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# Zinc speciation in organic waste drives its fate in amended soils

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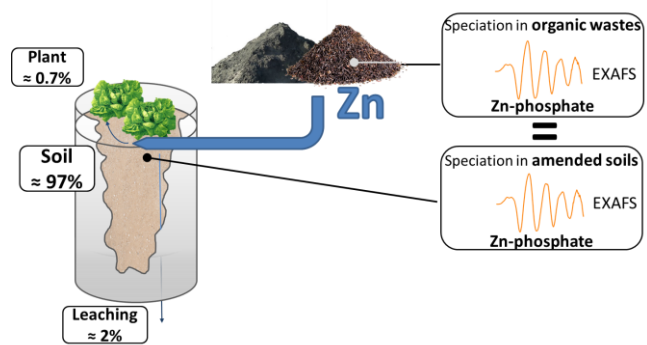
KEYWORDS. Trace element, agriculture, recycling, environmental fate, phosphate, contamination

17 ABSTRACT.

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

39 ABSTRACT ART

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## 42 **Introduction**

43 The rapid increase in the African population (by 1.3 billion people between 2017 and 2050<sup>1</sup>)  
44 combined with the high urbanization rate<sup>2</sup> has led to an urban and periurban agriculture boom.<sup>3, 4</sup>  
45 In developing countries, the market garden farming intensification is being achieved via inputs of  
46 biodegradable materials such as sewage sludge, livestock manure, green waste compost, etc., as  
47 soil fertilizers. These biodegradable materials, referred to as organic wastes (OWs), can supply a  
48 part or all of the nutrients needed for crops.<sup>4, 5</sup> However, many studies have highlighted negative  
49 impacts of agricultural OW recycling as fertilizers due to the presence of contaminants such as  
50 trace elements.<sup>6, 7</sup>

51 A recent assessment of periurban Dakar (Senegal) agrosystems highlighted trace element  
52 contamination of OW-amended cropped soils.<sup>8</sup> Zinc (Zn) accumulation in soil surface layers has  
53 been explained by long-term repeated Zn-rich OW application.<sup>8</sup> Short-term vegetable crop cycles  
54 led to sewage sludge (SS) or poultry manure (PM) application up to 9 times per year over a 24 to  
55 40 year period. The annual Zn input in periurban Dakar agrosystems ranged from 1369 to 5818  
56 g.ha<sup>-1</sup>year<sup>-1</sup>, which is alarmingly higher than the 454-539 g.ha<sup>-1</sup>year<sup>-1</sup> range in European countries  
57 and China.<sup>9-11</sup> Surprisingly, Zn contamination was similar in the two main periurban Dakar  
58 agrosystems (Pikine and Rufisque) despite the fact that the properties of the soils in these two  
59 regions differ markedly. One is an Arenosol (sandy soil, dune material) and the other a Fluvisol  
60 (sandy clay loam and moderately calcareous soil).<sup>12</sup> However, an analytical approach<sup>8</sup>, involving  
61 a comparison of Zn contents in long-term cultivated plots versus adjacent uncultivated plots, did  
62 not enable (i) accurate monitoring of the Zn fate following OW spreading in the three water–soil–  
63 plant system compartments, (ii) determination of the factors that could explain the similar fate of  
64 Zn in contrasted soil types.

65

66 X-ray absorption spectroscopy (XAS) is one of the most widely known structural techniques  
67 for direct determination of speciation of trace elements present in complex matrices and it has been  
68 successfully applied to describe Zn speciation in different OWs<sup>13-18</sup> or amended soils<sup>19-22</sup>.  
69 Kirpichtchikova et al.<sup>20</sup> and Formentini et al.<sup>21</sup> studied Zn speciation in soils affected by long-term  
70 application of sewage water and pig slurry, respectively. In both studies, Zn speciation in soils was  
71 dominated by its associations with secondary mineral phases (clay minerals and Fe  
72 oxyhydroxides). Zn speciation in OW was assessed by Formentini et al.<sup>21</sup>, revealing that nano-ZnS  
73 accounted for 100% of the speciation in the pig slurry. Yamamoto et al.<sup>22</sup> recently investigated Zn  
74 speciation in pig manure compost and in a soil amended with this compost for 23 years. They  
75 showed that oxidized species present in the compost, i.e. Zn-phosphate and Zn bound to OM, had  
76 persisted and accumulated in the amended soil. Although these studies agreed on the fact that Zn  
77 accumulated in the soil following OW spreading, their results were not consistent with respect to  
78 Zn speciation in OWs and in OW-amended soils.

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

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.

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## 91 **Materials and Methods**

### 92 **Organic waste and soil characteristics**

93 Arenosol (Pikine; sandy soil, dune material) and Fluvisol (Rufisque; sandy clay loam and  
94 moderately calcareous soil)<sup>12</sup> were selected for this study as they are the main soils in the periurban  
95 Dakar region, under the prevailing Sahelian tropical climatic conditions. The Arenosol texture was  
96 dominated by the sand fraction (96.2–97.1%). Silt and clay accounted for 15.3–15.7% and 24.9–  
97 28.8% of the Fluvisol content, respectively (Table 1, SI 1). The water holding capacity, total  
98 limestone, pH and organic carbon were much lower in the Arenosol than in the Fluvisol. Quartz,  
99 critobalite, sanidine and muscovite mainly accounted for the mineralogy of the Arenosol (SI 2).  
100 This contrasted with the Fluvisol mineralogy, in which several clay minerals (kaolinite,  
101 montmorillonite, palygorskite and kaolinite), calcite and quartz were detected.

