



Zinc speciation in organic waste drives its fate in amended soils

Nounagnon Richard Hodomihou, Frédéric Feder, Samuel Legros, Thiago Augusto, Enzo Lombi, Emmanuel Doelsch

► To cite this version:

Nounagnon Richard Hodomihou, Frédéric Feder, Samuel Legros, Thiago Augusto, Enzo Lombi, et al.. Zinc speciation in organic waste drives its fate in amended soils. Environmental Science and Technology, 2020. cirad-02982765

HAL Id: cirad-02982765

<https://hal.science/cirad-02982765>

Submitted on 28 Oct 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Zinc speciation in organic waste drives its fate in amended soils

Nounagnon Richard Hodomihou^{§#}, Frédéric Feder^{§#}, Samuel Legros^{§#}, Thiago Augusto

Formentini^{‡‡}, Enzo Lombi^α, Emmanuel Doelsch^{†#}*

[§] CIRAD, UPR Recyclage et risque, 18524 Dakar, Senegal

[#]Recyclage et Risque, Univ. Montpellier, CIRAD, Montpellier, France

[‡] Laboratory of Environmental Engineering, Federal University of Santa Maria (UFSM), 97105-900 Santa Maria, RS, Brazil

[‡] Department of Soil and Environment, Swedish University of Agricultural Sciences, SE-75007 Uppsala, Sweden

^α Future Industries Institute, University of South Australia, Adelaide, SA 5095, Australia

[†] CIRAD, UPR Recyclage et risque, F-34398 Montpellier, France

**Corresponding author. Emmanuel Doelsch, doelsch@cirad.fr*

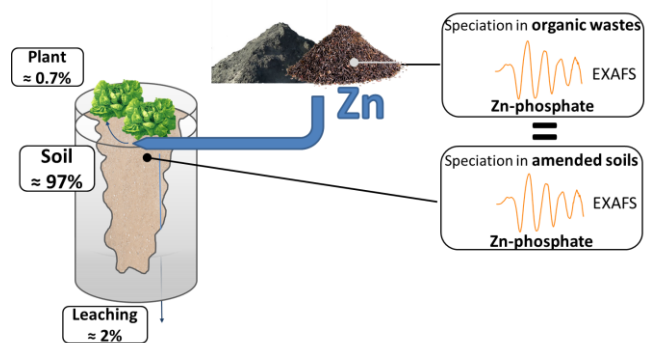
KEYWORDS. Trace element, agriculture, recycling, environmental fate, phosphate, contamination

ABSTRACT.

Recycling of organic waste (OW) as fertilizer on farmland is a widespread practice that fosters sustainable development via resource reuse. However, the advantages of OW fertilization should be weighed against the potentially negative environmental impacts due to the presence of contaminants such as zinc (Zn). Current knowledge on the parameters controlling the environmental fate of Zn following OW application on cultivated soils is scant. We addressed this shortcoming by combining soil column experiments and Zn speciation characterization in OWs and amended soils. Soil column experiments were first carried out using two contrasted soils (sandy soil and sandy clay loam) that were amended with sewage sludge or poultry manure and cropped with lettuce. The soil columns were irrigated with identical amounts of water twice a week and the leachates collected at the column outlet were monitored and analyzed. This scheme (OW application and lettuce crop cycle) was repeated for each treatment. Lettuce yields and Zn uptake were assessed at the end of each cycle. The soil columns were dismantled and seven soil layers were sampled and analysed at the end of the second cycle (total experiment time: 12 weeks). XAS analyses were then conducted to assess Zn speciation in OW and OW-amended soils. The results of this study highlighted that: (i) Zn fate in water–soil–plant compartments was similar, regardless the type of soil and OW, (ii) >97.6% of the Zn input from OW accumulated in the soil surface layer, (iii) Zn uptake by lettuce increased with repeated OW applications, and (iv) no radical change in Zn speciation was observed at the end of the 12-week experiment and phosphate was found to drive Zn speciation in both OW and amended soils (i.e. amorphous Zn-phosphate and Zn sorbed on hydroxylapatite). These results suggest that Zn speciation in OW is a key determinant controlling the environmental fate of this element in OW-amended soils.

39 ABSTRACT ART

40



41

Introduction

The rapid increase in the African population (by 1.3 billion people between 2017 and 2050¹) combined with the high urbanization rate² has led to an urban and periurban agriculture boom.^{3, 4} In developing countries, the market garden farming intensification is being achieved via inputs of biodegradable materials such as sewage sludge, livestock manure, green waste compost, etc., as soil fertilizers. These biodegradable materials, referred to as organic wastes (OWs), can supply a part or all of the nutrients needed for crops.^{4, 5} However, many studies have highlighted negative impacts of agricultural OW recycling as fertilizers due to the presence of contaminants such as trace elements.^{6, 7}

A recent assessment of periurban Dakar (Senegal) agrosystems highlighted trace element contamination of OW-amended cropped soils.⁸ Zinc (Zn) accumulation in soil surface layers has been explained by long-term repeated Zn-rich OW application.⁸ Short-term vegetable crop cycles led to sewage sludge (SS) or poultry manure (PM) application up to 9 times per year over a 24 to 40 year period. The annual Zn input in periurban Dakar agrosystems ranged from 1369 to 5818 g.ha⁻¹year⁻¹, which is alarmingly higher than the 454-539 g.ha⁻¹year⁻¹ range in European countries and China.⁹⁻¹¹ Surprisingly, Zn contamination was similar in the two main periurban Dakar agrosystems (Pikine and Rufisque) despite the fact that the properties of the soils in these two regions differ markedly. One is an Arenosol (sandy soil, dune material) and the other a Fluvisol (sandy clay loam and moderately calcareous soil).¹² However, an analytical approach⁸, involving a comparison of Zn contents in long-term cultivated plots versus adjacent uncultivated plots, did not enable (i) accurate monitoring of the Zn fate following OW spreading in the three water–soil–plant system compartments, (ii) determination of the factors that could explain the similar fate of Zn in contrasted soil types.

X-ray absorption spectroscopy (XAS) is one of the most widely known structural techniques for direct determination of speciation of trace elements present in complex matrices and it has been successfully applied to describe Zn speciation in different OWs¹³⁻¹⁸ or amended soils¹⁹⁻²². Kirpichtchikova et al.²⁰ and Formentini et al.²¹ studied Zn speciation in soils affected by long-term application of sewage water and pig slurry, respectively. In both studies, Zn speciation in soils was dominated by its associations with secondary mineral phases (clay minerals and Fe oxyhydroxides). Zn speciation in OW was assessed by Formentini et al.²¹, revealing that nano-ZnS accounted for 100% of the speciation in the pig slurry. Yamamoto et al.²² recently investigated Zn speciation in pig manure compost and in a soil amended with this compost for 23 years. They showed that oxidized species present in the compost, i.e. Zn-phosphate and Zn bound to OM, had persisted and accumulated in the amended soil. Although these studies agreed on the fact that Zn accumulated in the soil following OW spreading, their results were not consistent with respect to Zn speciation in OWs and in OW-amended soils.

The present study combined soil column experiments and Zn speciation analyses to characterize the fate of Zn in periurban Dakar agrosystems. Soil column experiments were first carried out using two contrasted soils that prevail in these agrosystems (i.e. an Arenosol from Pikine and a Fluvisol from Rufisque). Sewage sludge (SS) or poultry manure (PM) were applied at doses consistent with local agricultural practices and the soil columns were cropped with lettuce (*Lactuca sativa L.*). Laboratory studies were conducted to thoroughly control water and solute fluxes and to obtain an accurate measurement of the mass balance of Zn distribution in the water–soil–plant system. XAS analyses were then used to assess Zn speciation in OW and OW-amended soils from the soil column experiments.¹³⁻²²

88 This combined approach enabled us to: (i) monitor Zn fate in the three compartments of the
89 water–soil–plant system, and (ii) identify parameters controlling the fate of Zn following OW
90 application on contrasted types of soil.

FINAL PROOF

Materials and Methods

Organic waste and soil characteristics

Arenosol (Pikine; sandy soil, dune material) and Fluvisol (Rufisque; sandy clay loam and moderately calcareous soil)¹² were selected for this study as they are the main soils in the periurban Dakar region, under the prevailing Sahelian tropical climatic conditions. The Arenosol texture was dominated by the sand fraction (96.2–97.1%). Silt and clay accounted for 15.3–15.7% and 24.9–28.8% of the Fluvisol content, respectively (Table 1, SI 1). The water holding capacity, total limestone, pH and organic carbon were much lower in the Arenosol than in the Fluvisol. Quartz, critobalite, sanidine and muscovite mainly accounted for the mineralogy of the Arenosol (SI 2). This contrasted with the Fluvisol mineralogy, in which several clay minerals (kaolinite, montmorillonite, palygorskite and kaolinite), calcite and quartz were detected.

Sewage sludge (SS) and poultry manure (PM), are widely used as fertilizers in market gardens in periurban Dakar agrosystems. SS was sampled at the Pikine municipal wastewater treatment plant, and PM was sampled in a henhouse at Rufisque (SI 1). Both SS and PM had been stockpiled for long periods prior to being spread on the soil columns (>3 months) which is consistent with of market gardeners' practices. The ash content of SS (34%) was lower than that for PM (49%), whereas P concentrations were close for SS and PM (17.3 and 16.8 mg.kg⁻¹, respectively). The Zn concentration was higher in SS than in PM (1003 and 320 mg.kg⁻¹, respectively). The Zn concentration in SS was lower than the maximum permissible limits for land application in Europe (2500–4000 mg.kg⁻¹ DM), but higher than the most restrictive threshold values set by national legislation (Sweden: 800 mg.kg⁻¹; Netherlands: 300 mg.kg⁻¹).²³ The Zn concentration in PM was in very close agreement with Zn concentrations inventoried in United States, Canada, different European (Switzerland and Austria) and Asian (China and Japan) countries.²⁴

FINAL PROOF

115

116 Table 1: Soil and organic waste characteristics. Concentrations are expressed on a dry matter (DM)

117 basis. The analytical methods are described in SI 1 and SI 2.

| | | Arenosol | | Fluvisol | | Sewage sludge | Poultry manure |
|---|---------------------|--|--------------------------------------|---|--------------------------------------|--------------------------|---------------------------|
| | | <i>Surface layer (0-20 cm)</i> | <i>Deep layer (20-40 cm)</i> | <i>Surface layer (0-20 cm)</i> | <i>Deep layer (20-40 cm)</i> | | |
| Clay | % | 2.9 | 2.3 | 24.9 | 28.8 | - | - |
| Silt | % | 1.0 | 0.6 | 15.3 | 15.7 | - | - |
| Sand | % | 96.2 | 97.1 | 59.9 | 55.5 | - | - |
| Water-Holding Capacity | % | 20.0 | 16.0 | 36.0 | 40.0 | - | - |
| Total Limestone (CaCO ₃) | % | 6.0 | 2.5 | 24.8 | 23.9 | - | - |
| pH (water) | - | 7.7 | 7.2 | 8.6 | 8.8 | 6.2 | 8.3 |
| pH (KCl) | - | 7.6 | 7.0 | 7.3 | 7.7 | - | - |
| Organic Carbon | % | 0.52 | 0.11 | 1.24 | 0.51 | 35.4 | 26.7 |
| Total Nitrogen | % | 0.05 | 0.009 | 0.11 | 0.034 | 5 | 2.44 |
| C:N Ratio | - | 10.6 | 12.2 | 11.7 | 15 | 7.1 | 10.9 |
| Ash (at 500°C) | % | - | - | - | - | 34.0 | 49.0 |
| Total P | g.Kg ⁻¹ | 0.23 | 0.20 | 0.66 | 0.24 | 16.8 | 17.3 |
| Total Zn | mg.Kg ⁻¹ | 23 ± 2 | 5.1 ± 1.1 | 28.8 ± 1.3 | 20.7 ± 2.9 | 1003 ± 40 | 320 ± 30 |
| Mineralogy | | Quartz, cristobalite, sanidine, muscovite | | Quartz, calcite, montmorillonite, palygorskite, kaolinite | | - | - |

118

119

Soil column experiment

The soil columns consisted of polyethylene cylinders (50 cm h, 33 cm dia.) that were reconstituted to reproduce *in situ* conditions. Two soil layers (0–20 cm and 20–40 cm) were sampled in the Arenosol and Fluvisol. Soils were air dried, decumped and then reconstituted while maintaining the soil bulk densities measured *in situ* (1.65 kg.dm^{-3} for the Arenosol and 1.4 kg.dm^{-3} for the Fluvisol). The weight of Arenosol was $56 \text{ kg.column}^{-1}$ ($47 \text{ kg.column}^{-1}$ for Fluvisol). SS and PM were applied at the surface of the soil columns at 60 T.ha^{-1} ($0.51 \text{ kg.column}^{-1}$). Control soil columns without OW application (0 T.ha^{-1}) were also monitored. Three replicates per treatment (a treatment is defined as a type of soil amended with a type of OW) were performed, representing a total of 18 soil columns.

