

Zinc Speciation in Organic Waste Drives Its Fate in Amended Soils

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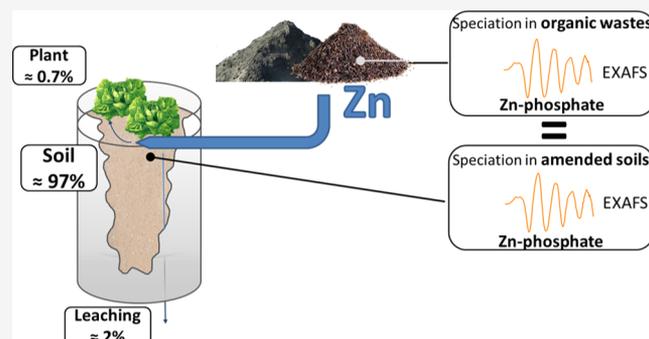
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ABSTRACT: Recycling of organic waste (OW) as fertilizer on farmland is a widespread practice that fosters sustainable development via resource reuse. However, the advantages of OW fertilization should be weighed against the potentially negative environmental 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 analyzed at the end of the second cycle (total experiment time: 12 weeks). X-ray absorption spectroscopy analyses were then conducted to assess Zn speciation in OW and OW-amended soils. The results of this study highlighted that (i) the fate of Zn in water–soil–plant compartments was similar, regardless of 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.



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, market garden farming intensification is being achieved via inputs of biodegradable materials, such as sewage sludge (SS), livestock manure, green waste compost, and so forth, 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 croppeds 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 SS or poultry manure (PM) application up to nine times per year over a 24–40 year period. The annual Zn input in periurban Dakar agrosystems ranged from 1369 to 5818 g ha⁻¹

year⁻¹, which is alarmingly higher than the 454–539 g ha⁻¹ year⁻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 approach,⁸ 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 and (ii) determination of the factors that could explain the similar fate of Zn in the contrasted soil types.

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Table 1. Soil and OW Characteristics^a

	arenosol		fluvisol		SS	poultry manure
	surface layer (0–20 cm)	deep layer (20–40 cm)	surface layer (0–20 cm)	deep layer (20–40 cm)		
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				

^aConcentrations are expressed on a dry matter (DM) basis. The analytical methods are described in the [Supporting Information S1 and S2](#).

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 OWs^{13–18} or amended soils.^{19–22} 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, that is, Zn phosphate and Zn bound to organic matter (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). SS or PM was 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}

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

MATERIALS AND METHODS

OW 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 ([Tables 1, S1](#)). The water holding capacity, total limestone, pH, and organic carbon were much lower in the arenosol than in the fluvisol. Quartz, cristobalite, sanidine, and muscovite mainly accounted for the mineralogy of the arenosol ([Supporting Information S2](#)). This contrasted with the fluvisol mineralogy, in which several clay minerals (kaolinite, montmorillonite, palygorskite, and kaolinite), calcite, and quartz were detected.

SS and 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 ([Supporting Information S1](#)). Both SS and PM had been stockpiled for long periods prior to being spread on the soil columns (>3 months) which is consistent with 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 the United States, Canada, and different European (Switzerland and Austria) and Asian (China and Japan) countries.²⁴

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 and 20–40 cm) were sampled in the arenosol and

Table 2. Mass Balances in the Soil Column Experiments^a

	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 ^b		1029 ± 41	328 ± 31		1029 ± 41	328 ± 31
(3) Zn leaching at the soil column outlet ^c	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 ^d	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 ^e	768 ± 163	1618 ± 230	912 ± 130	1366 ± 133	2267 ± 132	1567 ± 91
(6) Zn balance: (1) + (2) - ((3) + (4))	805 ± 67 ^{NSf}	1828 ± 110 ^{NS}	1126 ± 99 ^{NS}	1154 ± 100 ^{NS}	2183 ± 143 ^{NS}	1481 ± 131 ^{NS}