102 Sewage sludge (SS) and poultry manure (PM), are widely used as fertilizers in market gardens  
103 in periurban Dakar agrosystems. SS was sampled at the Pikine municipal wastewater treatment  
104 plant, and PM was sampled in a henhouse at Rufisque (SI 1). Both SS and PM had been stockpiled  
105 for long periods prior to being spread on the soil columns (>3 months) which is consistent with of  
106 market gardeners' practices. The ash content of SS (34%) was lower than that for PM (49%),  
107 whereas P concentrations were close for SS and PM (17.3 and 16.8 mg.kg<sup>-1</sup>, respectively). The Zn  
108 concentration was higher in SS than in PM (1003 and 320 mg.kg<sup>-1</sup>, respectively). The Zn  
109 concentration in SS was lower than the maximum permissible limits for land application in Europe  
110 (2500–4000 mg.kg<sup>-1</sup> DM), but higher than the most restrictive threshold values set by national  
111 legislation (Sweden: 800 mg.kg<sup>-1</sup>; Netherlands: 300 mg.kg<sup>-1</sup>).<sup>23</sup> The Zn concentration in PM was  
112 in very close agreement with Zn concentrations inventoried in United States, Canada, different  
113 European (Switzerland and Austria) and Asian (China and Japan) countries.<sup>24</sup>



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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.

		<b>Arenosol</b>		<b>Fluvisol</b>		<b>Sewage sludge</b>	<b>Poultry manure</b>
		<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 <sub>3</sub> )	%	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 <sup>-1</sup>	0.23	0.20	0.66	0.24	16.8	17.3
Total Zn	mg.Kg <sup>-1</sup>	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

120 **Soil column experiment**

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

130 Lettuces (*Lactuca sativa* L.) were cultivated 1 week after OW application. During the crop cycle  
131 (5 weeks), soil columns received 4 L of water twice a week, corresponding to 46.8 mm or 0.3 pore  
132 volume (PV) for the Arenosol and 0.25 PV for the Fluvisol. Leached soil solutions were sampled  
133 at the bottom of the soil columns weekly and analysed for pH, Zn concentration and dissolved  
134 organic carbon (DOC). Lettuce leaves were harvested at the end of the crop cycle. Dry biomass  
135 was weighed to determine yields and Zn uptake.

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

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

140

141 **Zinc speciation in organic wastes and soils**

142 X-ray absorption spectroscopy (XAS) was applied to assess the speciation of Zn in OW and the  
143 surface layer (0-3 cm) of amended soils (SS-amended Fluvisol, PM-amended Fluvisol and SS-  
144 amended Arenosol). Zn K-edge XAS spectra were recorded at the ESRF synchrotron (Grenoble,  
145 France) on the BM30B (FAME) beamline. Dried OW and soil samples were cryo-ground (Retsch  
146 MM400) and pressed into pellets before analysis. Spectra were measured at liquid helium  
147 temperature, to minimise beam-induced damage of the samples, in fluorescence mode with a 30-  
148 element solid-state Ge detector. The spectra of each sample were an average of three to seven  
149 scans, depending on the Zn concentration and the signal-to-noise ratio. The acquisition of EXAFS  
150 spectra for the PM-amended Arenosol was not possible due to the combination of a low Zn  
151 concentration and a very high Fe concentration. Each scan was measured on a different spot on  
152 the sample pellet to limit beam damage. Energy calibration was performed using metallic Zn  
153 reference foil recorded simultaneously with the samples. The absorption edge was defined at 9659  
154 eV, as indicated by the zero crossing of the second derivative of the Zn-foil spectrum. A similar  
155 procedure was applied to the previously acquired spectra of Zn reference compounds.  
156 Normalization and data reduction were performed according to standard methods<sup>25</sup> using Athena  
157 software.<sup>26</sup> A library of spectra from Zn reference compounds was used to identify Zn species in  
158 OW and soil (SI4). These references have been synthesized or purchased and described in previous  
159 published studies: Nano-ZnS and Amorphous Zn-Phosphate<sup>13</sup>; Zn sorbed on Goethite and Zn  
160 sorbed on Ferrihydrite<sup>27</sup>; Zn Cryptomelane<sup>28</sup>; Zn-Layered Double Hydroxide, Zn sorbed on  
161 hydroxy-Al interlayered montmorillonite<sup>29</sup>; Zn sorbed on Kaolinite<sup>30</sup>; Zn sorbed on  
162 Hydroxylapatite<sup>31</sup>; Zn-Malate, Zn-Histidine, Zn-Cysteine<sup>27,32</sup>; Zn-Methionine<sup>15,33</sup>; Zn-Phytate  
163<sup>15, 34</sup>; Zn-Oxalate, Crystalline Zn Phosphate and Sphalerite (reagent grade, Sigma Aldrich).  
164 Reference material spectra and sample spectra were measured in the same conditions. Least square

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

172

### 173 **Statistical Analysis**

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

178

## 179 **Results and Discussion**

### 180 **Accumulation of OW-borne Zn in the soil surface layer**

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

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

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

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

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

204 Overall, 99.6, 99.3 and 99.4% of OW-borne Zn accumulated in the upper soil layers (0–3 and  
205 3–6 cm) for the SS-amended Fluvisol, PM-amended Fluvisol and SS-amended Arenosol,  
206 respectively, whereas 97.6% of Zn accumulated in the 0–3 cm soil layer for the PM-amended  
207 Arenosol. This exogenous Zn accumulation in the upper soil layers after OW spreading has already  
208 been observed. For instance, Formentini et al.<sup>6</sup> assessed the impact of 11 years of pig slurry  
209 spreading in a clayey Hapludox soil. They concluded that most exogenous Zn accumulated within  
210 the topsoil layers, with assimilation by crops and leaching virtually negligible in the overall Zn  
211 balance.