Lettuces (*Lactuca sativa* L.) were cultivated 1 week after OW application. During the crop cycle (5 weeks), soil columns received 4 L of water twice a week, corresponding to 46.8 mm or 0.3 pore volume (PV) for the Arenosol and 0.25 PV for the Fluvisol. Leached soil solutions were sampled at the bottom of the soil columns weekly and analysed for pH, Zn concentration and dissolved organic carbon (DOC). Lettuce leaves were harvested at the end of the crop cycle. Dry biomass was weighed to determine yields and Zn uptake.

This scheme (OW application and lettuce crop cycle) was repeated for each treatment. At the end of the second cycle (total experiment time: 12 weeks), the soil columns were dismantled and seven soil layers were sampled and analysed.

The experimental procedure is described in further detail in SI 3.

Zinc speciation in organic wastes and soils

X-ray absorption spectroscopy (XAS) was applied to assess the speciation of Zn in OW and the surface layer (0-3 cm) of amended soils (SS-amended Fluvisol, PM-amended Fluvisol and SS-amended Arenosol). Zn K-edge XAS spectra were recorded at the ESRF synchrotron (Grenoble, France) on the BM30B (FAME) beamline. Dried OW and soil samples were cryo-ground (Retsch MM400) and pressed into pellets before analysis. Spectra were measured at liquid helium temperature, to minimise beam-induced damage of the samples, in fluorescence mode with a 30-element solid-state Ge detector. The spectra of each sample were an average of three to seven scans, depending on the Zn concentration and the signal-to-noise ratio. The acquisition of EXAFS spectra for the PM-amended Arenosol was not possible due to the combination of a low Zn concentration and a very high Fe concentration. Each scan was measured on a different spot on the sample pellet to limit beam damage. Energy calibration was performed using metallic Zn reference foil recorded simultaneously with the samples. The absorption edge was defined at 9659 eV, as indicated by the zero crossing of the second derivative of the Zn-foil spectrum. A similar procedure was applied to the previously acquired spectra of Zn reference compounds. Normalization and data reduction were performed according to standard methods²⁵ using Athena software.²⁶ A library of spectra from Zn reference compounds was used to identify Zn species in OW and soil (SI 4). These references have been synthesized or purchased and described in previous published studies: Nano-ZnS and Amorphous Zn-Phosphate¹³; Zn sorbed on Goethite and Zn sorbed on Ferrihydrite²⁷; Zn Cryptomelane²⁸; Zn-Layered Double Hydroxide, Zn sorbed on hydroxy-Al interlayered montmorillonite²⁹; Zn sorbed on Kaolinite³⁰; Zn sorbed on Hydroxylapatite³¹; Zn-Malate, Zn-Histidine, Zn-Cysteine^{27,32}; Zn-Methionine^{15,33}; Zn-Phytate^{15,34}; Zn-Oxalate, Crystalline Zn Phosphate and Sphalerite (reagent grade, Sigma Aldrich). Reference material spectra and sample spectra were measured in the same conditions. Least square

linear combination fitting (LCF, SI 5) was performed for each OW or amended soil spectrum over a k-range of 2.5-10.6 Å⁻¹. The residual factor of each LCF was calculated as follows: $R = \Sigma(k^3\chi(k)_{exp} - k^3\chi(k)_{fit})^2 / \Sigma(k^3\chi(k)_{exp})^2$. At each step of the fitting, an additional reference spectrum was added and retained in the result if the following two conditions were true: (i) the residual factor decreased by 20% or more, and (ii) the additional reference had a contribution equal to or higher than 10% among Zn-species used for the fit. The uncertainty of this LCF method was estimated at ±15%.²⁵

Statistical Analysis

Data are presented as means of three independent soil columns and mean values were taken for statistical analyses using one-way ANOVA. Significant differences were further analysed using the Student–Newman–Keuls test to identify differences between modalities. The differences were considered significant if $p \leq 0.05$.

Results and Discussion

Accumulation of OW-borne Zn in the soil surface layer

The different mass balance terms in the soil column experiments are shown in Table 2. Note that the Zn mass balance ((Initial Zn content in the soil column + Zn input from OW) – (Zn leaching at the soil column outlet + Zn uptake by lettuce)) was not statistically different from the final Zn content in the soil column, indicating that the different mass balance terms had been accurately quantified and no compartments (soil, plant or leaching) were overlooked. Since Zn concentrations in the OWs varied (see Table 1), Zn inputs in the amended soils were different: SS application provided 3.1-fold more Zn than PM (1029 and 328 mg, respectively, for the whole experiment).

For the Fluvisol columns, there was no significant difference between the leached Zn concentration at the outlet when comparing the control and the amended columns, indicating that exogenous Zn (i.e. Zn derived from OW) was not leached from the Fluvisol column. In contrast, Arenosol promoted leaching of a minor fraction of the exogenous Zn. The leached Zn at the outlet of the Arenosol columns represented 0.15% of the Zn input in the SS-amended soil and 1.9% of the Zn input in the PM-amended soil.

For both soils, OW application enhanced Zn uptake by lettuce as compared to the control soil. Total Zn uptake by lettuce (cumulated for the two cycles) was similar regardless of the treatment (soil+OW), ranging from 0.36% (SS-amended Fluvisol) to 0.68% (PM-amended Fluvisol) of the Zn inputs.

Soil column dismantling and analysis at the end of the two crop cycles highlighted the accumulated Zn distribution through the soil profile (Figure 1). In the Fluvisol, exogeneous Zn remained entirely in the 0–3 cm surface layer for both SS- and PM-amended soils. In the Arenosol, exogenous Zn was distributed in the 0–3 cm and 3–6 cm layers for the SS-amended soil and 0–3

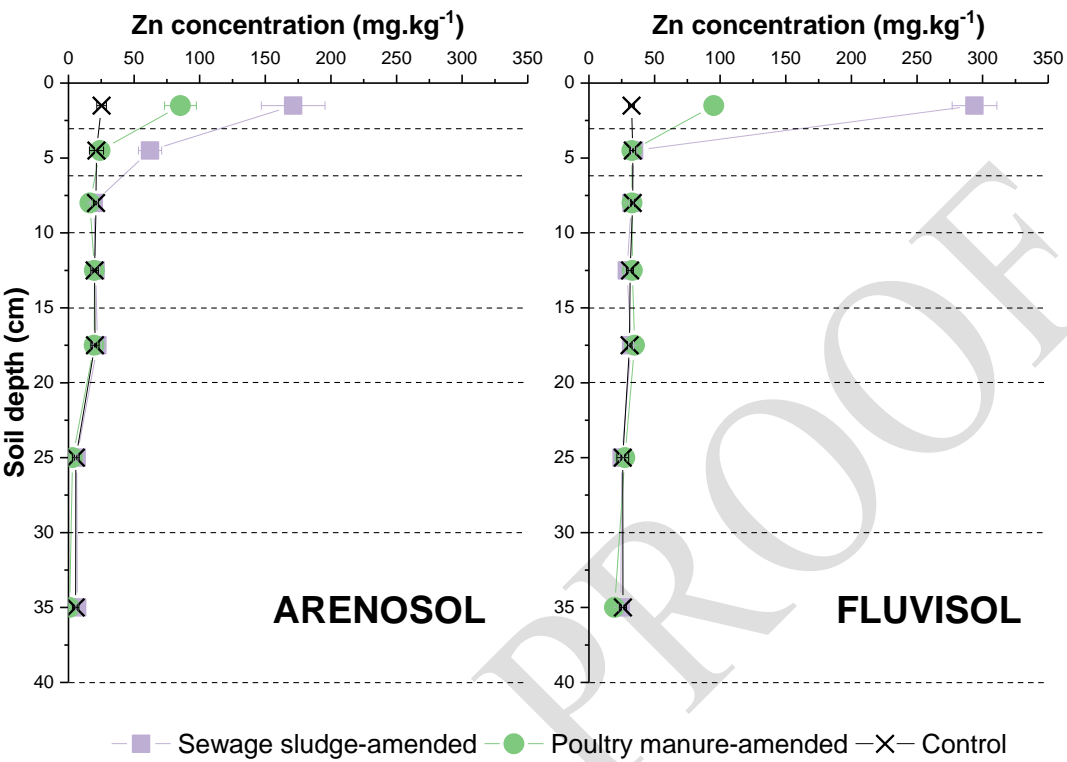
cm for the PM-amended soil. Zn derived from OWs was therefore not transferred through the soil profile to deeper layers.

Overall, 99.6, 99.3 and 99.4% of OW-borne Zn accumulated in the upper soil layers (0–3 and 3–6 cm) for the SS-amended Fluvisol, PM-amended Fluvisol and SS-amended Arenosol, respectively, whereas 97.6% of Zn accumulated in the 0–3 cm soil layer for the PM-amended Arenosol. This exogenous Zn accumulation in the upper soil layers after OW spreading has already been observed. For instance, Formentini et al.⁶ assessed the impact of 11 years of pig slurry spreading in a clayey Hapludox soil. They concluded that most exogenous Zn accumulated within the topsoil layers, with assimilation by crops and leaching virtually negligible in the overall Zn balance.

This study specifically highlighted a soil effect. The Arenosol promoted leaching of a small fraction of Zn in drained water (SI 6) and migration from 0 to 6 cm depth (Figure 1). The sandy texture of the Arenosol associated with its high hydraulic conductivity might have favored particulate or dissolved Zn movement. Conversely, higher clay, carbonate and organic matter contents, basic pH and the higher cation exchange capacity of the Fluvisol might have favored Zn accumulation in the surface layer (Figure 1).

An OW effect was also highlighted. We observed a 1 pH unit time-course decrease in the solution collected at the outlet of the SS-amended Arenosol (SI 6). This decrease in pH is common and attributed to the acidic effect of OW mineralization and the ammonium nitrification process^{27, 35, 36}. It is well established that pH is the major driver of Zn solubility in soils³⁷ and the observed decrease in pH favoured Zn leaching in the SS-amended Arenosol. However, Zn leaching at the outlet of the PM-amended Arenosol column (1.9% of the Zn input) was surprising as the pH of the soil solution was stable and slightly alkaline (pH=7.3-8) throughout the experiment (SI 6).

Nevertheless, Zn leaching was closely correlated with the DOC at the column outlet (SI 7). Complexation with organic ligands could have mobilized a fraction of exogenous Zn. Several studies concluded that colloidal transport can favour trace element transfer in soils following OW spreading. For example, Karathanasis et al.³⁸ studied Cu, Zn and Pb elution in a soil monolith. They demonstrated the elution of significant soluble metal loads in association with water-dispersible biosolid colloids. Similarly, Yamamoto et al.²² studied the fate of P, Zn and Cu in soil affected by a long-term application of swine manure compost. They demonstrated that continual compost application enhanced the formation of a soil water dispersible colloid in which Zn, Cu and P were accumulated.



237 Figure 1: Zn concentration (mg.kg⁻¹) in the Arenosol and Fluvisol soil layers at the end of the soil
238 column experiment. Dashed lines represent the analysed soil layers.