^aThe Zn content is expressed in mg. ^bZn input from OW = Zn_{OWC1} + Zn_{OWC2}, where Zn_{OWC1} is the Zn input from SS or PM for cycle 1, and Zn_{OWC2} is the Zn input from SS or PM for cycle 2. ^cZn leaching at the soil column outlet = $\sum_{i=1}^n [\text{Zn}]_i \times F_i$, where $[\text{Zn}]_i$ is the Zn concentration measured in the leachate at week i , 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 Zn calculated after normalization by Zn leaching measured for the control soil column. ^dZn uptake by lettuce = Zn_{PC1} + Zn_{PC2}, where Zn_{PC1} is the mass Zn uptake by lettuce for cycle 1, and Zn_{PC2} is the mass Zn uptake by lettuce for cycle 2. Percentage of OW-derived Zn calculated after normalization by Zn uptake measured for the control soil column. ^eFinal Zn content in the soil column = $\sum_{j=1}^m [\text{Zn}]_j \times \text{MSL}_j$, where $[\text{Zn}]_j$ is the Zn concentration measured in soil layer j , and MSL_j is the mass of soil layer j . m is the number of soil layers ($m = 7$). ^fNS = no significant difference between the final Zn content in the soil column (5) and the Zn balance (6) at the 5% level.

fluvisol. Soils were air-dried, crumbled, 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 kg column⁻¹ (47 kg column⁻¹ for fluvisol). SS and PM were applied at the surface of the soil columns at 60 T ha⁻¹ (0.51 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.

Lettuce (*L. sativa* L.) was cultivated 1 week after the 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 analyzed 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 analyzed.

The experimental procedure is described in further detail in the Supporting Information S3.

Zinc Speciation in OWs and Soils. 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 minimize beam-induced damage of the samples, in the 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 extended X-ray absorption fine structure (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 a 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 the soil (Supporting Information S4). These references have been synthesized or purchased and described in previously published studies: nano-ZnS and amorphous Zn-phosphate;¹³ Zn sorbed on goethite and Zn sorbed on ferrihydrite;²⁷ Zn cryptomelane;²⁸ Zn-layered double hydroxide, Zn sorbed on hydroxy-Al interlayered montmorillonite;²⁹ Zn sorbed on kaolinite;³⁰ Zn sorbed on hydroxylapatite;³¹ Zn-malate, Zn-histidine, Zn-cysteine;^{27,32} Zn-methionine;^{15,33} Zn-phytate;^{15,34} and 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, Supporting Information S5) was performed for each OW or amended soil spectrum over a k -range of 2.5–10.6 cÅ⁻¹. The residual factor of each LCF was calculated as follows: $R = \frac{\sum(k^3\chi(k)_{\text{exp}} - k^3\chi(k)_{\text{fit}})^2}{\sum(k^3\chi(k)_{\text{exp}})^2}$. 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 analyzed using the Student–Newman–Keuls test to identify differences between modalities. The differences were considered significant if $p \leq 0.05$.