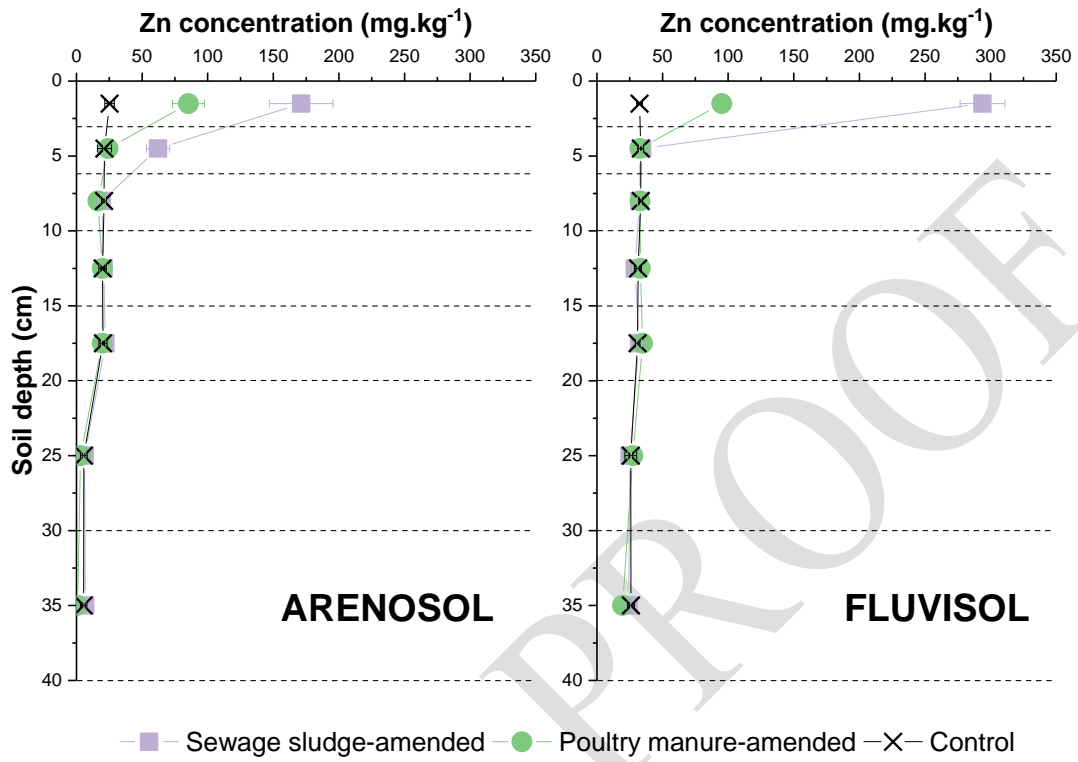
212 This study specifically highlighted a soil effect. The Arenosol promoted leaching of a small  
213 fraction of Zn in drained water (SI 6) and migration from 0 to 6 cm depth (Figure 1). The sandy  
214 texture of the Arenosol associated with its high hydraulic conductivity might have favored  
215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

218 An OW effect was also highlighted. We observed a 1 pH unit time-course decrease in the  
219 solution collected at the outlet of the SS-amended Arenosol (SI 6). This decrease in pH is common  
220 and attributed to the acidic effect of OW mineralization and the ammonium nitrification process<sup>27</sup>,  
221 <sup>35, 36</sup>. It is well established that pH is the major driver of Zn solubility in soils<sup>37</sup> and the observed  
222 decrease in pH favoured Zn leaching in the SS-amended Arenosol. However, Zn leaching at the  
223 outlet of the PM-amended Arenosol column (1.9% of the Zn input) was surprising as the pH of the  
224 soil solution was stable and slightly alkaline (pH=7.3-8) throughout the experiment (SI 6).

225 Nevertheless, Zn leaching was closely correlated with the DOC at the column outlet (SI 7).  
226 Complexation with organic ligands could have mobilized a fraction of exogenous Zn. Several  
227 studies concluded that colloidal transport can favour trace element transfer in soils following OW  
228 spreading. For example, Karathanasis et al.<sup>38</sup> studied Cu, Zn and Pb elution in a soil monolith.  
229 They demonstrated the elution of significant soluble metal loads in association with water-  
230 dispersible biosolid colloids. Similarly, Yamamoto et al.<sup>22</sup> studied the fate of P, Zn and Cu in soil  
231 affected by a long-term application of swine manure compost. They demonstrated that continual  
232 compost application enhanced the formation of a soil water dispersible colloid in which Zn, Cu  
233 and P were accumulated.  
234

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237 Figure 1: Zn concentration (mg.kg<sup>-1</sup>) 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 <sup>a</sup>	-	1029 ± 41	328 ± 31	-	1029 ± 41	328 ± 31
(3) Zn leaching at the soil column outlet <sup>b</sup>	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 <sup>c</sup>	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 <sup>d</sup>	768 ± 163	1618 ± 230	912 ± 130	1366 ± 133	2267 ± 132	1567 ± 91
(6) Zn balance: (1) + (2) – ((3) + (4))	805 ± 67 <sup>NS e</sup>	1828 ± 110 <sup>NS</sup>	1126 ± 99 <sup>NS</sup>	1154 ± 100 <sup>NS</sup>	2183 ± 143 <sup>NS</sup>	1481 ± 131 <sup>NS</sup>

240 <sup>a</sup> 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 <sup>b</sup> 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 <sup>c</sup> 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  $Zn_{P\ C2}$  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 <sup>d</sup> Final Zn content in the soil column =  $\sum_{j=1}^m [Zn]_j \times MSl_j$ , where  $[Zn]_j$  is the Zn concentration measured in soil layer j, and  $MSl_j$   
249 is the mass of soil layer j. m is the number of soil layers (m=7).

250 <sup>e</sup> NS= no significant difference between the final Zn content in the soil column (5) and the Zn balance (6) at the 5% level.