239 Table 2: Mass balances in the soil column experiments. The Zn content is expressed in mg.

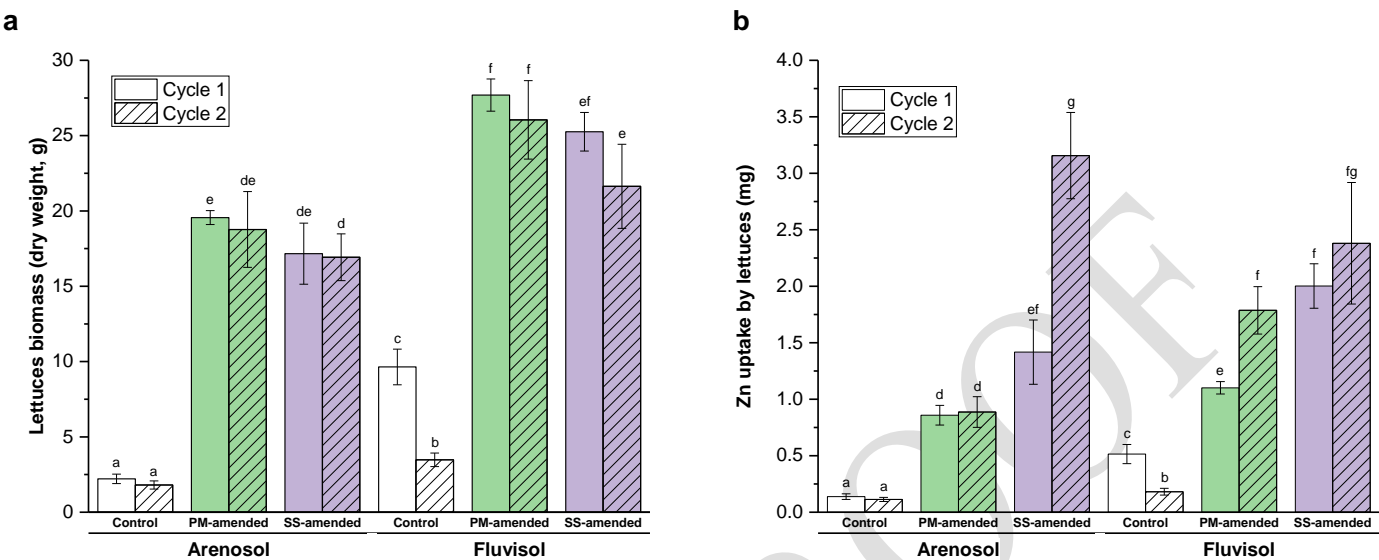
| | Arenosol | | | Fluvisol | | |
|--|--------------------------|----------------------------|----------------------------|--------------------------|----------------------------|----------------------------|
| | Control | SS-amended | PM-amended | Control | SS-amended | PM-amended |
| (1) Initial Zn content in the soil column | 809 ± 67 | 809 ± 67 | 809 ± 67 | 1168 ± 98 | 1168 ± 98 | 1168 ± 98 |
| (2) Zn input from OW ^a | - | 1029 ± 41 | 328 ± 31 | - | 1029 ± 41 | 328 ± 31 |
| (3) Zn leaching at the soil column outlet ^b | 3.7 ± 0.3 | 5.2 ± 0.5 (0.15%±0.08%) | 9.9 ± 0.9 (1.9%±0.56%) | 12.6 ± 2.2 | 9.3 ± 3.5 (0%±0.50%) | 11.9 ± 1.9 (0%±1.02%) |
| (4) Zn uptake by lettuce ^c | 0.2 ± 0.04 | 4.6 ± 0.7 (0.42%±0.09%) | 1.8 ± 0.2 (0.46%±0.12%) | 0.7 ± 0.1 | 4.4 ± 0.7 (0.36%±0.10%) | 2.9 ± 0.3 (0.68%±0.18%) |
| (5) Final Zn content in the soil column ^d | 768 ± 163 | 1618 ± 230 | 912 ± 130 | 1366 ± 133 | 2267 ± 132 | 1567 ± 91 |
| (6) Zn balance: (1) + (2) – ((3) + (4)) | 805 ± 67 ^{NS e} | 1828 ± 110 ^{NS} | 1126 ± 99 ^{NS} | 1154 ± 100 ^{NS} | 2183 ± 143 ^{NS} | 1481 ± 131 ^{NS} |
| 240 ^a Zn input from OW = $Zn_{OW\ C1} + Zn_{OW\ C2}$, where $Zn_{OW\ C1}$ is the Zn input from SS or PM for cycle 1 and $Zn_{OW\ C2}$ is the Zn input | | | | | | |
| 241 from SS or PM for cycle 2. | | | | | | |
| 242 ^b Zn leaching at the soil column outlet = $\sum_{i=1}^n [Zn]_i \times F_i$, where $[Zn]_i$ is the Zn concentration measured in the leachate at week i, | | | | | | |
| 243 and F_i is the water flux measured at the bottom of the column at week i. n is the number of weeks (n = 12). Percentage of OW-derived | | | | | | |
| 244 Zn calculated after normalization by Zn leaching measured for the control soil column. | | | | | | |
| 245 ^c Zn uptake by lettuce = $Zn_{P\ C1} + Zn_{P\ C2}$, where $Zn_{P\ C1}$ is the mass Zn uptake by lettuce for cycle 1, and $Zn_{P\ C1}$ is the mass Zn | | | | | | |
| 246 uptake by lettuce for cycle 2. Percentage of OW-derived Zn derived calculated after normalization by Zn uptake measured for the control | | | | | | |
| 247 soil column. | | | | | | |
| 248 ^d Final Zn content in the soil column = $\sum_{j=1}^m [Zn]_j \times MS_{lj}$, where $[Zn]_j$ is the Zn concentration measured in soil layer j, and MS_{lj} | | | | | | |
| 249 is the mass of soil layer j. m is the number of soil layers (m=7). | | | | | | |
| 250 ^e NS= no significant difference between the final Zn content in the soil column (5) and the Zn balance (6) at the 5% level. | | | | | | |

Zinc uptake by lettuce increases with repeated organic wastes application

For both soils, PM or SS application significantly increased the lettuce biomass in comparison to the unfertilized control soil (Figure 2a). No significant differences in yields were found between the first and second lettuce crop cycle within a same treatment (except for the Fluvisol control, for which a decrease in dry biomass was observed). This highlights the fertilization value of OW, which represents a potential alternative to inorganic fertilizers for crop production.³⁹

Significantly higher Zn uptake by lettuce was measured in the OW-amended soils than in the control soils (Figure 2b). Moreover, we observed a significant increase in Zn uptake by lettuce between the first and second OW application for the SS-amended Arenosol and PM-amended Fluvisol. This was also observed for the other two treatments (PM-amended Arenosol and SS-amended Fluvisol), but these findings were not statistically significant.

If this trend, i.e. constant crop yield combined with increased Zn uptake, were to be confirmed by long-term experiments with repeated OW application and successive crop cycles, OW fertilization could represent an opportunity to improve the Zn content of staple food crops. Such agronomic biofortification⁴⁰ could help tackle Zn deficiency in human populations which is a cause of illness and death in developing countries.⁴¹ The advantages of using OW to increase the plant Zn concentration should, however, be assessed together with the potential uptake of toxic trace elements such as Cd or Pb.



271 Figure 2 (a) Mean harvested lettuce dry biomass per soil column (g) and (b) mean Zn uptake by
272 lettuces per soil column (mg). Different letters represents significant differences between
273 treatments at the 5% level. PM: Poultry manure; SS: Sewage sludge

274

275

276 **Phosphate drives Zn speciation in organic wastes and amended soils**

277 The quantitative LCF results (expressed as a percentage of each Zn species) obtained for both
278 OW and OW-amended soils (0-3 cm soil layer) collected at the end of the experiment are shown
279 in Figure 3. The experimental data were modelled with two Zn references per sample and total
280 contributions ranged from 89 to 111% (SI 5, SI8). Zn species contributions were normalized to
281 100% for easier comparison. The R-factor of the LCFs ranged from 0.029 to 0.063.

282

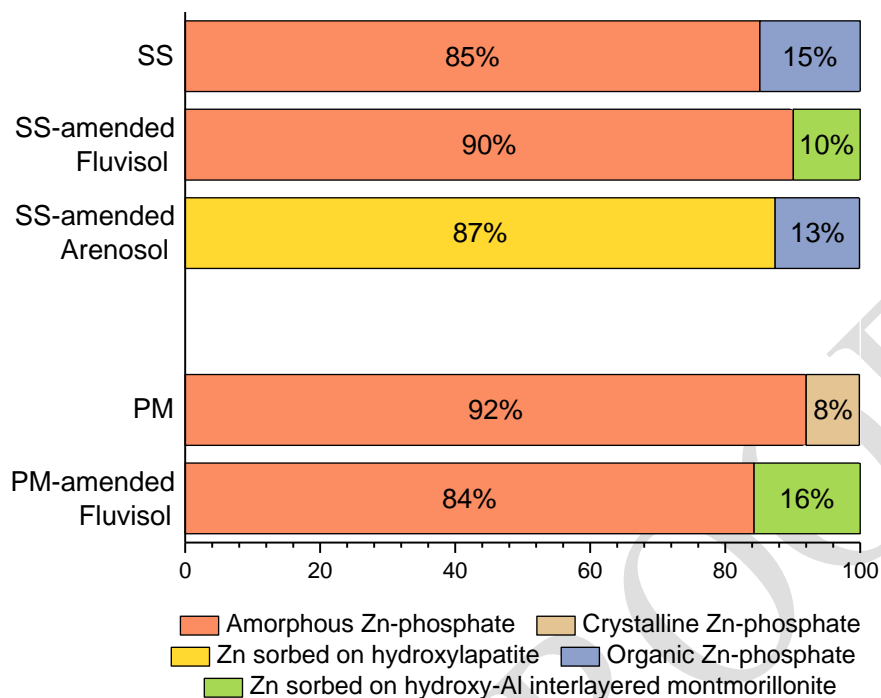


Figure 3: Zn speciation determined from the linear combination fitting of the Zn K-edge extended X-ray absorption fine-structure spectroscopy data (PM = poultry manure, SS = sewage sludge).

Zn speciation in OWs

Zinc phosphate (organic, amorphous or crystalline) accounted for 100% of Zn speciation in SS and PM, which is in agreement with the high affinity of Zn for phosphate compounds.⁴² Amorphous Zn-phosphate was found to be the main Zn species in SS (85%) and PM (92%). The second Zn species was another form of Zn-phosphate: organic Zn-phosphate (15% in SS) or crystalline Zn-phosphate (8% in PM). Hopeite (crystalline Zn-phosphate) has already been documented in previous studies as a major Zn phase in OWs.^{15, 16, 18, 22, 43}

In the present study, the amorphous Zn phosphate reference closely matched the Zn speciation of PM and SS. These findings are in accordance with those of a recent survey of Zn speciation in

a large series of OW sampled in full-scale plants¹³ where it was reported for the first time that the main Zn species in compost or stockpiled OW was amorphous Zn-phosphate (40–100%). In this survey, Le Bars et al.¹³ also demonstrated that nano-sized Zn sulfide (nano-ZnS, with a crystallite size of 3 ± 0.4 nm) was a major Zn species in liquid agricultural OW and SS. This contrasts with our result as zinc phosphate accounted for 100% of Zn speciation in the studied SS. Nevertheless, these discrepancies could be explained by the chemical instability of nano-ZnS which become a minor species after OW composting or stockpiling.^{13, 16} As the SS and PM in the present study had been stockpiled for a long period (>3 months), they were exposed to atmospheric conditions, which favors nano-ZnS oxidative-dissolution and could explain why nano-ZnS were no longer observed and were replaced by Zn-phosphate species.

Zn speciation in amended soils

The best LCFs for both SS-amended and PM-amended Fluvisol were achieved by combining the same references at almost the same proportions. Amorphous Zn-phosphate was the main species, i.e. 84% for PM-amended Fluvisol and 90% for SS-amended Fluvisol. Zn sorbed on hydroxy-Al interlayered montmorillonite (HIM) was the secondary Zn species, i.e. 16% for PM-amended Fluvisol and 10% for SS-amended Fluvisol. The latter mineral reference was supported by the XRD clay mineral findings in the Fluvisol (SI 2). For SS-amended Fluvisol, the Zn speciation pattern was in very close agreement with the Zn distribution in the 0–3 cm soil layer: the proportion of exogenous Zn derived from SS represented 90% of the total soil Zn concentration while the proportion inherited from the pedo-geochemical background represented 10% (Figure 1). This agreement was less satisfactory for PM-amended Fluvisol: Zn speciation was characterized as 84% Amorphous Zn phosphate + 16% Zn sorbed on HIM, whereas the proportion

of exogenous Zn derived from PM represented 66% of the total soil Zn concentration while the proportion of endogenous Zn represented 34% (Figure 1). In this case, the poor quality of the EXAFS spectra (SI 5), as well as the uncertainty of the LCF method ($\pm 15\%$), could explain this discrepancy. The SS-amended Arenosol contained 87% of Zn sorbed on hydroxylapatite and 13% of Zn-phytate, an organic Zn-phosphate already detected in the SS. Zn sorbed on hydroxylapatite was not detected in SS, in which amorphous Zn-phosphate was found to be the main Zn species. However, the featureless shape of the Zn sorbed on the hydroxylapatite EXAFS spectrum suggested that this phase was a Zn-sorption surface complex or a poorly crystalline Zn-phosphate precipitate.³¹ This change of speciation (amorphous Zn-phosphate to Zn sorbed on hydroxylapatite) was not fully understood but could be explained by the acidification of the soil solution (-1 pH unit, SI 6) due to organic matter (OM) mineralization. In brief, no radical change in Zn speciation was observed at the end of the 12-week experiment (two OW applications and two lettuce crop cycles) and phosphate was the main driver of Zn speciation in both OWs and amended soils.

Previous studies and new findings: the benefits of assessing the source speciation to predict the environmental fate

To our knowledge, no previous studies have assessed the fate of OW-borne amorphous Zn-phosphate species in the soil after OW spreading. More importantly, our results differed substantially from those of previous studies using XAS techniques.¹⁹⁻²² Mamindy-Pajany et al.¹⁹ described Zn speciation in a soil mixed with SS and spiked with a Zn nitrate solution. Their results (58% Zn sorbed to Fe oxyhydroxides and 42% Zn bound to OM) highlighted the soil retention mechanism with respect to Zn rather than the fate of exogenous OW-derived Zn. In two studies by Kirpichtchikova et al.²⁰ and Formentini et al.²¹, Zn speciation in soils affected by long-term sewage water and pig slurry application, was dominated by its associations with secondary mineral

phases (clay minerals and Fe oxyhydroxides). Surprisingly, nano-ZnS accounted for 100% of the Zn speciation in the pig slurry²¹, but nano-ZnS was not detected in the amended soil. The authors assumed that the nano-scale of the ZnS favoured oxidation of this species in the soil, in turn releasing Zn that was subsequently retained by the soil matrix. We think that an identical mechanism could explain the Zn speciation in the soil amended by sewage water²⁰, since the conditions in liquid OW are often reducing hence leading to the formation of nano-ZnS¹³, which might have oxidized and dissolved after sewage water spreading.

