Combining X-ray absorption spectroscopy (XAS) and diffusive gradients in thin films (DGT) to probe speciation and dynamic of heavy metals in soils amended with organic wastes

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Abstract

Applications of so-called organic wastes are recommended in agricultural fields where soil organic matter content is low. However, these materials could pose some hazard to humans, animals, or to the environment through the assessment of the dynamic of potential pollutants such as trace metals. This study thus aimed at evaluating the speciation of copper (Cu) and zinc (Zn) in various organic wastes exhibiting moderate to high levels of trace metals, their dynamic in a soil after amendment and their mutual correlation. Trace metals speciation was determined by X-ray absorption spectroscopy (XAS) while the temporal dynamic remobilization in soil/waste mixtures was monitored using the diffusive gradient in thin films (DGT) technique. Results indicated that predominant pools of species in wastes were inorganic for Zn (>60%) and organic for Cu (>50%). During mineralization, we detected an increase in the remobilization of trace elements in soil/waste mixtures, which was more noticeable for Zn than for Cu.

Introduction

Agricultural recycling is recognized as an alternative to stockpiling or incineration. However, benefits of using organic wastes as soil amendment should be assessed together with the potential environmental and toxicological effects of trace elements [1]. In addition, the biochemical conditions of the medium are substantially altered during organic waste mineralization through changes in the organic matter stock and dynamics and in the physicochemical properties (e.g., pH, Eh) of the soil solution. Indeed, mineralization of organic matter could influence the remobilization of trace metals, whose speciation characterization is essential for dynamic understanding.

Based on total amounts of trace metals in organic wastes we previously highlighted accumulation of Cu and Zn in their fine particles [2] and their association with major elements, statistical analysis, revealed sulfur or phosphorus bearing phases and any correlation with organic carbon. However, such interactions could be concealed by the abundant quantity of carbon in coarse particles of wastes. Studies devoted to trace metals speciation in organic wastes are still scarce and were mainly focused on the speciation and availability of heavy metals after spreading on soils [3] and rely mainly on sequential metals extraction using a series of reagents. However, it is well known that reagents are not completely selective in dissolution of phases and usually modify the physicochemical properties of soil substantially. A better insight into speciation by combining different analytical approaches with X-ray absorption spectroscopy (XAS), which allows identifying major chemical species in situ with minor or no-pretreatments [4]. In addition, the potential resupply of trace elements from soil to solution could be measured by the DGT technique (diffusive gradients in thin films; [5]).

It is noteworthy that this technique enables an *in situ* investigation of trace element dynamic in soil. In addition, DIFS modeling of DGT measurements allows a quantitative interpretation of trace metals dynamic in terms of fundamental kinetic and equilibrium resupply parameters.

Materials and methods

Geographical origin and type of organic waste raw materials

Seventeen different organic wastes of diverse origins (urban or agricultural), collected from five different regions over three countries (Madagascar, Senegal, France), located in temperate or tropical environments were selected for this study [2]. Each organic waste was analyzed for their major elements and heavy metal concentrations.

XAS data collection on organic wastes

The XAS spectra (including near-edge structure region or XANES, and extended X-ray absorption fine structure region or EXAFS) of samples were collected at liquid helium temperature in fluorescence mode for the Cu and Zn K-edge at the FAME CRG beamline of the European synchrotron Radiation Facility (ESRF, Grenoble, France). The beam energy was selected using a Si (220) double crystal monochromator with sagital focusing. Fluorescence spectra were collected using a Canberra 30-element Ge detector. We used a combination of principal component analysis (PCA), target transformation (TT), and linear combination fitting (LCF) to fit spectra of organic wastes at Cu and Zn K-edge. The quality of the fit was assessed with the normalized sum-square (NSS) equation. PCA and TT were performed with the SixPack software and LCF were obtained with using Athena software from 2.5 to 10.5 Å. Relevant reference compounds were identified in a large collection of pure Zn or Cu minerals and species.