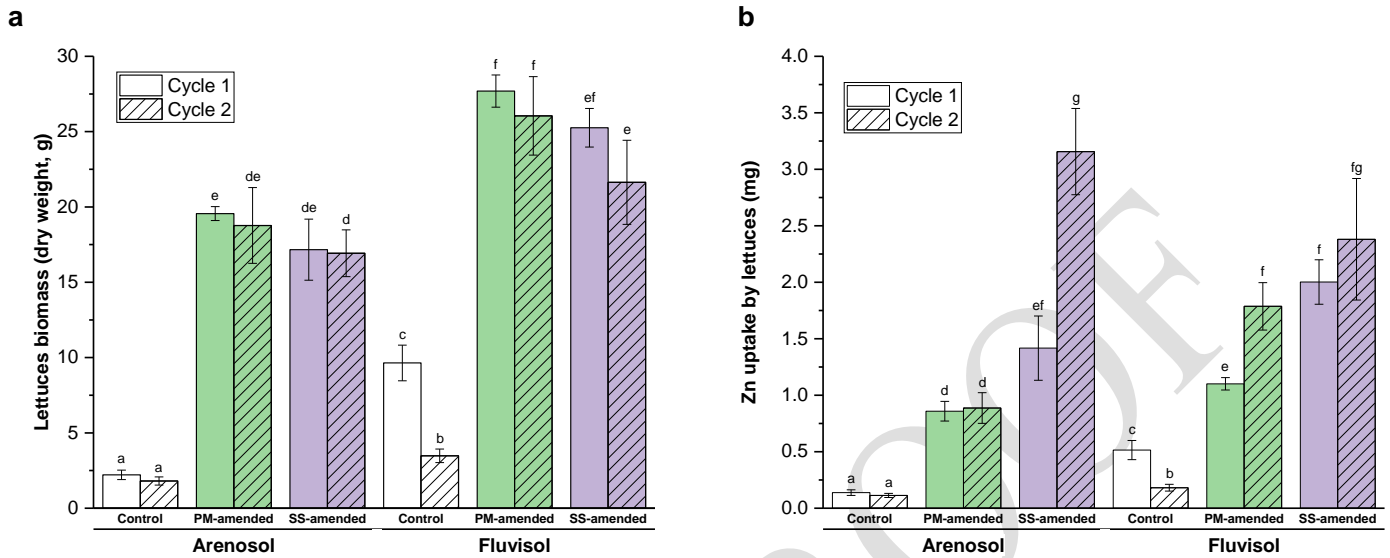
251 **Zinc uptake by lettuce increases with repeated organic wastes application**

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

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

262 If this trend, i.e. constant crop yield combined with increased Zn uptake, were to be confirmed  
263 by long-term experiments with repeated OW application and successive crop cycles, OW  
264 fertilization could represent an opportunity to improve the Zn content of staple food crops. Such  
265 agronomic biofortification<sup>40</sup> could help tackle Zn deficiency in human populations which is a cause  
266 of illness and death in developing countries.<sup>41</sup> The advantages of using OW to increase the plant  
267 Zn concentration should, however, be assessed together with the potential uptake of toxic trace  
268 elements such as Cd or Pb.

269



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

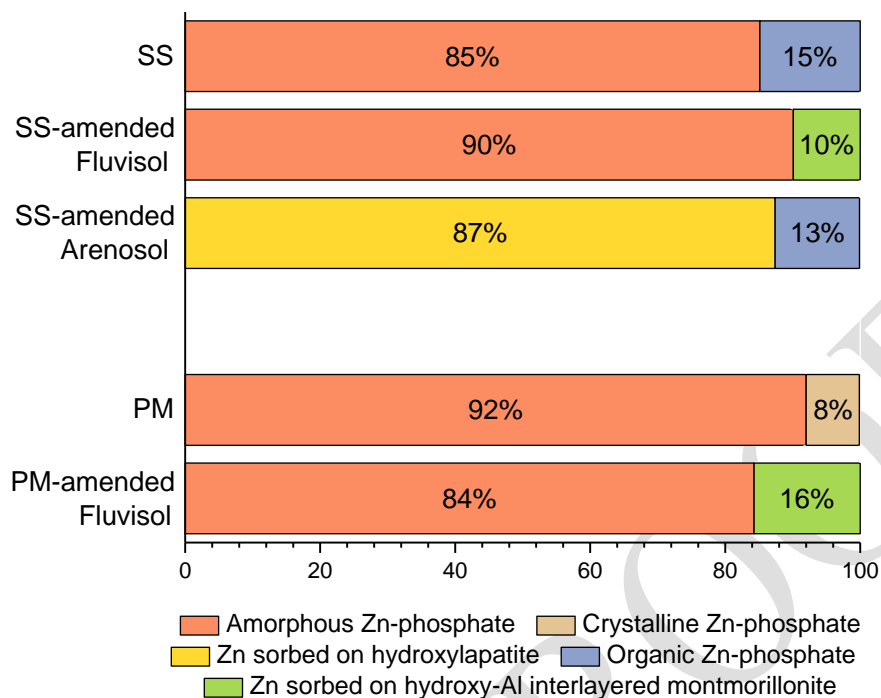
274

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



283  
 284 Figure 3: Zn speciation determined from the linear combination fitting of the Zn K-edge extended  
 285 X-ray absorption fine-structure spectroscopy data (PM = poultry manure, SS = sewage sludge).