Yamamoto et al.²² investigated Zn speciation in pig manure compost and in a soil amended with this compost for 23 years. Their results highlighted that oxidized species present in the compost, i.e. Zn-phosphate and Zn bound to OM, had persisted and accumulated in the amended soil. Our results confirmed that Zn present in OW stockpiled for a long period (>3 months) did not undergo a considerable change in speciation after OW application and was mainly accumulated in the soil surface horizon, despite the highly contrasting properties of both studied soils.

After application of fresh OW with a high Zn-sulfide content, the final Zn speciation would be soil dependent as the sulfide would oxidize and release Zn, which in turn would be sorbed/precipitated on the soil matrix.^{13, 21} Conversely, if the OW had been stockpiled/composted with sufficient phosphate present, then OW-borne Zn-phosphate species accumulate and persist in the amended soil.

The results of the present study and the aforementioned studies jointly point towards the same conclusion. Speciation of trace elements in the source, i.e. OW, is the main driver that controls the Zn fate in the soil-plant-water compartments following OW application. Neglecting trace element speciation in the contamination source (OW in this case) hampers gaining further insight into the environmental fate of contaminants in amended soils.

Acknowledgements

This study was part of the "Negative externalities of land cultivation intensification in periurban areas" project funded by West and Central African Council for Agricultural Research and Development (CORAF/WE CARD). The authors wish to thank LMI IESOL for hosting and IMAGO (IRD, Dakar) for laboratory analysis. The authors are grateful to the French Agricultural Research Centre for International Development (CIRAD) for funding the PhD scholarship of Richard Hodomihou. We are grateful to the European Synchrotron Radiation Facility (ESRF) for providing access to the synchrotron radiation facilities. E. Doelsch has received funding from the EU Horizon 2020 Framework Programme for Research and Innovation under the Marie Skłodowska-Curie actions agreement N°795614.



Supporting Information

Soil, plant, leached water and organic waste sampling procedure, analytical methods and experimental design; X-ray diffraction; Zn K-edge EXAFS spectra and radial distribution function of reference compounds; linear combination fitting results; variations in pH, DOC and Zn in the drained water at the soil column outlets; Comparison of EXAFS spectra and radial distribution function of reference compounds.

383 **References**

- 384 1. United Nations, D. o. E. a. S. A., Population Division, *World Population Prospects: The*
385 *2017 Revision*. 2017; Vol. Volume I: Comprehensive Tables (ST/ESA/SER.A/399), p 346.
- 386 2. United Nations, D. o. E. a. S. A., Population Division, *World Urbanization Prospects: The*
387 *2014 Revision*. 2014; Vol. Highlights (ST/ESA/SER.A/352), p 27.
- 388 3. Orsini, F.; Kahane, R.; Nono-Womdim, R.; Gianquinto, G., Urban agriculture in the
389 developing world: a review. *Agronomy for Sustainable Development* **2013**, 33, (4), 695-720.
- 390 4. De Bon, H.; Parrot, L.; Moustier, P., Sustainable urban agriculture in developing countries.
391 A review. *Agronomy for Sustainable Development* **2010**, 30, (1), 21-32.
- 392 5. Diallo, F.; Masse, D.; Diarra, K.; Feder, F., Impact of organic fertilisation on lettuce
393 biomass production according to the cultivation duration in tropical soils. *Acta Agriculturae*
394 *Scandinavica, Section B — Soil & Plant Science* **2020**, 70, (3), 215-223.
- 395 6. Formentini, T.; Mallmann, F.; Pinheiro, A.; Fernandes, C.; Bender, M.; da, V., M; Dos, S.,
396 DR; Doelsch, E., Copper and zinc accumulation and fractionation in a clayey Hapludox soil
397 subject to long-term pig slurry application. *The Science of the total environment* **2015**, 536, 831-
398 839
- 399 7. Legros, S.; Doelsch, E.; Feder, F.; Moussard, G.; Sansoulet, J.; Gaudet, J. P.; Rigaud, S.;
400 Doelsch, I. B.; Saint Macary, H.; Bottero, J. Y., Fate and behaviour of Cu and Zn from pig slurry
401 spreading in a tropical water-soil-plant system. *Agr. Ecosyst. Environ.* **2013**, 164, 70-79.
- 402 8. Hodomihou, N. R.; Feder, F.; Masse, D.; Agbossou, K. E.; Amadji, G. L.; Ndour-Badiane,
403 Y.; Doelsch, E., Diagnosis of periurban Dakar (Senegal) agrosystem contamination by trace
404 elements. *Biotechnol. Agron. Soc.* **2016**, 20, (3), 397-407.
- 405 9. Belon, E.; Boisson, M.; Deportes, I. Z.; Eglin, T. K.; Feix, I.; Bispo, A. O.; Galsomies, L.;
406 Leblond, S.; Guellier, C. R., An inventory of trace elements inputs to French agricultural soils. *Sci.*
407 *Tot. Environ.* **2012**, 439, 87-95.
- 408 10. Nicholson, F. A.; Smith, S. R.; Alloway, B. J.; Carlton-Smith, C.; Chambers, B. J., An
409 inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Tot. Environ.*
410 **2003**, 311, (1-3), 205-219.
- 411 11. Luo, L.; Ma, Y.; Zhang, S.; Wei, D.; Zhu, Y.-G., An inventory of trace element inputs to
412 agricultural soils in China. *J. Environ. Manage.* **2009**, 90, (8), 2524-2530.
- 413 12. Working Group Wrb, I., *World Reference Base for Soil Resources 2014. International Soil*
414 *Classification System for Naming Soils and Creating Legends for Soil Maps*. 2014.
- 415 13. Le Bars, M.; Legros, S.; Levard, C.; Chaurand, P.; Tella, M.; Rovezzi, M.; Browne, P.;
416 Rose, J.; Doelsch, E., Drastic Change in Zinc Speciation during Anaerobic Digestion and
417 Composting: Instability of Nanosized Zinc Sulfide. *Environ. Sci. Technol.* **2018**, 52, (22), 12987-
418 12996.
- 419 14. Legros, S.; Doelsch, E.; Masion, A.; Rose, J.; Borshneck, D.; Proux, O.; Hazemann, J. L.;
420 Saint-Macary, H.; Bottero, J. Y., Combining Size Fractionation, Scanning Electron Microscopy,
421 and X-ray Absorption Spectroscopy to Probe Zinc Speciation in Pig Slurry. *J. Environ. Qual.* **2010**,

- 39, (2), 531-540.
15. Legros, S.; Levard, C.; Marcato-Romain, C.-E.; Guiresse, M.; Doelsch, E., Anaerobic Digestion Alters Copper and Zinc Speciation. *Environ. Sci. Technol.* **2017**, *51*, (18), 10326-10334.
 16. Donner, E.; Howard, D. L.; de Jonge, M. D.; Paterson, D.; Cheah, M. H.; Naidu, R.; Lombi, E., X-ray Absorption and Micro X-ray Fluorescence Spectroscopy Investigation of Copper and Zinc Speciation in Biosolids. *Environ. Sci. Technol.* **2011**, *45*, (17), 7249-7257.
 17. Donner, E.; Ryan, C. G.; Howard, D. L.; Zarcinas, B.; Scheckel, K. G.; McGrath, S. P.; de Jonge, M. D.; Paterson, D.; Naidu, R.; Lombi, E., A multi-technique investigation of copper and zinc distribution, speciation and potential bioavailability in biosolids. *Environ. Pollut.* **2012**, *166*, (0), 57-64.
 18. Lombi, E.; Donner, E.; Tavakkoli, E.; Turney, T. W.; Naidu, R.; Miller, B. W.; Scheckel, K. G., Fate of Zinc Oxide Nanoparticles during Anaerobic Digestion of Wastewater and Post-Treatment Processing of Sewage Sludge. *Environ. Sci. Technol.* **2012**, *46*, (16), 9089-9096.
 19. Mamindy-Pajany, Y.; Sayen, S.; Mosselmans, J. F. W.; Guillon, E., Copper, Nickel and Zinc Speciation in a Biosolid-Amended Soil: pH Adsorption Edge, μ -XRF and μ -XANES Investigations. *Environ. Sci. Technol.* **2014**, *48*, (13), 7237-7244.
 20. Kirpichtchikova, T. A.; Manceau, A.; Spadini, L.; Panfili, F.; Marcus, M. A.; Jacquet, T., Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. *Geochim. Cosmochim. Acta* **2006**, *70*, (9), 2163-2190.
 21. 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. *Environ. Pollut.* **2017**, *222*, 495-503.
 22. Yamamoto, K.; Hashimoto, Y.; Kang, J.; Kobayashi, K., Speciation of Phosphorus Zinc and Copper in Soil and Water-Dispersible Colloid Affected by a Long-Term Application of Swine Manure Compost. *Environ. Sci. Technol.* **2018**, *52*, (22), 13270-13278.
 23. Inglezakis, V. J.; Zorpas, A. A.; Karagiannidis, A.; Samaras, P.; Voukkali, I.; Sklari, S., EUROPEAN UNION LEGISLATION ON SEWAGE SLUDGE MANAGEMENT. *Fresenius Environmental Bulletin* **2014**, *23*, (2A), 635-639.
 24. Romeo, A.; Vacchina, V.; Legros, S.; Doelsch, E., Zinc fate in animal husbandry systems. *Metallomics* **2014**, *11*, (6), 1999-2009.
 25. Doelsch, E.; Basile-Doelsch, I.; Rose, J.; Masion, A.; Borschneck, D.; Hazemann, J. L.; SaintMacary, H.; Bottero, J. Y., New Combination of EXAFS Spectroscopy and Density Fractionation for the Speciation of Chromium within an Andosol. *Environ. Sci. Technol.* **2006**, *40*, (24), 7602-7608.
 26. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **2005**, *12*, (4), 537-541.
 27. Tella, M.; Bravin, M. N.; Thuriès, L.; Cazevielle, P.; Chevassus-Rosset, C.; Collin, B.; Chaurand, P.; Legros, S.; Doelsch, E., Increased zinc and copper availability in organic waste amended soil potentially involving distinct release mechanisms. *Environ. Pollut.* **2016**, *212*, 299-306.

- 463 28. Hammer, D.; Keller, C.; McLaughlin, M. J.; Hamon, R. E., Fixation of metals in soil
464 constituents and potential remobilization by hyperaccumulating and non-hyperaccumulating
465 plants: Results from an isotopic dilution study. *Environ. Pollut.* **2006**, *143*, (3), 407-415.
- 466 29. Jacquat, O.; Voegelin, A.; Villard, A.; Marcus, M. A.; Kretzschmar, R., Formation of Zn-
467 rich phyllosilicate, Zn-layered double hydroxide and hydrozincite in contaminated calcareous
468 soils. *Geochim. Cosmochim. Acta* **2008**, *72*, (20), 5037-5054.
- 469 30. Jacquat, O.; Voegelin, A.; Kretzschmar, R., Local coordination of Zn in hydroxy-
470 interlayered minerals and implications for Zn retention in soils. *Geochim. Cosmochim. Acta* **2009**,
471 *73*, (2), 348-363.
- 472 31. Panfili, F.; Manceau, A.; Sarret, G.; Spadini, L.; Kirpichtchikova, T.; Bert, V.; Laboudigue,
473 A.; Marcus, M. A.; Ahamdach, N.; Libert, M.-F., The effect of phytostabilization on Zn speciation
474 in a dredged contaminated sediment using scanning electron microscopy, X-ray fluorescence,
475 EXAFS spectroscopy, and principal components analysis. *Geochim. Cosmochim. Acta* **2005**, *69*,
476 (9), 2265-2284.
- 477 32. Kelly, R. A.; Andrews, J. C.; DeWitt, J. G., An X-ray absorption spectroscopic
478 investigation of the nature of the zinc complex accumulated in *Datura innoxia* plant tissue culture.
479 *Microchem. J.* **2002**, *71*, (2-3), 231-245.
- 480 33. González, J. C.; Peariso, K.; Penner-Hahn, J. E.; Matthews, R. G., Cobalamin-Independent
481 Methionine Synthase from *Escherichia coli*: A Zinc Metalloenzyme. *Biochemistry* **1996**, *35*, (38),
482 12228-12234.
- 483 34. Sarret, G.; Saumitou-Laprade, P.; Bert, V.; Proux, O.; Hazemann, J. L.; Traverse, A. S.;
484 Marcus, M. A.; Manceau, A., Forms of zinc accumulated in the hyperaccumulator *Arabidopsis*
485 *halleri*. *Plant Physiol.* **2002**, *130*, (4), 1815-1826.
- 486 35. Doelsch, E.; Masion, A.; Moussard, G.; Chevassus-Rosset, C.; Wojciechowicz, O., Impact
487 of pig slurry and green waste compost application on heavy metal exchangeable fractions in
488 tropical soils. *Geoderma*. **2010**, *155*, (3-4), 390-400.
- 489 36. Feder, F.; Bochu, V.; Findeling, A.; Doelsch, E., Repeated pig manure applications modify
490 nitrate and chloride competition and fluxes in a Nitisol. *Sci. Tot. Environ.* **2015**, *511*, 238-248.
- 491 37. McBride, M.; Sauve, S.; Hendershot, W., Solubility control of Cu, Zn, Cd and Pb in
492 contaminated soils. *Eur. J. Soil Sci.* **1997**, *48*, (2), 337-346.
- 493 38. Karathanasis, A. D.; Johnson, D. M. C.; Matocha, C. J., Biosolid Colloid-Mediated
494 Transport of Copper, Zinc, and Lead in Waste-Amended Soils. *J. Environ. Qual.* **2005**, *34*, (4),
495 1153-1164.
- 496 39. Hernández, T.; Chocano, C.; Moreno, J.-L.; García, C., Use of compost as an alternative
497 to conventional inorganic fertilizers in intensive lettuce (*Lactuca sativa* L.) crops—Effects on soil
498 and plant. *Soil and Tillage Research* **2016**, *160*, 14-22.
- 499 40. McGrath, S. P.; Chambers, B. J.; Taylor, M. J.; Carlton-Smith, C. H., Biofortification of
500 zinc in wheat grain by the application of sewage sludge. *Plant Soil.* **2012**, *361*, (1), 97-108.
- 501 41. Black, R. E., Zinc Deficiency, Infectious Disease and Mortality in the Developing World.
502 *The Journal of Nutrition* **2003**, *133*, (5), 1485S-1489S.