Incubation experiment and DGT

For incubation experiment, a nitisol was sampled in the 0–25 cm horizon (La Réunion, France). This soil exhibits a fairly low total concentration in a range of trace elements compared to contaminated organic wastes (Table 1). Organic wastes were supplied at a rate equivalent to 80 t ha^{-1} DM and incubated with the soil for 37 days. The moisture content was brought to 70% of the water-holding capacity and was controlled by weighting, and readjusted if necessary, during the experiments. The DGT units were inserted into the soil/waste mixture in triplicate. The study also included a treatment without organic waste (control soil). The DGT devices were progressively retrieved at 6 time points: 12, 24, 53, ~150, ~480 and ~890 hours. The calculated flux of metals from soil to the DGT device (F_{DGT}) provides information on the ability of the solid phase to resupply the soil solution with dissolved metals (for details, see [5]). In addition, soil solution was extracted by centrifugation to measure some physicochemical parameters: pH, trace elements total concentrations and dissolved organic carbon. The mineralization of organic matters in soil/waste mixtures was also deduced from the temporal monitoring of CO_2 release.

Results and discussion

Raw organic wastes and their size fractions were analyzed by XAS spectroscopy. Visual examination of Zn and Cu K-edge XANES spectra provided information on oxidation state of absorbing atom and its surrounding symmetry. For all organic wastes Zn was present in +2 oxidation states in combination of tetrahedral and distorted octahedral geometry. In addition to light neighbors (O/N), a contribution of S atoms in Td configuration was clearly observed. For copper, Cu(II) and Cu(I) were identified surrounded by O/N or S in different samples. We denoted that sulfide Cu and Zn species are present in the same samples. Results from LCF of EXAFS spectra indicated that predominant pools of species were inorganic for Zn (>60%) and organic for Cu (>50%) irrespective to the kind of wastes or its origin (urban *vs* agricultural). Predominant inorganic species for Zn corresponded to fairly adsorbed Zn in Td geometry while minorities are minerals with Zn incorporated

in the structure (phylosilicate, phosphate and silicate). For Cu, predominant species corresponded to metal complexed by organic acid or amino acid, whose proportions differed within the samples without any clear trend corresponding to the kind of waste. Sulfur-bearing species for Zn and Cu were observed in the less mature wastes and Cu(I) was exclusive to these samples. These results showed that Cu and Zn speciation is correlated to the maturity of organic matter (OM).

Furthermore, we compared speciation in raw organic wastes with that in small particles and coarse ones. For all organic wastes, speciation of Cu and Zn are similar in raw waste and coarse fractions. For both elements in some wastes, we observed a difference for fine particles *vs* the rest of waste. These differences in small particles fractions are present for wastes characterized by low maturity of OM compare to others analyzed.

Simultaneously, to assess the impact of organic waste mineralization on trace element speciation, we have monitored the labile fraction by DGT. The flux of Zn accumulated by DGT (F_{DGT}) in the soil and waste mixture was significantly different from soil control for all wastes except MSWC_M. Up to 8 percent of Zn in experiment with FF-MSWC was labile. For Cu fluxes of labile metals in presence of wastes decreased more rapidly with incubation time and were greater than soil control. This would suggest that DGT technique is more efficient to assess metals dynamic in an agricultural soil than chemical extractions.

Moreover, physical-chemical parameters acquired on soil solutions will enable us to achieve quantitative interpretations of DGT measurements in terms of fundamental kinetic and equilibrium resupply parameters. The monitoring of organic matters mineralization in soil/waste mixtures will also enable to link trace metal dynamic with added organic matters.

Conclusion and perspectives

These results showed that Cu and Zn speciation is correlated to the maturity of organic matter and indicated clearly dynamic remobilization of trace elements after organic amendment of contaminated organic wastes with potential uptake by the biota and percolation to groundwater.

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Acknowledgments

This study was part of the ISARD project, funded by ANR (Agence Nationale de la Recherche, France) under Grant ANR-08-STRA-15-01. We thank P. Cambier, M. N'Dienor, T. Rafolisy and L. Thuries who provided us with the samples and considerable advice on sample selection and Gleb Pokrovski and Andreas Voeglin for XAS reference spectra.

Table 1. Trace elements contents in investigated soil and organic wastes (mg kg^{-1} of dry matter).

	Soil	FF-MSWC_M	MSWC_M	FF-MSWC_S	MSWC_S	SS1_S	MC-Pi__F
		Madagascar	Madagascar	Senegal	Senegal	Senegal	France
Cu	34	280±50	48±15	340±30	24±26	340±30	180±20
Zn	170	1 900±600	240±80	2190±400	100±30	1 000±100	700±100

FF-MSWC = fine fraction from municipal solid waste compost; MSWC = municipal solid waste compost; SS = sewage sludge; PSC = pig slurry compost [2].

