ESRF	**Experiment title:** Changes in Zn and Cu speciation after introduction of energetic plants in a sludge-impacted agricultural soil	**Experiment number:** **30-02- 983**
Beamline: BM30B-FAME	**Date of experiment:** from: 08/09/2010 at 08:00 to 13/09/2010 at 08:00	**Date of report:** March 6, 2011
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Report:

The objective of proposal CRG2009-24001 was to use EXAFS data of selected soil samples to follow the possible changes in Zn and Cu speciation along a sandy soil due to *miscanthus* cropping for an energetic purpose. This objective is part of a French ANR project called RESACOR (REconversion des Sols Agricoles Contaminés: impact des cultures à vocation énergétique sur la biodisponibilité des elements en trace en relation avec la réponse des ORganismes du sol) aimed at studying the pedo-geochemical responses of contaminated agricultural soils to changes in land use.

Materials and methods

Rather than following Zn speciation along a reference profile where no *miscanthus* have been introduced and the second one where *miscanthus* have been introduced one year ago as initially schedule in the proposal, we decided to analyze *rhizospheric* and *bulk* soil samples collected at various 12mx12m areas at the studied site.

The first area (area 0 on Figure 1) corresponds to a place where no *miscanthus* have been introduced, the second area (area 1 on Figure 1) corresponds to a place where *miscanthus* have been introduced one year ago and the third area (area 3 on Figure 1) corresponds to a place where *miscanthus* have been introduced three years ago.

Zn K-edge EXAFS data were collected at liquid He temperature in fluorescence mode with the 30-element Canberra Ge solid state detector. Because of the high Fe concentration in the studied samples, it was necessary to reduce the Fe Kα contribution to the fluorescence signal with 4 to 7 Al foils. Consequently, no additional foils could be used to reduce the Rayleigh scattering (i.e. Cu foils at the Zn K-edge) because doing so would have significantly dampened the Zn Kα signal.

With this setup, between 5 and 8 EXAFS scans were necessary to achieve a good signal/noise ratio for each soil sample.

Results

The Zn K-edge EXAFS signals of the 6 samples analyzed are displayed in Figure 1. For each area, the EXAFS signals of the bulk and rhizospheric soils are compared in order to emphasize a possible change in Zn speciation related to *miscanthus* introduction. Such a comparison shows that, despite slight differences from one area to the other (likely reflecting sampling heterogeneities), the EXAFS data of bulk and rhizospheric soils are similar. This result suggests that *miscanthus* has no effect on Zn speciation in the rhizosphere, at least at a 3 years timescale.

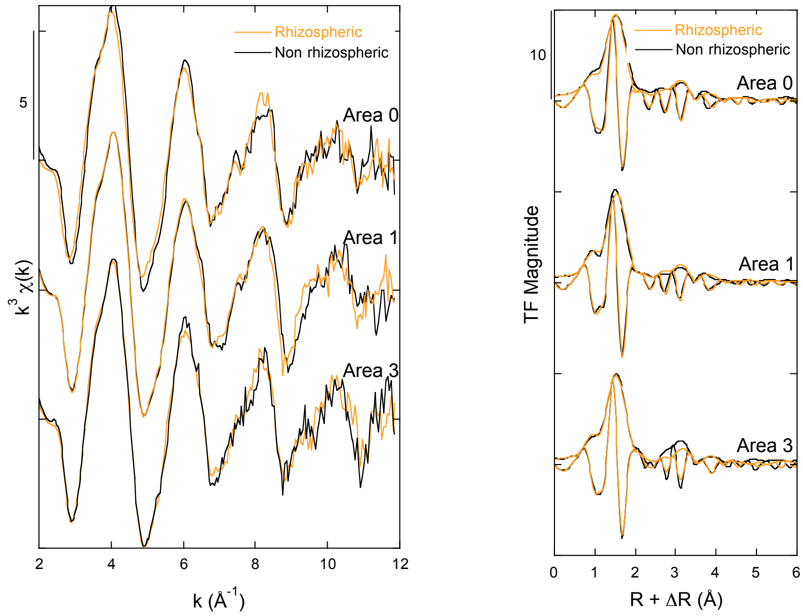


Figure 1 : Comparison between bulk (black) and rhizospheric (orange) soils for each of the three studied areas.