503 42. B., B.; Wedepohl, K. H., Zinc. In *Handbook of Geochemistry*, Wedepohl, K. H., Ed.
504 Springer-Verlag: Berlin, 1978; Vol. II/3.

505 43. Yamamoto, K.; Hashimoto, Y., Chemical Species of Phosphorus and Zinc in Water-
506 Dispersible Colloids from Swine Manure Compost. *J. Environ. Qual.* **2017**, 46, (2), 461-465.

507

508

FINAL PROOF

Supporting Information

Zinc speciation in organic waste drives its fate in amended soils

Nounagnon Richard Hodomihou^{§#}, Frédéric Feder^{§#}, Samuel Legros^{§#}, Thiago Augusto

Formentini^{‡‡}, Enzo Lombi^α, Emmanuel Doelsch^{†#}*

[§] CIRAD, UPR Recyclage et risque, 18524 Dakar, Senegal

[#]Recyclage et Risque, Univ. Montpellier, CIRAD, Montpellier, France

[‡] Laboratory of Environmental Engineering, Federal University of Santa Maria (UFSM), 97105-900 Santa Maria, RS, Brazil

[‡] Department of Soil and Environment, Swedish University of Agricultural Sciences, SE-75007

Uppsala, Sweden^α Future Industries Institute, University of South Australia, Adelaide, SA 5095, Australia

[†] CIRAD, UPR Recyclage et risque, F-34398 Montpellier, France

524

525 *Corresponding author. Emmanuel Doelsch, doelsch@cirad.fr

526

527 number of pages 15

528 number of figures 6

529 number of tables 1

FINAL PROOF

SI 1 Soil, plant, leached water and organic waste sampling procedure and analytical methods

Soils

Soils were sampled in the 0-20 and 20-40 cm layers from two sites located in suburban agricultural areas (Pikine and Rufisque market gardening areas located on an Arenosol and a Fluvisol, respectively) of Dakar (Senegal). Only steel or plastic tools were used for sampling in order to avoid trace element contamination of soils. After air-drying and declumping the aggregates, soils samples were sieved through a 2 mm mesh sieve.

After organic matter (OM) dissolution and carbonate removal, soil particle size analyses (sand, silt and clay) were conducted using the combined pipette sieving and sedimentation method (NF X 31-107). The total limestone or carbonate content in soil was estimated by the volumetric method (ISO 10693). Total nitrogen (ISO 13878) and total carbon (ISO 10694) were determined by dry combustion with an elemental NC 2100 Soil Analyzer (Thermo Electron Corp.), and organic carbon was determined according to the difference with mineral carbon as calculated from the carbonate content (ISO 10694). Soil and OW pH were determined according to the potentiometric method in the supernatant of the soil–water and OW-water suspension with 1:2 and 1:5 ratios, respectively (ISO 10390). For total P and Zn analyses, sieved soil sub-samples were ground to 100 µm particle size in zirconium material before dissolution. After 2 h calcination at 500°C, total dissolution was performed by acid digestion using a mixture of hydrofluoric (HF), nitric (HNO₃) and perchloric (HClO₄) acids (ISO 14869-1). Total P and Zn concentrations were then determined using inductively coupled plasma mass spectrometry (ICP-MS). Furthermore, two reference standard certified soil samples, i.e. CRM 7001 (light sandy soil) and CRM 7004 (loam), were used to assess the accuracy of the results according to the ISO 9001 certification of the laboratory. The variation coefficient for both of these checks must be less than 5%.

At the end of the second cycle, the soil columns were dismantled and seven soil layers were sampled as follows: 0-3, 3-6, 6-10, 10-15, 15-20, 20-30 and 30-40 cm. Soils were air-dried, sieved through a 2 mm mesh sieve, and ground to 100 μm using a planetary grinder made of zirconium oxide to avoid trace element contamination. Zn contents were determined by ICP-MS after 2 h calcination of the soil samples at 500°C, followed by total dissolution using a mixture of hydrofluoric (HF), nitric acid (HNO_3) and perchloric acid (HClO_4) (ISO 14869-1). Furthermore, two reference standard certified soil samples: CRM 7001 (light sandy soil) and CRM 7004 (loam) were used to assess the accuracy of the results according to the ISO 9001 certification of the laboratory. Deviations from the certified values of these controls were less than 5%.

Leached water

pH, dissolved organic carbon (DOC) and Zn were analysed in the leached water. For this purpose, weekly leachate samples collected at 40 cm depth (i.e. at the bottom of the soil columns) were filtered using grade GF/D Whatman microfiber filter paper (pore size 2.7 μm) and subdivided in three subsamples. pH was determined in the first leachate subsamples immediately after sampling. The second leachate subsamples were conditioned and acidified with 2.5% ultrapure nitric acid (v/v) in 10 mL scintillation flasks (previously washed with a 10% nitric acid bath and rinsed with ultrapure water), and stored at 4°C. The Zn concentration in acidified leachate subsamples was determined using ICP-MS. The third leachate subsamples conditioned in 20 mL brown amber glass bottles (prewashed in a 10% NaOH bath and rinsed with ultrapure water), were treated with 0.1% sodium azide (NaN_3) and stored at 4°C until use. DOC in azide-treated leachate subsamples was determined using a Total Organic Carbon (TOC) Analyzer (Shimadzu, TOC-L) in NPOC mode. Samples were bubbled for 90 s with 1.5% HCl to eliminate carbonates before

oven injection (680°C). The DOC measurement quality was checked with the certified reference sample MISSIPPI-03 and the variation coefficient was less than 10%.

Plants

Freshly harvested leaves of mature lettuce plant samples were rinsed several times with distilled water, cut into small pieces, and oven-dried at 60°C to constant mass. Then these samples were ground into powder separately through a grinder made of zirconium oxide (bowls and balls) in order to avoid trace element contamination. Total digestion of ground lettuce samples consisted of introducing 1 g of each ground lettuce sample into a platinum crucible which was subsequently placed in a muffle furnace for 2 h calcination at 500°C. After cooling, the ash was moistened with a few drops of ultrapure water, and 2 mL of 6N HCl was added. Dry evaporation was then carried out on a warming plate. Hydrofluoric acid was added to the ash residue and then evaporated again on a warming plate. The silica contained in the ash thus volatilized as SiF₆. The ash residue was taken up in 2 mL of 6N HCl and filtered through Whatman No.42 filter paper into a 50 mL vial. The filter containing the residue was placed in the same crucible and then calcined at 500°C. Finally, the crucible was rinsed with 1 mL of 6N HCl, and then with ultrapure water (18.2 MΩ.cm) from a Millipore Milli-Q system, and transferred to the same vial. The vial was gauged and then homogenized by manual stirring. Furthermore, three strawberry plant samples (*Fragaria vesca*) with internal references were also analyzed for verification and validation of the results. Deviations from the certified values of these controls were always less than 5%. All reagents used were Merck analytical grade (AR). The Zn concentration in digestates was determined by inductively coupled plasma mass spectrometry (ICP-MS, Varian Ultramass).

596 *Organic wastes*

597 Sewage sludge (SS) was sampled at the Pikine municipal wastewater treatment plant. This
598 lagoon-type plant is run on the basis of biological processes with free culture in basins and
599 produces 1905 t of activated sludge per year. SS are sun dried in a refining tank.

600 Poultry manure (PM) from laying hens was sampled in a henhouse at Rufisque. The manure is
601 mixed with litter (sawdust or rice husking waste) used as a henhouse substrate.

602 Both SS and PM had been stockpiled for long periods prior to being spread on the soil columns
603 (>3 months), which is consistent with market gardeners' practices.

604 Organic waste was dried at 40°C then ground with a grinder made of zirconium oxide (bowls
605 and balls) in order to avoid trace element contamination, and then ground and sieved through a 1
606 mm mesh sieve. The characteristics of these OW soils were obtained using standard soil analysis
607 methods.

608

609

SI 2 X-ray diffraction

X-ray diffractograms of the soils were obtained with a Philips PW 3710 X-ray diffractometer using CoK α radiation at 40 kV and 40 mA (a counting time of 12 s per 0.02° step was used for the 2 h range 5–75°)

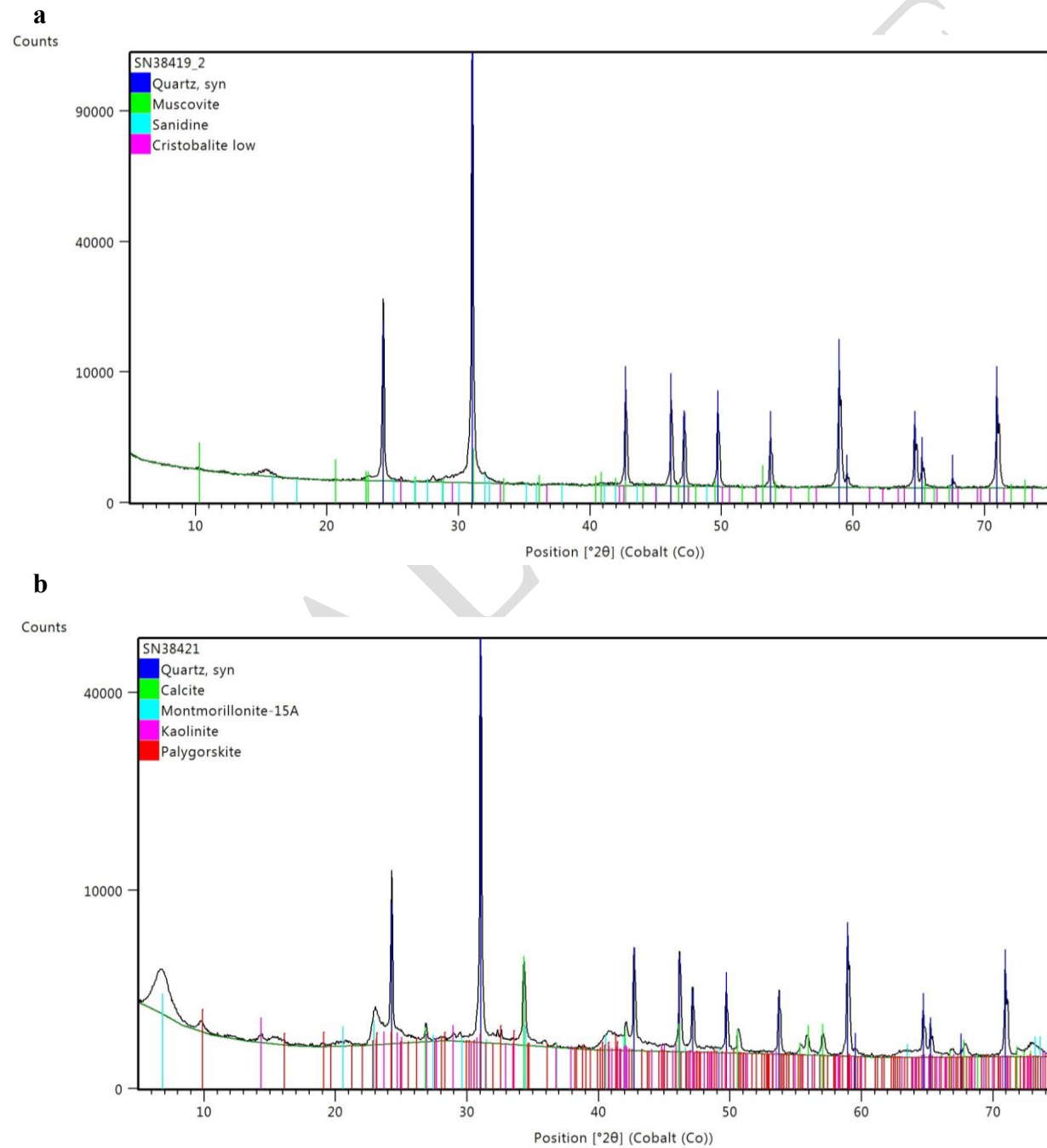


Figure SI-2: X-ray diffractograms for (a) Arenosol and (b) Fluvisol

SI 3 Experimental design

The soil columns were composed of cylindrical polyethylene columns (50 cm h; 33 cm dia.). The bottom of each column was covered by a nylon membrane (Nitex, 50 μm mesh) to prevent any soil particle release. The bottom was perforated with five holes (1 cm dia.) to collect the drained water. At the outlet, each column is equipped with a funnel and a polyethylene bottle to collect the leachate. Two soil layers (0-20 and 20-40 cm) were sampled for the Arenosol and the Fluvisol. Soils were air dried, decumped and then assembled while maintaining the soil bulk densities measured *in situ* (2.65 kg.dm⁻³).