286  
 287 *Zn speciation in OWs*

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

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

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

306

#### 307 *Zn speciation in amended soils*

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

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

332

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

335 To our knowledge, no previous studies have assessed the fate of OW-borne amorphous Zn-  
336 phosphate species in the soil after OW spreading. More importantly, our results differed  
337 substantially from those of previous studies using XAS techniques.<sup>19-22</sup> Mamindy-Pajany et al.<sup>19</sup>  
338 described Zn speciation in a soil mixed with SS and spiked with a Zn nitrate solution. Their results  
339 (58% Zn sorbed to Fe oxyhydroxides and 42% Zn bound to OM) highlighted the soil retention  
340 mechanism with respect to Zn rather than the fate of exogenous OW-derived Zn. In two studies  
341 by Kirpichtchikova et al.<sup>20</sup> and Formentini et al.<sup>21</sup>, Zn speciation in soils affected by long-term  
342 sewage water and pig slurry application, was dominated by its associations with secondary mineral

343 phases (clay minerals and Fe oxyhydroxides). Surprisingly, nano-ZnS accounted for 100% of the  
344 Zn speciation in the pig slurry<sup>21</sup>, but nano-ZnS was not detected in the amended soil. The authors  
345 assumed that the nano-scale of the ZnS favoured oxidation of this species in the soil, in turn  
346 releasing Zn that was subsequently retained by the soil matrix. We think that an identical  
347 mechanism could explain the Zn speciation in the soil amended by sewage water<sup>20</sup>, since the  
348 conditions in liquid OW are often reducing hence leading to the formation of nano-ZnS<sup>13</sup>, which  
349 might have oxidized and dissolved after sewage water spreading.

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

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

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



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376

## 377 **Supporting Information**

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

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FINAL PROOF

509 Supporting Information

510 Zinc speciation in organic waste drives its fate in  
511 amended soils

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FINAL PROOF

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

531 *Soils*

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

537 After organic matter (OM) dissolution and carbonate removal, soil particle size analyses (sand,  
538 silt and clay) were conducted using the combined pipette sieving and sedimentation method (NF  
539 X 31-107). The total limestone or carbonate content in soil was estimated by the volumetric method  
540 (ISO 10693). Total nitrogen (ISO 13878) and total carbon (ISO 10694) were determined by dry  
541 combustion with an elemental NC 2100 Soil Analyzer (Thermo Electron Corp.), and organic  
542 carbon was determined according to the difference with mineral carbon as calculated from the  
543 carbonate content (ISO 10694). Soil and OW pH were determined according to the potentiometric  
544 method in the supernatant of the soil–water and OW-water suspension with 1:2 and 1:5 ratios,  
545 respectively (ISO 10390). For total P and Zn analyses, sieved soil sub-samples were ground to 100  
546 µm particle size in zirconium material before dissolution. After 2 h calcination at 500°C, total  
547 dissolution was performed by acid digestion using a mixture of hydrofluoric (HF), nitric (HNO<sub>3</sub>)  
548 and perchloric (HClO<sub>4</sub>) acids (ISO 14869-1). Total P and Zn concentrations were then determined  
549 using inductively coupled plasma mass spectrometry (ICP-MS). Furthermore, two reference  
550 standard certified soil samples, i.e. CRM 7001 (light sandy soil) and CRM 7004 (loam), were used  
551 to assess the accuracy of the results according to the ISO 9001 certification of the laboratory. The  
552 variation coefficient for both of these checks must be less than 5%.



553 At the end of the second cycle, the soil columns were dismantled and seven soil layers were  
554 sampled as follows: 0-3, 3-6, 6-10, 10-15, 15-20, 20-30 and 30-40 cm. Soils were air-dried, sieved  
555 through a 2 mm mesh sieve, and ground to 100 µm using a planetary grinder made of zirconium  
556 oxide to avoid trace element contamination. Zn contents were determined by ICP-MS after 2 h  
557 calcination of the soil samples at 500°C, followed by total dissolution using a mixture of  
558 hydrofluoric (HF), nitric acid (HNO<sub>3</sub>) and perchloric acid (HClO<sub>4</sub>) (ISO 14869-1). Furthermore,  
559 two reference standard certified soil samples: CRM 7001 (light sandy soil) and CRM 7004 (loam)  
560 were used to assess the accuracy of the results according to the ISO 9001 certification of the  
561 laboratory. Deviations from the certified values of these controls were less than 5%.

#### 562 *Leached water*

563 pH, dissolved organic carbon (DOC) and Zn were analysed in the leached water. For this  
564 purpose, weekly leachate samples collected at 40 cm depth (i.e. at the bottom of the soil columns)  
565 were filtered using grade GF/D Whatman microfiber filter paper (pore size 2.7 µm) and subdivided  
566 in three subsamples. pH was determined in the first leachate subsamples immediately after  
567 sampling. The second leachate subsamples were conditioned and acidified with 2.5% ultrapure  
568 nitric acid (v/v) in 10 mL scintillation flasks (previously washed with a 10% nitric acid bath and  
569 rinsed with ultrapure water), and stored at 4°C. The Zn concentration in acidified leachate  
570 subsamples was determined using ICP-MS. The third leachate subsamples conditioned in 20 mL  
571 brown amber glass bottles (prewashed in a 10% NaOH bath and rinsed with ultrapure water), were  
572 treated with 0.1% sodium azide (NaN<sub>3</sub>) and stored at 4°C until use. DOC in azide-treated leachate  
573 subsamples was determined using a Total Organic Carbon (TOC) Analyzer (Shimadzu, TOC-L)  
574 in NPOC mode. Samples were bubbled for 90 s with 1.5% HCl to eliminate carbonates before