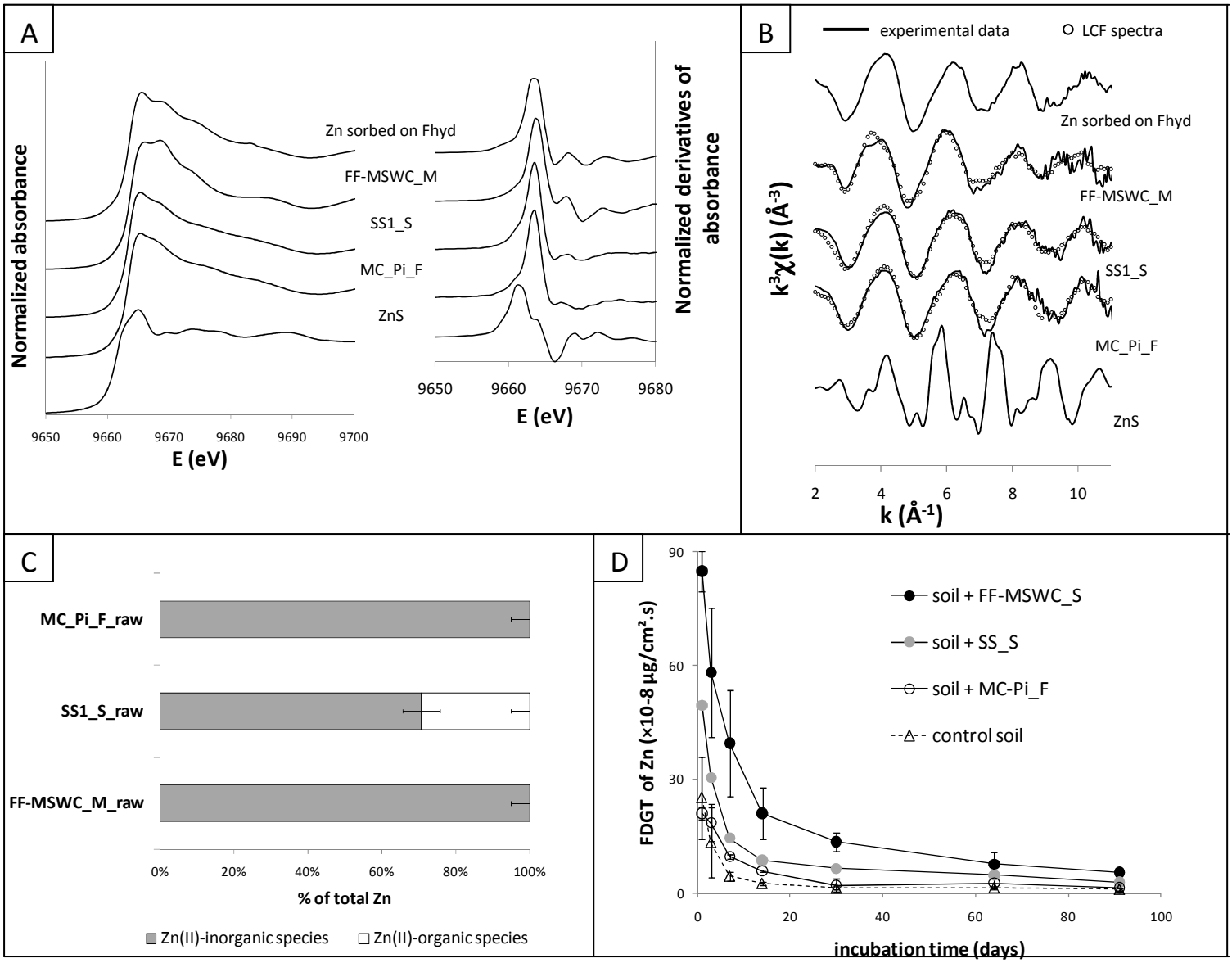

Figure 1. A/ Normalized XANES spectra at Zn K-edge and corresponding first derivatives. B/ EXAFS spectra at Zn K-edge. C/ Proportion of each bearing phase in raw wastes from LCF results of EXAFS spectra. D/ Fluxes of Zn resupply from the solid phase (F_{DGT})