Figure SI 3: Soil column

Sewage sludge (SS) and poultry manure (PM) were applied at 60 t DM/ha (60 T.ha⁻¹). Control soil columns without OW application (0 T.ha⁻¹) were also included. Predried OWs were uniformly spread on the soil surface and immediately incorporated into the surface soil layer (0–2 cm) by hand before sowing. About 25 lettuce (*Lactuca sativa* L., Eden variety) seeds were sown in the soil column subsurface and covered with a thin soil layer (about 2 mm depth). After germination,

at the 3 to 4 leaf stage, the seedlings were thinned in order to leave a dozen vigorous lettuce plants per column. Lettuces (*Lactuca sativa* L.) were cultivated 1 week after OW application. Each lettuce crop cycle lasted 5 weeks.

The pore volume (PV) of each soil column was calculated using the equation reported by Feder et al. (2015)³⁶:

[Pore volume] = Porosity × Volume of the soil column.

with Porosity = $1 - \frac{AD}{RD}$

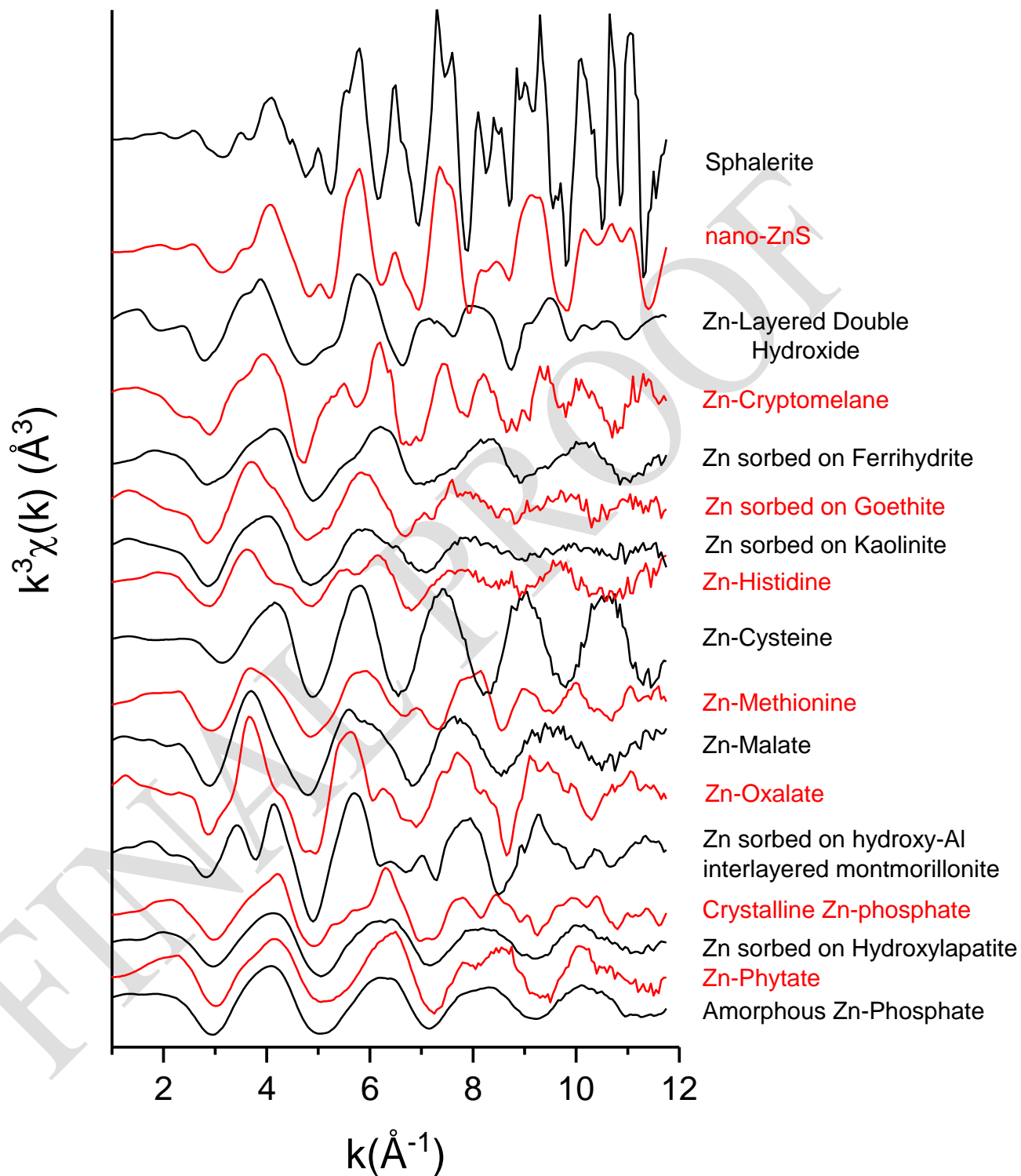
where AD (kg.dm⁻³) corresponds to the apparent density or bulk density measured for each soil *in situ*, and RD corresponds to the real particle density (expressed in kg.dm⁻³) estimated at 2.65 kg .dm⁻³ for both soils.

Each column received 8 L of water weekly, corresponding to 0.6 PV for the Arenosol columns and 0.5 PV for the Fluvisol columns. Water (4 L) was applied on fixed days (Monday and Thursday). 24 h after each water supply, the leachates drained and collected at the column outlets were sampled. On a weekly basis, the two leachate samples from the same soil column were combined and stored before analysis.

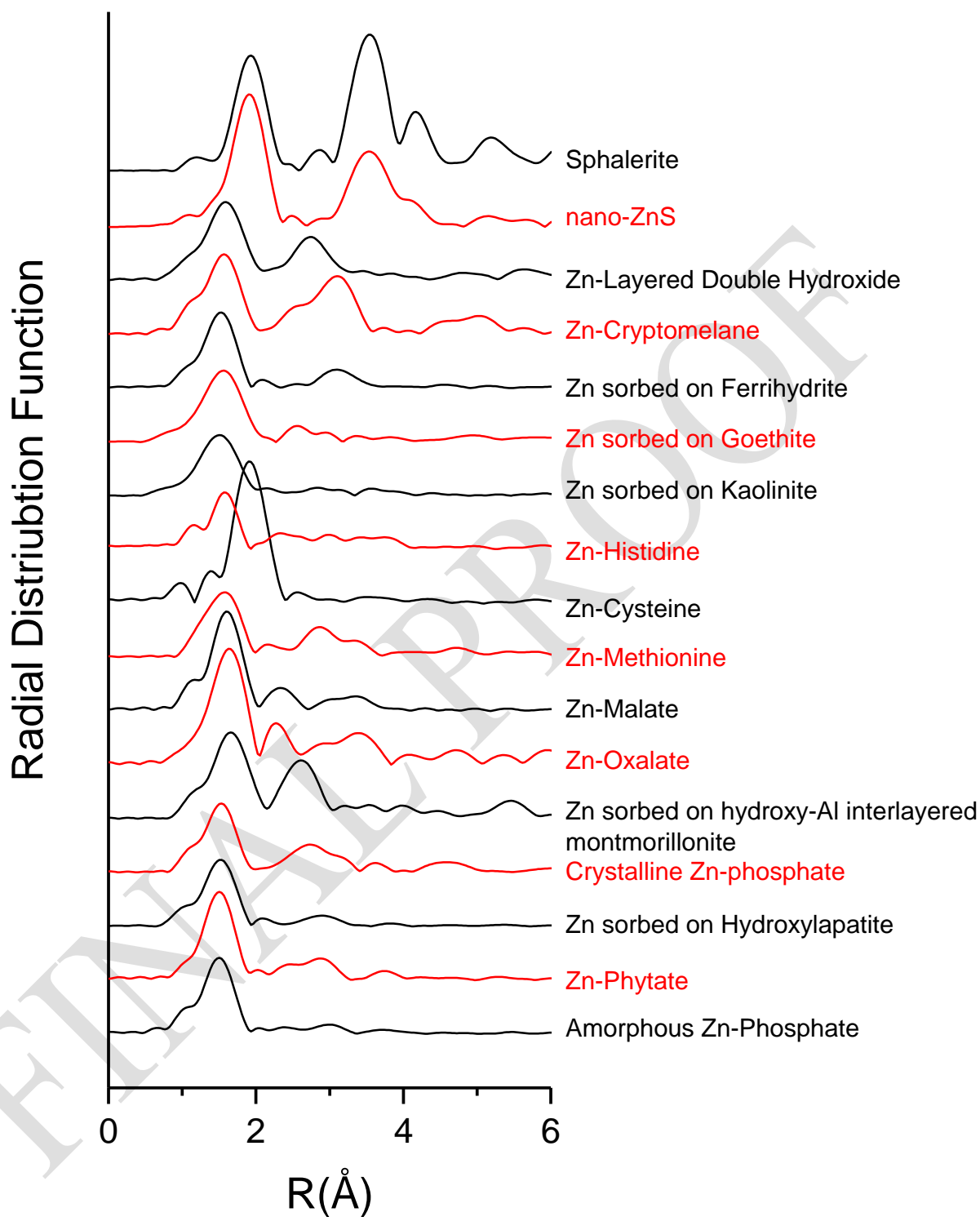
At the end of the lettuce crop cycle, only the above-ground parts (leaves) of the plants were harvested. The plants were cut, then washed three times successively with tap water, and rinsed twice with distilled and ultra-pure water. The lettuces were dried in an oven at 60°C to constant weight and the dry biomass was weighed to determine the lettuce yields.

After the first lettuce harvest, the whole experiment (OW application, lettuce crop, water irrigation and sampling) was repeated a second time.

Three replicates were performed for each treatment (a treatment is defined as a soil and an OW) representing a total of 18 soil columns.

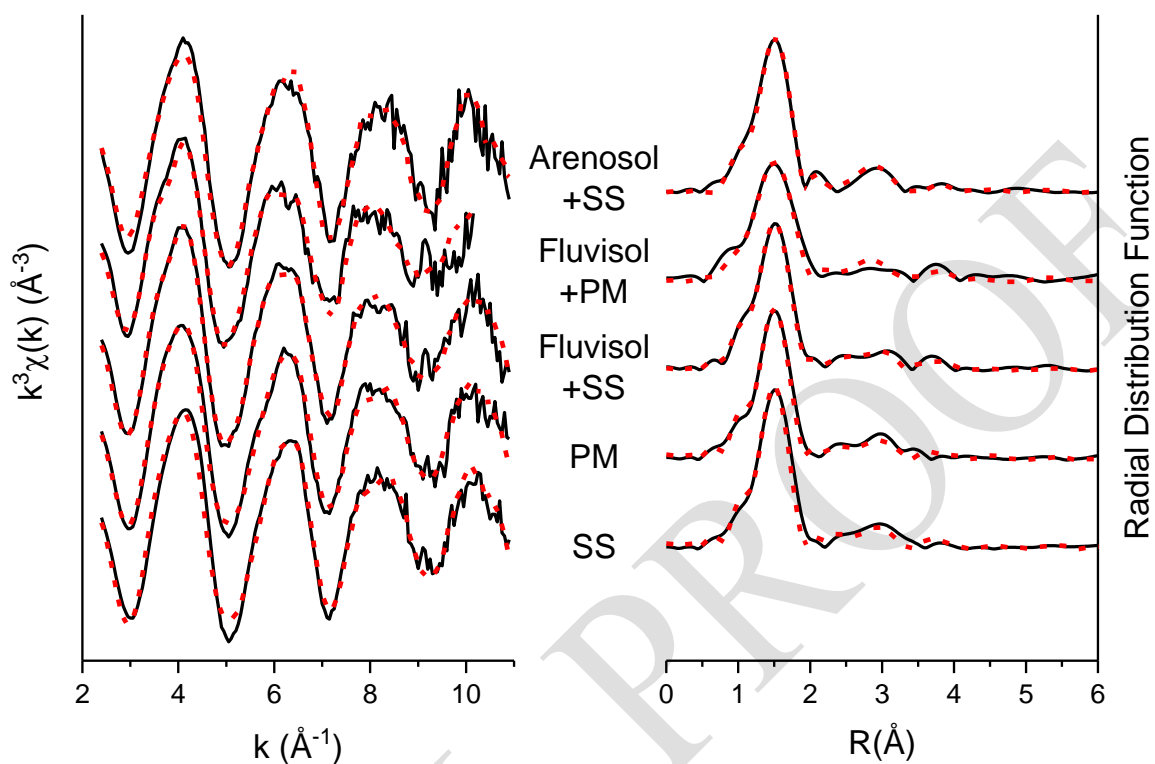


656
 657 Figure SI 4a: Zn K-edge extended X-ray absorption fine-structure spectroscopy spectra of all
 658 reference compounds.