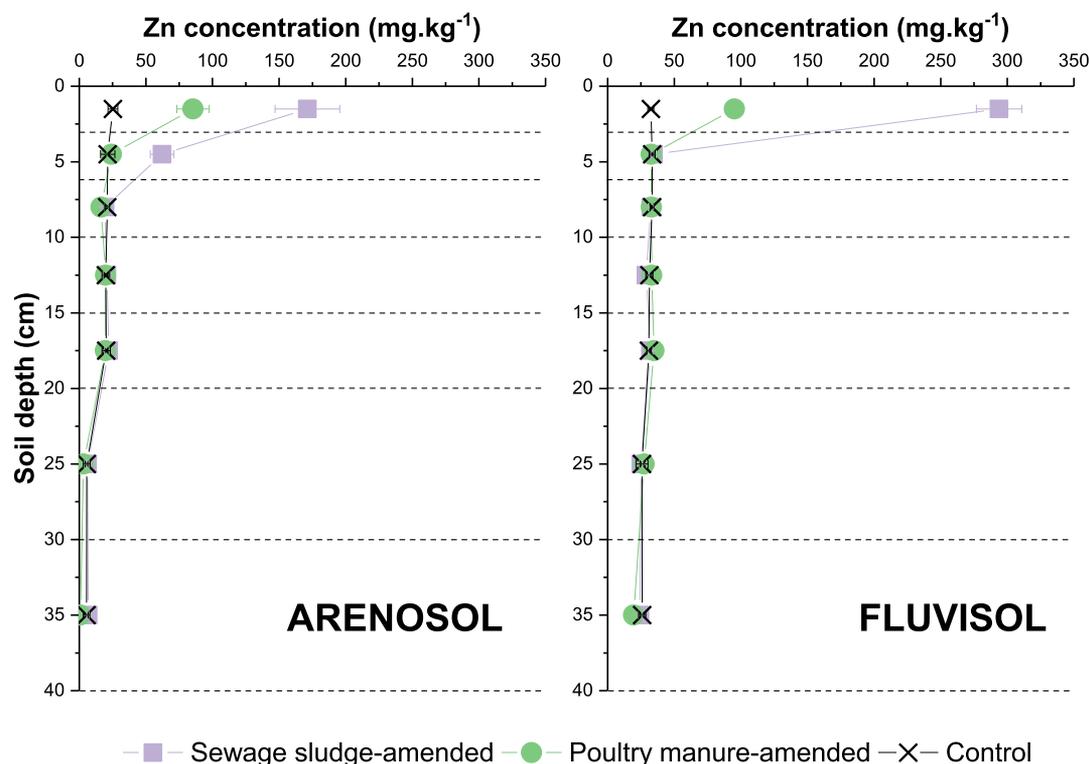


Figure 1. Zn concentration (mg kg^{-1}) in the arenosol and fluvisol soil layers at the end of the soil column experiment. Dashed lines represent the analyzed soil layers.

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, exogenous 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 and 3–6 cm layers for the SS-amended soil and 0–3 and 3–6 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 (Supporting Information S6) 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 OM 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 (Supporting Information S6). 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 favored Zn leaching in the SS-amended arenosol. However, Zn

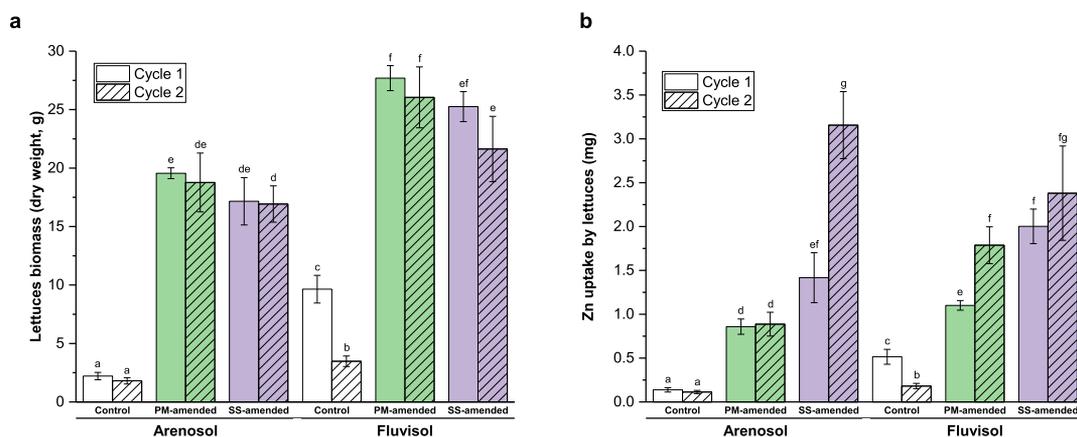


Figure 2. (a) Mean harvested lettuce dry biomass per soil column (g) and (b) mean Zn uptake by lettuces per soil column (mg). Different letters represent significant differences between treatments at the 5% level. PM: poultry manure; SS: sewage sludge.