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

577 *Plants*

578 Freshly harvested leaves of mature lettuce plant samples were rinsed several times with distilled  
579 water, cut into small pieces, and oven-dried at 60°C to constant mass. Then these samples were  
580 ground into powder separately through a grinder made of zirconium oxide (bowls and balls) in  
581 order to avoid trace element contamination. Total digestion of ground lettuce samples consisted of  
582 introducing 1 g of each ground lettuce sample into a platinum crucible which was subsequently  
583 placed in a muffle furnace for 2 h calcination at 500°C. After cooling, the ash was moistened with  
584 a few drops of ultrapure water, and 2 mL of 6N HCl was added. Dry evaporation was then carried  
585 out on a warming plate. Hydrofluoric acid was added to the ash residue and then evaporated again  
586 on a warming plate. The silica contained in the ash thus volatilized as SiF<sub>6</sub>. The ash residue was  
587 taken up in 2 mL of 6N HCl and filtered through Whatman No.42 filter paper into a 50 mL vial.  
588 The filter containing the residue was placed in the same crucible and then calcined at 500°C.  
589 Finally, the crucible was rinsed with 1 mL of 6N HCl, and then with ultrapure water (18.2 MΩ.cm)  
590 from a Millipore Milli-Q system, and transferred to the same vial. The vial was gauged and then  
591 homogenized by manual stirring. Furthermore, three strawberry plant samples (*Fragaria vesca*)  
592 with internal references were also analyzed for verification and validation of the results. Deviations  
593 from the certified values of these controls were always less than 5%. All reagents used were Merck  
594 analytical grade (AR). The Zn concentration in digestates was determined by inductively coupled  
595 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.

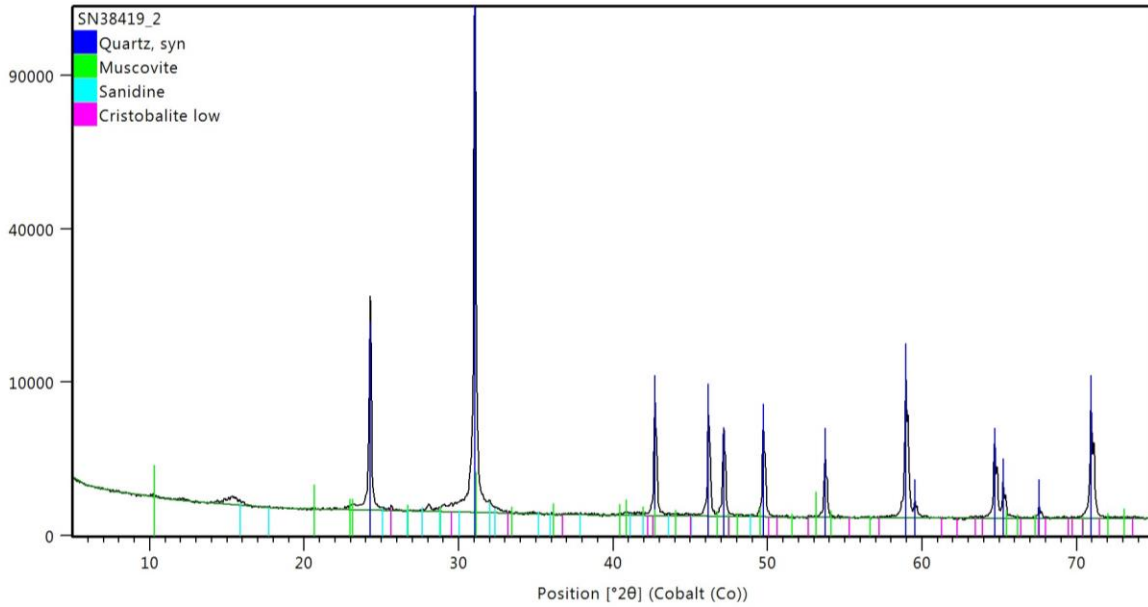
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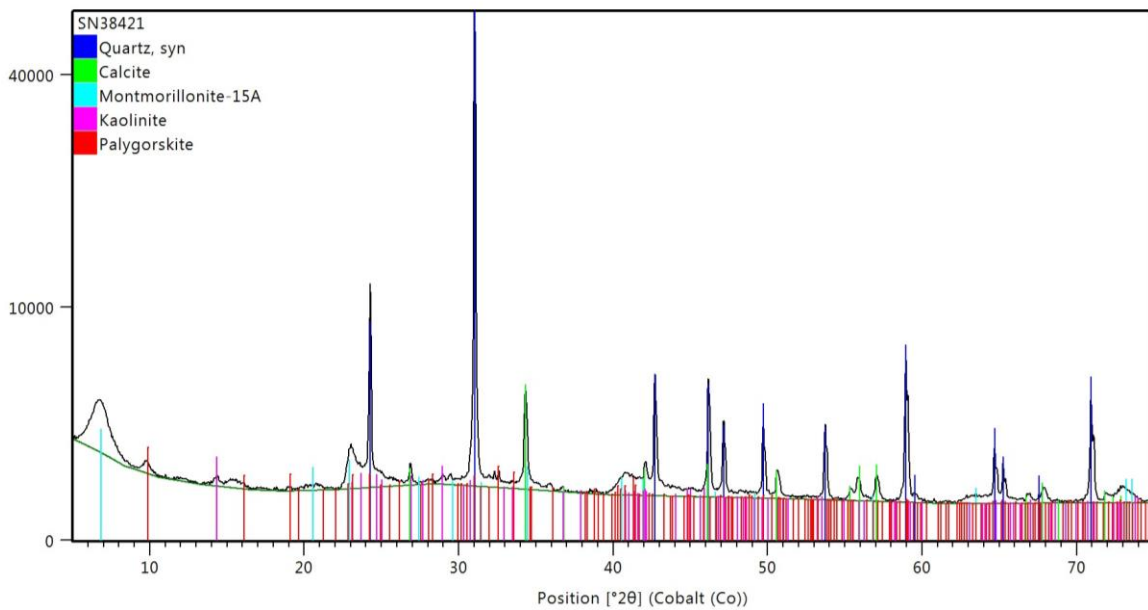
610 **SI 2 X-ray diffraction**