659

660 Figure SI 4b: Radial distribution function (window Kaiser-Bessel, $dk=2$) of all reference
 661 compounds.



663
664 Figure SI 5: Experimental (black) and modeled (dotted, red) Zn K-edge extended X-ray absorption
665 fine-structure spectroscopy spectra and radial distribution function (window Kaiser-Bessel, $dk=2$)
666 for each sample of OW and soil + OW. SS= sewage sludge, PM=poultry manure

668 Table SI 5: Detailed linear combination fitting results. SS = sewage sludge, PM = poultry manure

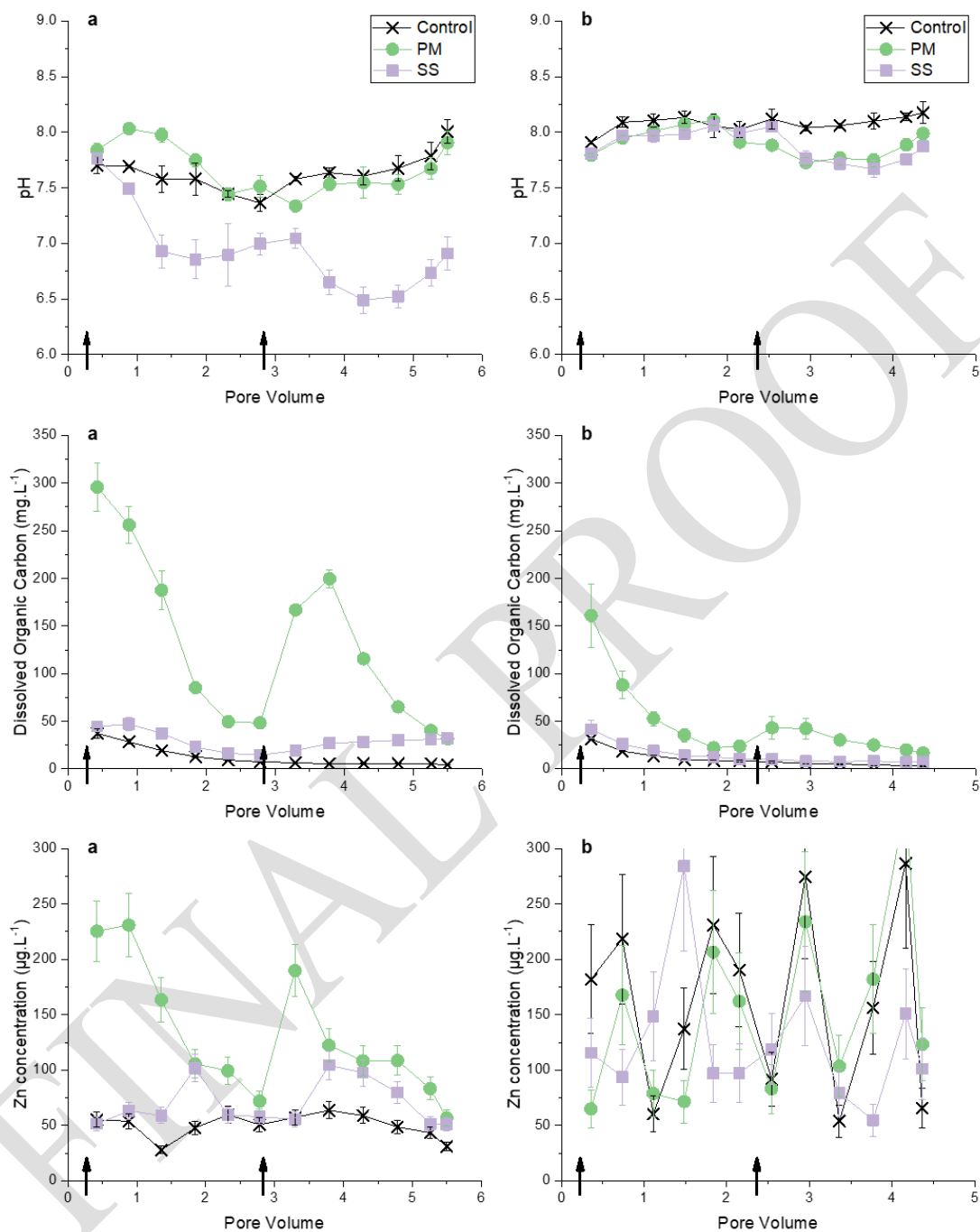
| | Amorphous Zn- phosphate | Zn- phytate | Cristalline Zn- phosphate | Zn sorbed on hydroxylapatite | Zn sorbed on hydroxy-Al interlayered montmorillonite | R- factor* |
|------------------|-------------------------------|----------------|---------------------------------|---------------------------------|---|---------------|
| Arenosol + SS | | 14% | | 97% | | 0.050 |
| Fluvisol + PM | 75% | | | | 14% | 0.063 |
| Fluvisol + SS | 91% | | | | 10% | 0.029 |
| PM | 96 % | | 10% | | | 0.030 |
| SS | 86 % | 15 % | | | | 0.037 |

669 *R-factor = $\Sigma(k^3\chi(k)_{exp} - k^3\chi(k)_{fit})^2 / \Sigma(k^3\chi(k)_{exp})^2$

670

671

672 **SI 6 variations in pH, DOC and Zn in the drained water at the soil column outlets.**



673

674 Figure SI 6: Variations in pH, DOC and Zn concentrations in drained water at the outlet of the (a)

675 Arenosol columns and (b) Fluvisol columns. Arrows represent the OW applications. PM: Poultry

676 manure; SS: Sewage sludge

SI 7 Zn concentration as a function of the dissolved organic carbon concentration in drained water at the soil column outlets.

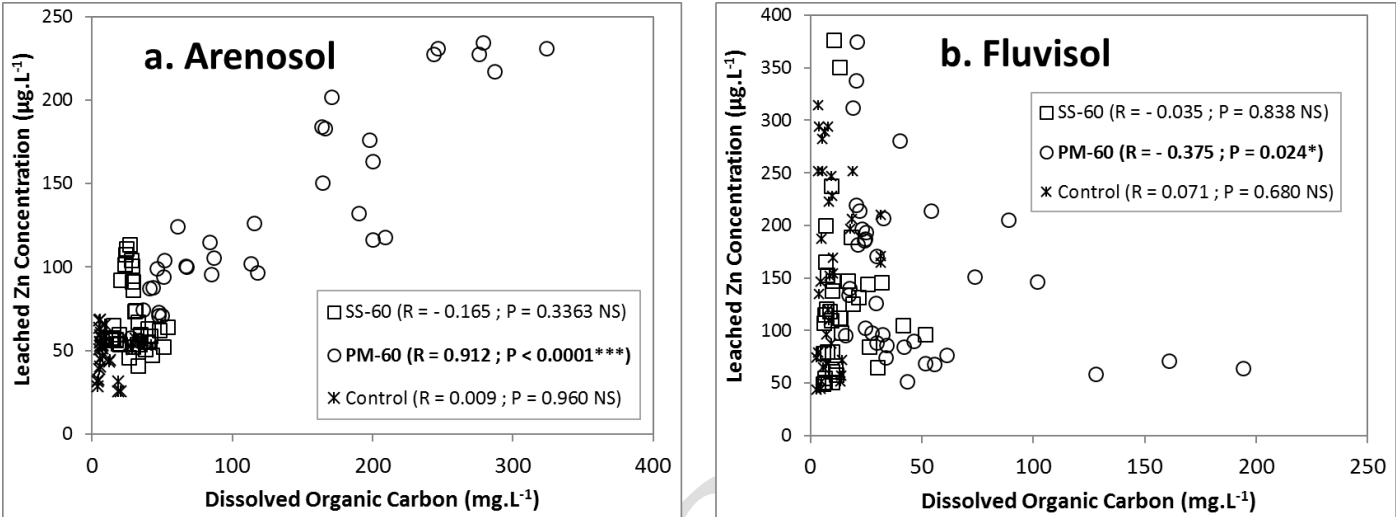


Figure SI 7: Zn concentration as a function of dissolved organic carbon in drained water at the column outlets of the Arenosol (a) and Fluvisol (b). R corresponds to the Pearson linear correlation coefficient; NS = not significant; Significance level: * = $p < 0.05$, and *** = $p < 0.0001$.

SI 8 X-ray absorption spectroscopy – comparison of reference compounds.

The EXAFS spectra of Zn sorbed on hydroxyapatite, amorphous Zn phosphate and Zn sorbed on Ferrihydrite look very similar, although some minor features can be observed. But, these distinct features are much easier to detect on the radial distribution function. The radial distribution function obtained from Fourier transforming the reduced EXAFS data consists of different peaks resulting from Zn-backscatter interactions. The peaks between 2 and 4 Å indicate the presence of atoms in the next-nearest shells around Zn. For amorphous Zn phosphate, Zn sorbed on hydroxylapatite and Zn sorbed on Ferrihydrite, the radial distances of these peaks are different (see arrows), thus indicating a modification of the local Zn environment for these three references.

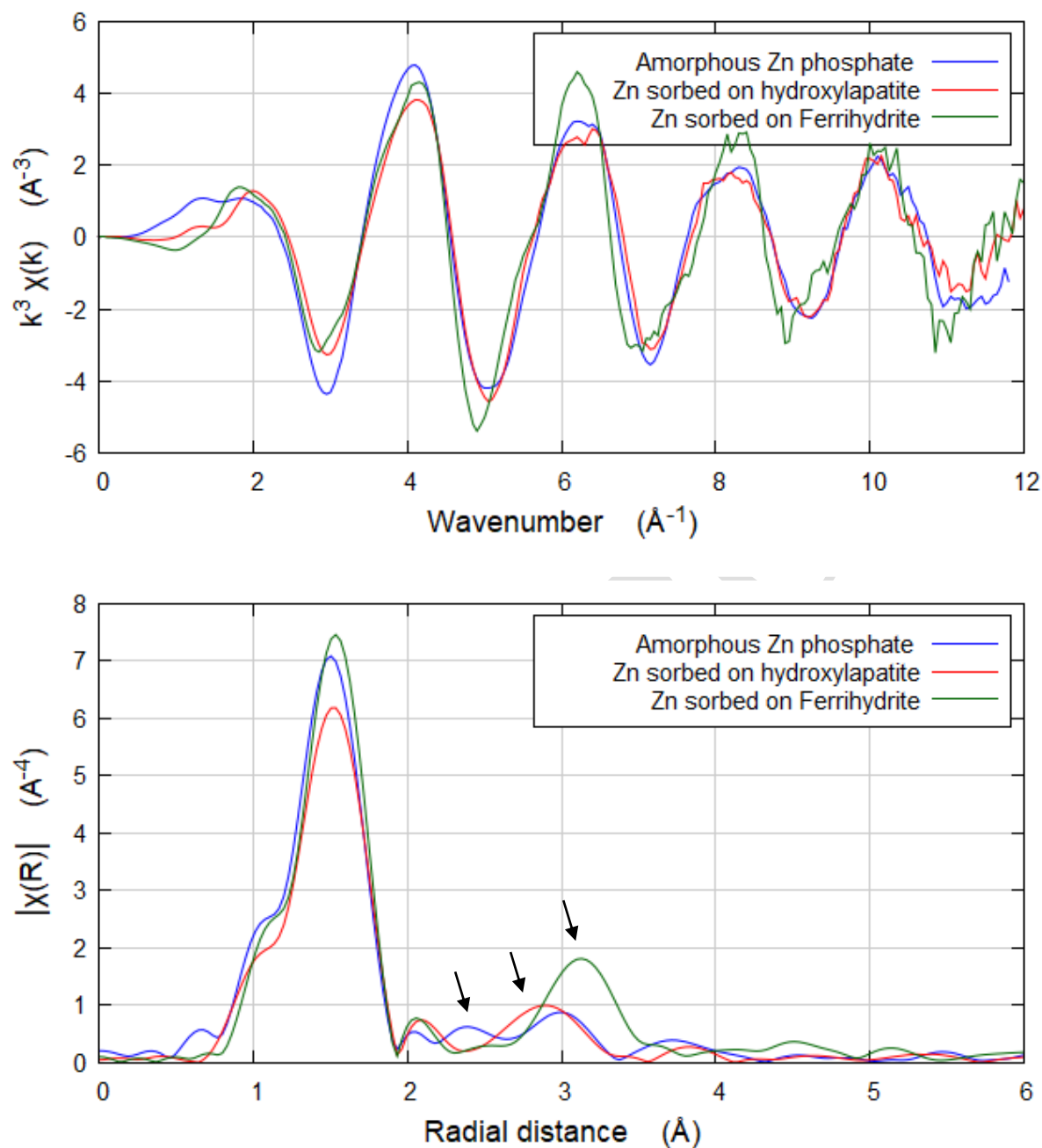


Figure SI 8: Zn K-edge extended X-ray absorption fine-structure spectroscopy spectra and radial distribution function (window Kaiser-Bessel, dk=2) for amorphous Zn phosphate, Zn sorbed on hydroxylapatite and Zn sorbed on Ferrihydrite.