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 (Supporting Information S6). Nevertheless, Zn leaching was closely correlated with the DOC at the column outlet (Supporting Information S7). Complexation with organic ligands could have mobilized a fraction of exogenous Zn. Several studies concluded that colloidal transport can favor 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.

Zinc Uptake by Lettuce Increases with Repeated OWs 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 cycles within the 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, that is, 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.

Phosphate Drives Zn Speciation in OWs and Amended Soils. The quantitative LCF results (expressed as a percentage of each Zn species) obtained for both OW and OW-amended soils (0–3 cm soil layer) collected at the end of the experiment are shown in Figure 3. The experimental data

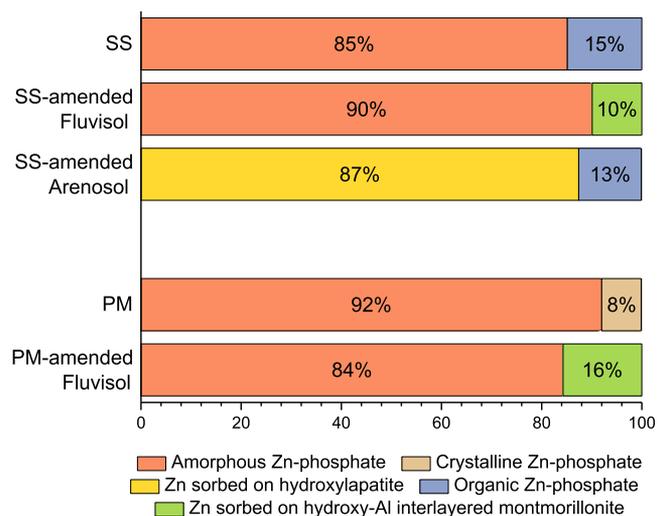


Figure 3. Zn speciation determined from the linear combination fitting of the Zn K-edge EXAFS spectroscopy data (PM = poultry manure, SS = sewage sludge).

were modeled with two Zn references per sample and total contributions ranged from 89 to 111% (Supporting Information S5, S18). Zn species contributions were normalized to 100% for easier comparison. The *R*-factor of the LCFs ranged from 0.029 to 0.063.

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 nanosized 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 becomes 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, that is, 84% for PM-amended fluvisol and 90% for SS-amended fluvisol. Zn sorbed on hydroxy-Al interlayered montmorillonite (HIM) was the secondary Zn species, that is, 16% for PM-amended fluvisol and 10% for SS-amended fluvisol. The latter mineral reference was supported by the X-ray diffraction clay mineral findings in the fluvisol (Supporting Information S2). 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 Zn concentration in the total soil, while the proportion of endogenous Zn represented 34% (Figure 1). In this case, the poor quality of the EXAFS spectra (Supporting Information S5), 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, Supporting Information S6) due to 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 slurry,²¹ but nano-ZnS was not detected in the amended soil. The authors assumed that the nano-scale of ZnS favored 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 water,²⁰ since the conditions in liquid OW are often reducing, hence leading to the formation of nano-ZnS,¹³ 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, that is, 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 the 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 toward the same conclusion. Speciation of trace elements in the source, that is, 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.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c02721>.

Soil, plant, leached water, and OW sampling procedure, analytical methods, and experimental design; X-ray diffraction; Zn K-edge EXAFS spectra and radial distribution function of reference compounds; LCF results; variations in pH, DOC, and Zn in the drained water at the soil column outlets; and comparison of EXAFS spectra and radial distribution function of reference compounds (PDF)

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Notes

The authors declare no competing financial interest.

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