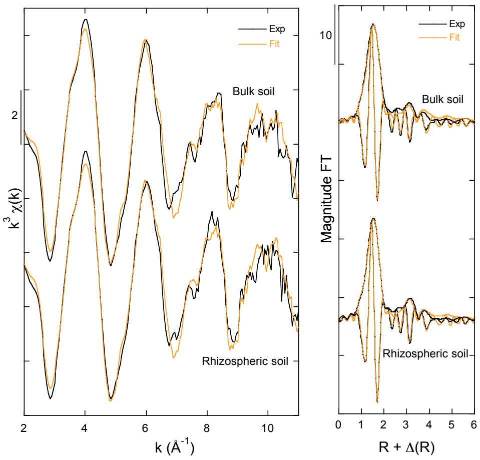
This hypothesis of a lack of effect of *miscanthus* on Zn speciation in the rhizosphere is confirmed by the quantitative results of EXAFS data analysis following a Least-Square Fitting (LSF) procedure (Table 1 and Figure 2). Although a Principal Component Analysis (PCA) could not be performed because of the similarity of the 6 EXAFS spectra analyzed, LSF procedure indicates an homogeneous speciation of Zn, with fourfold Zn sorbed at the surface of ferrihydrite and associated with phosphorous in phytate (likely representing organic Zn) and sixfold Zn incorporated within the structure of a dioctahedral phyllosilicate (represented here by illite).

Table 1 : Quantitative results of the LSF procedure performed on the 6 analyzed soil samples.

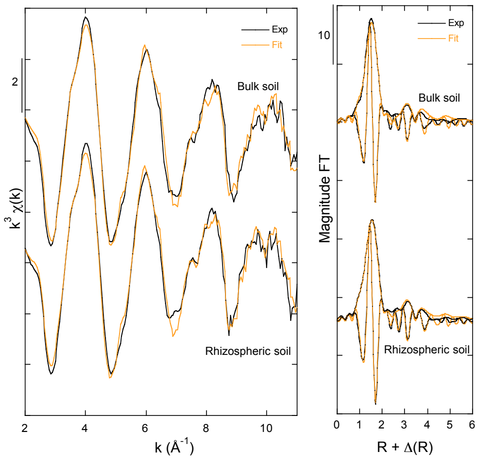
	AREA 0		**AREA 2**		**AERA 3**	
	Rhizospheric	Bulk	Rhizospheric	Bulk	Rhizospheric	Bulk
Fourfold Zn / Ferrihydrite	52	43	49	40	37	45
Fourfold Zn Phytate	17	22	19	31	31	24
Sixfold Zn in Illite	29	33	32	29	32	30
Σ components	98	98	100	100	100	99
Reduced-Chi^2	0.164	0.191	0.139	0.131	0.157	0.243

(1) The sum of component was set free during the LSF procedure. (2) Reduced-Chi^2 calculated as .

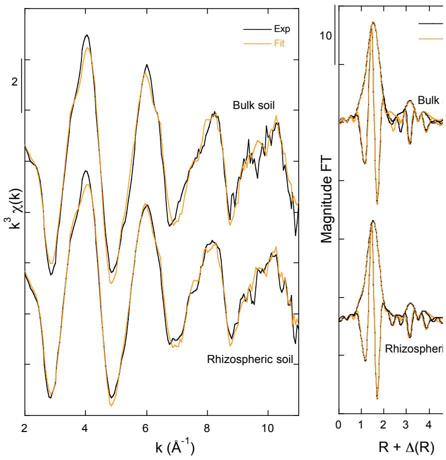
Fourfold Zn sorbed at the surface of ferrihydrite and associated with phosphorous in phytate (likely representing organic Zn) likely represent anthropogenic Zn, whereas sixfold Zn incorporated within the structure of a dioctahedral phyllosilicate (represented here by illite) is more likely associated to geogenic Zn.



AREA 0 (No *miscanthus*)



AREA 1 (One year *miscanthus*)



AREA 3 (Three years *miscanthus*)

Figure 2 : Experimental (black) and LSF fits (orange) of bulk and rhizospheric soils collected at the three studied areas.

The slight variations in the relative proportions of these Zn species between bulk and rhizospheric soils can be related to the samples heterogeneity rather than to an effect of *miscanthus* on Zn speciation in the rhizosphere. These results confirm the lack of effect of *miscanthus* on Zn speciation in the rhizosphere, at least at a three years timescale.

These experiments should be extended over a larger timescale (up to 10 years) before concluding that *miscanthus* can be grown on Zn impacted soils without any risk of enhanced mobility or bioavailability due to a change in Zn speciation.

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