611 X-ray diffractograms of the soils were obtained with a Philips PW 3710 X-ray diffractometer  
612 using CoK $\alpha$  radiation at 40 kV and 40 mA (a counting time of 12 s per 0.02° step was used for the  
613 2 h range 5–75°)

614 **a**  
Counts



615 **b**  
Counts



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

617 **SI 3 Experimental design**

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



625  
626 Figure SI 3: Soil column

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

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

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

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

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

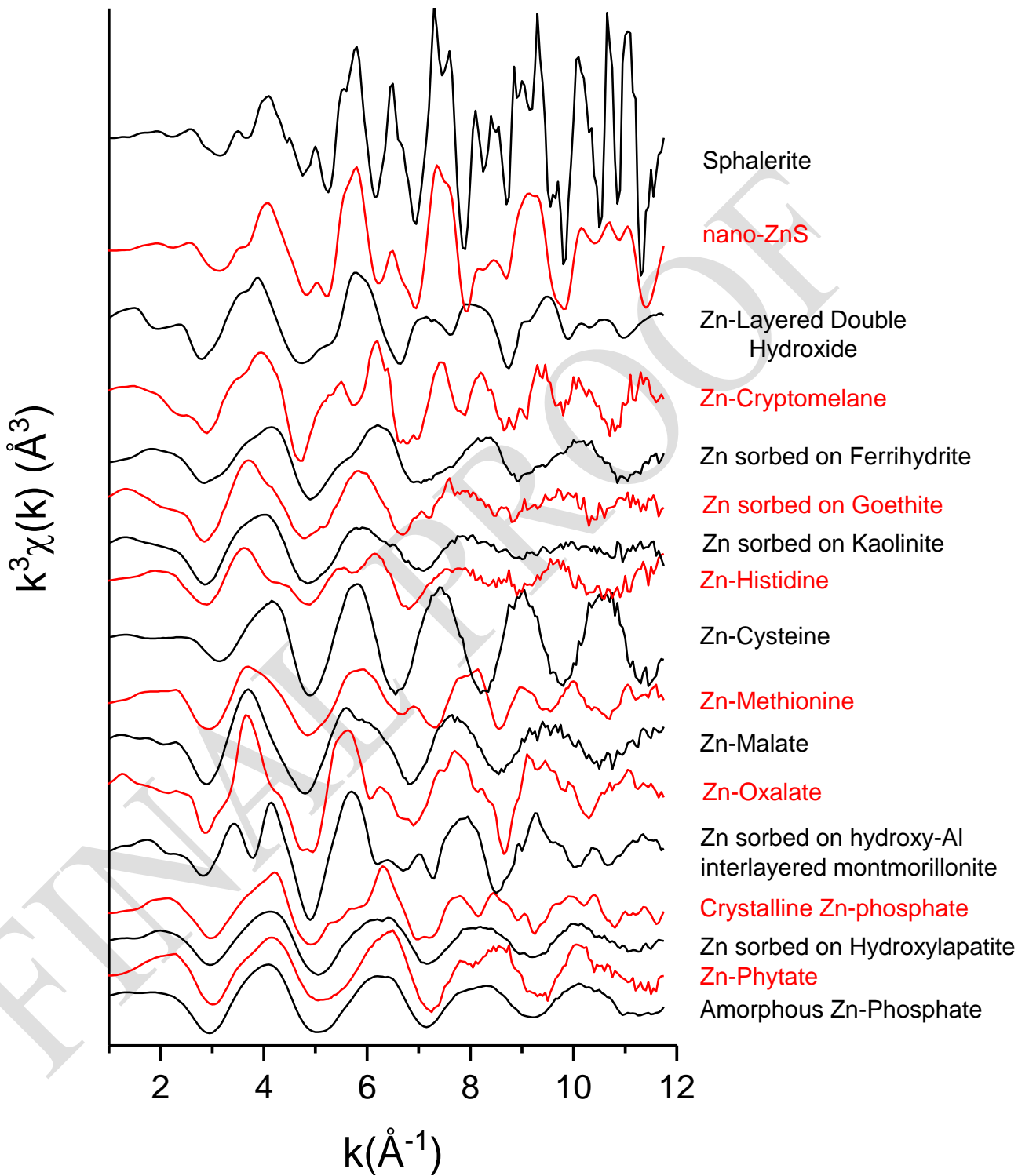
639 where AD (kg.dm<sup>-3</sup>) corresponds to the apparent density or bulk density measured for each soil  
640 *in situ*, and RD corresponds to the real particle density (expressed in kg.dm<sup>-3</sup>) estimated at 2.65 kg  
641 .dm<sup>-3</sup> for both soils.