References

1. United Nations, D. o. E. a. S. A., Population Division, *World Population Prospects: The 2017 Revision*. 2017; Vol. Volume I: Comprehensive Tables (ST/ESA/SER.A/399), p 346.
2. United Nations, D. o. E. a. S. A., Population Division, *World Urbanization Prospects: The 2014 Revision*. 2014; Vol. Highlights (ST/ESA/SER.A/352), p 27.
3. Orsini, F.; Kahane, R.; Nono-Womdim, R.; Gianquinto, G., Urban agriculture in the developing world: a review. *Agronomy for Sustainable Development* **2013**, 33, (4), 695-720.
4. De Bon, H.; Parrot, L.; Moustier, P., Sustainable urban agriculture in developing countries. A review. *Agronomy for Sustainable Development* **2010**, 30, (1), 21-32.
5. Diallo, F.; Masse, D.; Diarra, K.; Feder, F., Impact of organic fertilisation on lettuce biomass production according to the cultivation duration in tropical soils. *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science* **2020**, 70, (3), 215-223.
6. Formentini, T.; Mallmann, F.; Pinheiro, A.; Fernandes, C.; Bender, M.; da, V., M; Dos, S., DR; Doelsch, E., Copper and zinc accumulation and fractionation in a clayey Hapludox soil subject to long-term pig slurry application. *The Science of the total environment* **2015**, 536, 831-839.
7. Legros, S.; Doelsch, E.; Feder, F.; Moussard, G.; Sansoulet, J.; Gaudet, J. P.; Rigaud, S.; Doelsch, I. B.; Saint Macary, H.; Bottero, J. Y., Fate and behaviour of Cu and Zn from pig slurry spreading in a tropical water-soil-plant system. *Agr. Ecosyst. Environ.* **2013**, 164, 70-79.
8. Hodomihou, N. R.; Feder, F.; Masse, D.; Agbossou, K. E.; Amadji, G. L.; Ndour-Badiane, Y.; Doelsch, E., Diagnosis of periurban Dakar (Senegal) agrosystem contamination by trace elements. *Biotechnol. Agron. Soc.* **2016**, 20, (3), 397-407.
9. Belon, E.; Boisson, M.; Deportes, I. Z.; Eglin, T. K.; Feix, I.; Bispo, A. O.; Galsomies, L.; Leblond, S.; Guellier, C. R., An inventory of trace elements inputs to French agricultural soils. *Sci. Tot. Environ.* **2012**, 439, 87-95.
10. Nicholson, F. A.; Smith, S. R.; Alloway, B. J.; Carlton-Smith, C.; Chambers, B. J., An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Tot. Environ.* **2003**, 311, (1-3), 205-219.
11. Luo, L.; Ma, Y.; Zhang, S.; Wei, D.; Zhu, Y.-G., An inventory of trace element inputs to agricultural soils in China. *J. Environ. Manage.* **2009**, 90, (8), 2524-2530.
12. Working Group Wrb, I., *World Reference Base for Soil Resources 2014. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*. 2014.
13. Le Bars, M.; Legros, S.; Levard, C.; Chaurand, P.; Tella, M.; Rovezzi, M.; Browne, P.; Rose, J.; Doelsch, E., Drastic Change in Zinc Speciation during Anaerobic Digestion and Composting: Instability of Nanosized Zinc Sulfide. *Environ. Sci. Technol.* **2018**, 52, (22), 12987-12996.
14. Legros, S.; Doelsch, E.; Masion, A.; Rose, J.; Borshneck, D.; Proux, O.; Hazemann, J. L.; Saint-Macary, H.; Bottero, J. Y., Combining Size Fractionation, Scanning Electron Microscopy, and X-ray Absorption Spectroscopy to Probe Zinc Speciation in Pig Slurry. *J. Environ. Qual.* **2010**,

- 39, (2), 531-540.
15. Legros, S.; Levard, C.; Marcato-Romain, C.-E.; Guiresse, M.; Doelsch, E., Anaerobic Digestion Alters Copper and Zinc Speciation. *Environ. Sci. Technol.* **2017**, *51*, (18), 10326-10334.
16. Donner, E.; Howard, D. L.; de Jonge, M. D.; Paterson, D.; Cheah, M. H.; Naidu, R.; Lombi, E., X-ray Absorption and Micro X-ray Fluorescence Spectroscopy Investigation of Copper and Zinc Speciation in Biosolids. *Environ. Sci. Technol.* **2011**, *45*, (17), 7249-7257.
17. Donner, E.; Ryan, C. G.; Howard, D. L.; Zarcinas, B.; Scheckel, K. G.; McGrath, S. P.; de Jonge, M. D.; Paterson, D.; Naidu, R.; Lombi, E., A multi-technique investigation of copper and zinc distribution, speciation and potential bioavailability in biosolids. *Environ. Pollut.* **2012**, *166*, (0), 57-64.
18. Lombi, E.; Donner, E.; Tavakkoli, E.; Turney, T. W.; Naidu, R.; Miller, B. W.; Scheckel, K. G., Fate of Zinc Oxide Nanoparticles during Anaerobic Digestion of Wastewater and Post-Treatment Processing of Sewage Sludge. *Environ. Sci. Technol.* **2012**, *46*, (16), 9089-9096.
19. Mamindy-Pajany, Y.; Sayen, S.; Mosselmans, J. F. W.; Guillon, E., Copper, Nickel and Zinc Speciation in a Biosolid-Amended Soil: pH Adsorption Edge, μ -XRF and μ -XANES Investigations. *Environ. Sci. Technol.* **2014**, *48*, (13), 7237-7244.
20. Kirpichtchikova, T. A.; Manceau, A.; Spadini, L.; Panfili, F.; Marcus, M. A.; Jacquet, T., Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. *Geochim. Cosmochim. Acta* **2006**, *70*, (9), 2163-2190.
21. 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. *Environ. Pollut.* **2017**, *222*, 495-503.
22. Yamamoto, K.; Hashimoto, Y.; Kang, J.; Kobayashi, K., Speciation of Phosphorus Zinc and Copper in Soil and Water-Dispersible Colloid Affected by a Long-Term Application of Swine Manure Compost. *Environ. Sci. Technol.* **2018**, *52*, (22), 13270-13278.
23. Inglezakis, V. J.; Zorpas, A. A.; Karagiannidis, A.; Samaras, P.; Voukkali, I.; Sklari, S., EUROPEAN UNION LEGISLATION ON SEWAGE SLUDGE MANAGEMENT. *Fresenius Environmental Bulletin* **2014**, *23*, (2A), 635-639.
24. Romeo, A.; Vacchina, V.; Legros, S.; Doelsch, E., Zinc fate in animal husbandry systems. *Metallomics* **2014**, *11*, (6), 1999-2009.
25. Doelsch, E.; Basile-Doelsch, I.; Rose, J.; Masion, A.; Borschneck, D.; Hazemann, J. L.; SaintMacary, H.; Bottero, J. Y., New Combination of EXAFS Spectroscopy and Density Fractionation for the Speciation of Chromium within an Andosol. *Environ. Sci. Technol.* **2006**, *40*, (24), 7602-7608.
26. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **2005**, *12*, (4), 537-541.
27. Tella, M.; Bravin, M. N.; Thuriès, L.; Cazevieille, P.; Chevassus-Rosset, C.; Collin, B.; Chaurand, P.; Legros, S.; Doelsch, E., Increased zinc and copper availability in organic waste amended soil potentially involving distinct release mechanisms. *Environ. Pollut.* **2016**, *212*, 299-306.

- 781 28. Hammer, D.; Keller, C.; McLaughlin, M. J.; Hamon, R. E., Fixation of metals in soil
782 constituents and potential remobilization by hyperaccumulating and non-hyperaccumulating
783 plants: Results from an isotopic dilution study. *Environ. Pollut.* **2006**, *143*, (3), 407-415.
- 784 29. Jacquat, O.; Voegelin, A.; Villard, A.; Marcus, M. A.; Kretzschmar, R., Formation of Zn-
785 rich phyllosilicate, Zn-layered double hydroxide and hydrozincite in contaminated calcareous
786 soils. *Geochim. Cosmochim. Acta* **2008**, *72*, (20), 5037-5054.
- 787 30. Jacquat, O.; Voegelin, A.; Kretzschmar, R., Local coordination of Zn in hydroxy-
788 interlayered minerals and implications for Zn retention in soils. *Geochim. Cosmochim. Acta* **2009**,
789 *73*, (2), 348-363.
- 790 31. Panfili, F.; Manceau, A.; Sarret, G.; Spadini, L.; Kirpichtchikova, T.; Bert, V.; Laboudigue,
791 A.; Marcus, M. A.; Ahamdach, N.; Libert, M.-F., The effect of phytostabilization on Zn speciation
792 in a dredged contaminated sediment using scanning electron microscopy, X-ray fluorescence,
793 EXAFS spectroscopy, and principal components analysis. *Geochim. Cosmochim. Acta* **2005**, *69*,
794 (9), 2265-2284.
- 795 32. Kelly, R. A.; Andrews, J. C.; DeWitt, J. G., An X-ray absorption spectroscopic
796 investigation of the nature of the zinc complex accumulated in *Datura innoxia* plant tissue culture.
797 *Microchem. J.* **2002**, *71*, (2-3), 231-245.
- 798 33. González, J. C.; Peariso, K.; Penner-Hahn, J. E.; Matthews, R. G., Cobalamin-Independent
799 Methionine Synthase from *Escherichia coli*: A Zinc Metalloenzyme. *Biochemistry* **1996**, *35*, (38),
800 12228-12234.
- 801 34. Sarret, G.; Saumitou-Laprade, P.; Bert, V.; Proux, O.; Hazemann, J. L.; Traverse, A. S.;
802 Marcus, M. A.; Manceau, A., Forms of zinc accumulated in the hyperaccumulator *Arabidopsis*
803 *halleri*. *Plant Physiol.* **2002**, *130*, (4), 1815-1826.
- 804 35. Doelsch, E.; Masion, A.; Moussard, G.; Chevassus-Rosset, C.; Wojciechowicz, O., Impact
805 of pig slurry and green waste compost application on heavy metal exchangeable fractions in
806 tropical soils. *Geoderma*. **2010**, *155*, (3-4), 390-400.
- 807 36. Feder, F.; Bochu, V.; Findeling, A.; Doelsch, E., Repeated pig manure applications modify
808 nitrate and chloride competition and fluxes in a Nitisol. *Sci. Tot. Environ.* **2015**, *511*, 238-248.
- 809 37. McBride, M.; Sauve, S.; Hendershot, W., Solubility control of Cu, Zn, Cd and Pb in
810 contaminated soils. *Eur. J. Soil Sci.* **1997**, *48*, (2), 337-346.
- 811 38. Karathanasis, A. D.; Johnson, D. M. C.; Matocha, C. J., Biosolid Colloid-Mediated
812 Transport of Copper, Zinc, and Lead in Waste-Amended Soils. *J. Environ. Qual.* **2005**, *34*, (4),
813 1153-1164.
- 814 39. Hernández, T.; Chocano, C.; Moreno, J.-L.; García, C., Use of compost as an alternative
815 to conventional inorganic fertilizers in intensive lettuce (*Lactuca sativa* L.) crops—Effects on soil
816 and plant. *Soil and Tillage Research* **2016**, *160*, 14-22.
- 817 40. McGrath, S. P.; Chambers, B. J.; Taylor, M. J.; Carlton-Smith, C. H., Biofortification of
818 zinc in wheat grain by the application of sewage sludge. *Plant Soil.* **2012**, *361*, (1), 97-108.
- 819 41. Black, R. E., Zinc Deficiency, Infectious Disease and Mortality in the Developing World.
820 *The Journal of Nutrition* **2003**, *133*, (5), 1485S-1489S.

821 42. B., B.; Wedepohl, K. H., Zinc. In *Handbook of Geochemistry*, Wedepohl, K. H., Ed.
822 Springer-Verlag: Berlin, 1978; Vol. II/3.

823 43. Yamamoto, K.; Hashimoto, Y., Chemical Species of Phosphorus and Zinc in Water-
824 Dispersible Colloids from Swine Manure Compost. *J. Environ. Qual.* **2017**, 46, (2), 461-465.

825

826

FINAL PROOF