago Formentini * (Universidade Federal de Santa Maria, Brazil)

Dr. Emmanuel Doelsch * (CIRAD, France)

Dr. Samuel Legros * (CIRAD, France)

Dr. Fabio Mallmann (Universidade Federal de Santa Maria, Brazil)

REPORT

Context

Spreading Zn-rich organic wastes (OWs) on farmlands is a very common practice. It accounts for 78% of the exogenous Zn inputs in cultivated soils in France. Assessing the impacts of this practice should consider the Zn speciation in its origin (OWs) as well as within the soil after long-term OW amendments, under realistic field conditions. However, this requires years or decades of fieldwork and is hence very rare. Consequently, such studies are lacking.

Zinc sulfide (ZnS) may dominate the Zn speciation in several types of OWs. However, only a few studies have identified this species, notably due to sampling, storage and analytical shortcomings. Direct observation of ZnS (in the form of nano-sized particles) is as recent as 2014 in sewage sludge [1] and 2016 in pig slurry [2]. There is little information on their fate in the environment.

Samples Analyzed

We used XAS to analyze the speciation and molecular environment of Zn in well-preserved OWs as well as in soils following OW amendments in three controlled, field-scale, long-term experiments, according to the table below:

Field experiment	Type of soil	Type of organic waste applied	Experiment duration
#1 (Santa Maria, RS, Brazil)	Sandy loam	Pig slurry	2000-2008
#2 (Ponta Grossa, PR, Brazil)	Clay loam	Dairy manure	2005-2014
#3 (Castro, PR, Brazil)	Clayey	Dairy manure	2005-2014

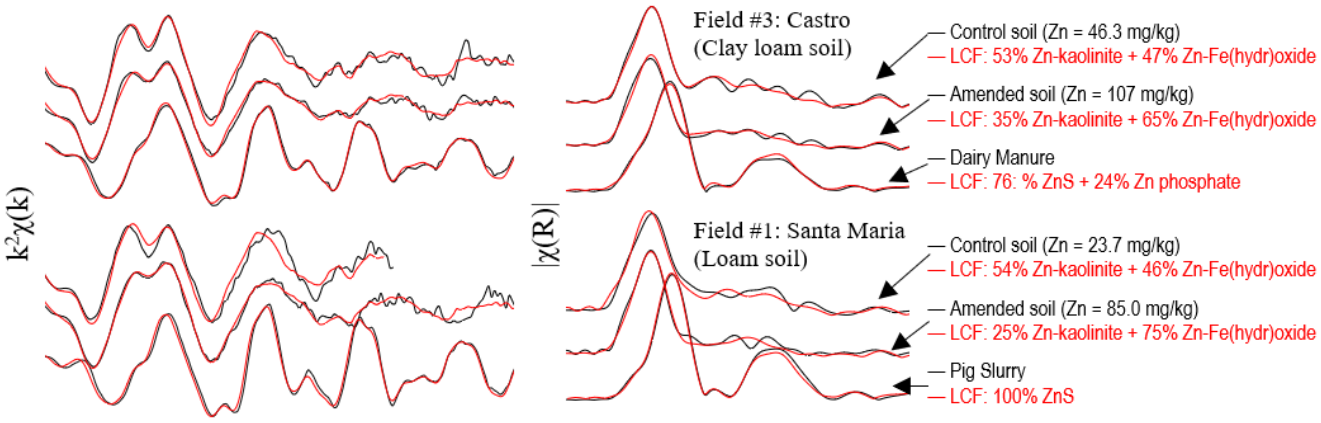
[1] Kim, B. et al. (2014). *Journal of Environmental Quality* 43, 908–916. https://doi.org/10.2134/jeq2013.10.0418.

[2] Formentini, T.A. et al. (2017). *Environmental Pollution* 222, 495–503. http://dx.doi.org/10.1016/j.envpol.2016.11.056.

Results

The concentration of Zn in the control soils, i.e., the soils containing only natural Zn levels, was rather low: 23.7 mg/kg in field #1 (Santa Maria), 24.1 mg/kg in field #2 (Ponta Grossa), and 46.3 mg/kg in field #3 (Castro). Because of increasing noise at high k values, only an extended XANES was recorded for the control soils of fields #1 and #2. For the soils amended with organic waste and for the organic wastes itself (higher Zn concentrations), we could record good quality EXAFS up to high k values.

The figure below summarizes the EXAFS recorded for the samples from fields #1 and #3, together with the results of the LCF procedure conducted to elucidate the Zn speciation in each case. In both field experiments, ZnS dominated the Zn speciation in the organic wastes applied: 100% ZnS in the pig slurry applied to field #1 and 76% ZnS in the dairy manure applied to field #3. This confirmed the hypothesis that ZnS might be a dominant species in these types of wastes, though this has been overlooked due to little attention during sample collection and preservation.



The fate of organic waste borne ZnS was very similar in both field experiments, despite the soils featuring different textures and different mineralogy. Zn-kaolinite and Zn-Fe(hydr)oxide accounted for about 50% each of the Zn speciation in the natural soils (no organic waste amendments). In the soils amended with pig slurry or dairy manure, the proportion of Zn-Fe(hydr)oxide increased considerably, indicating that these are the species responsible for the Zn uptake in the amended soils.

Noteworthy, ZnS was not detected in the amended soils, despite the increase in Zn concentration caused by the organic waste amendments. This is rather surprising due to the expected low solubility of these species. The occurrence of ZnS as nano-sized particles has been proposed as an explanation for its high instability in the soil.

Publications

Given the relevance and originality of the results, we will complement our dataset by investigating other field experiments, where other types of soils and organic wastes are also considered. The final goal is to understand to which extent the soil features and/or the speciation of Zn in the source control the long-term environmental fate of Zn in agroecosystems. This was partially accomplished during experiment *A30-2 1146* and will be finalized in a new experiment for which beamtime is being requested. A manuscript with comprehensive data and discussion should be submitted for publication soon.