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

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

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

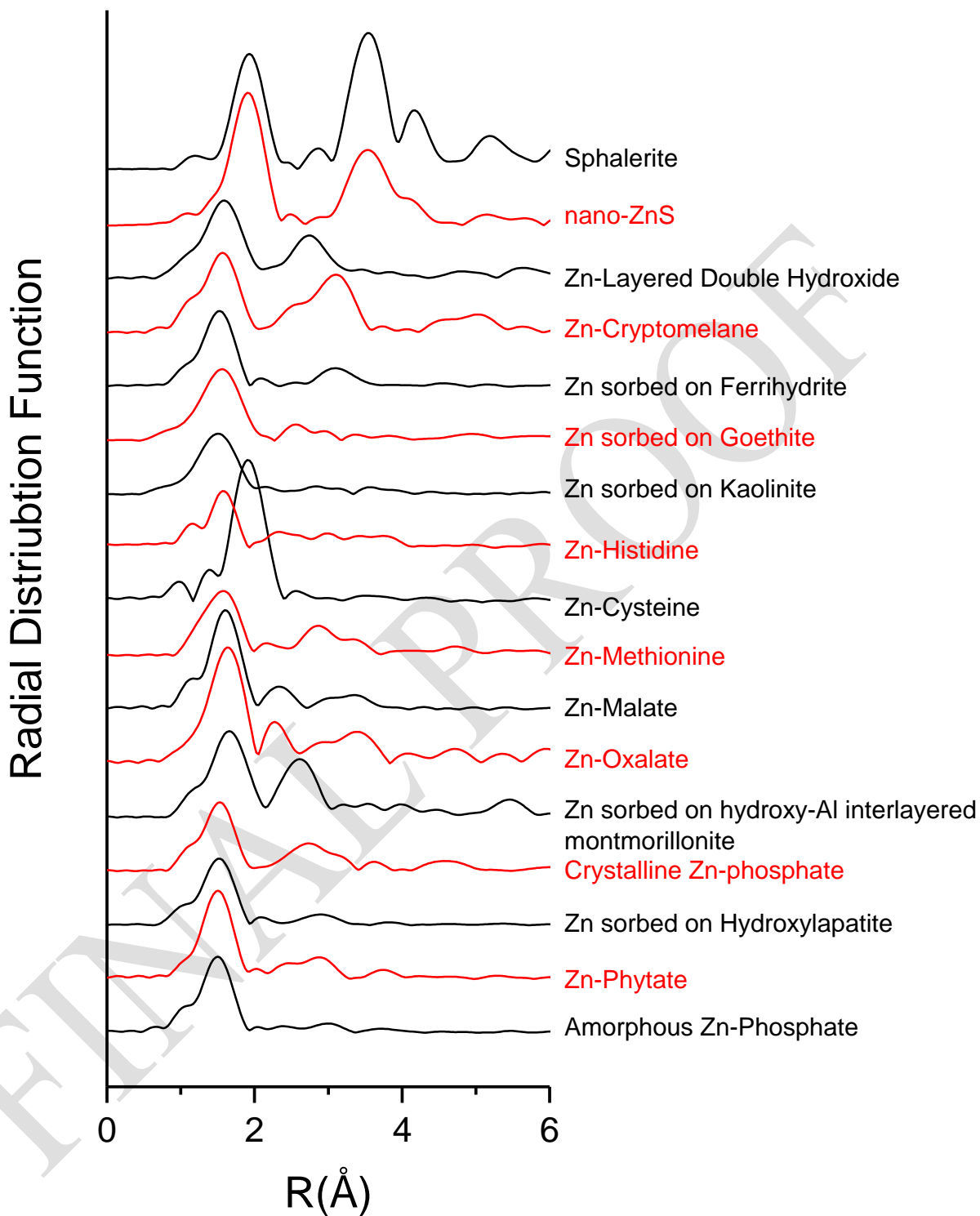
653 Three replicates were performed for each treatment (a treatment is defined as a soil and an OW)  
654 representing a total of 18 soil columns.



656

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

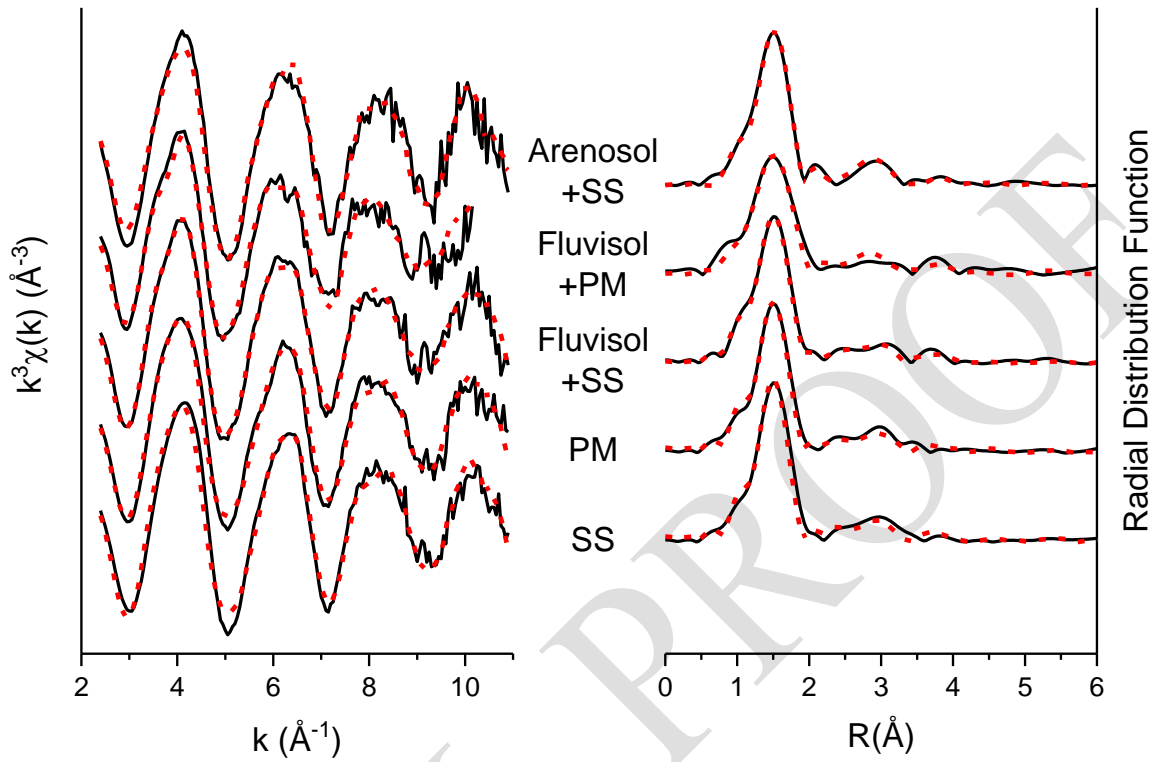
658 reference compounds.



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

667

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

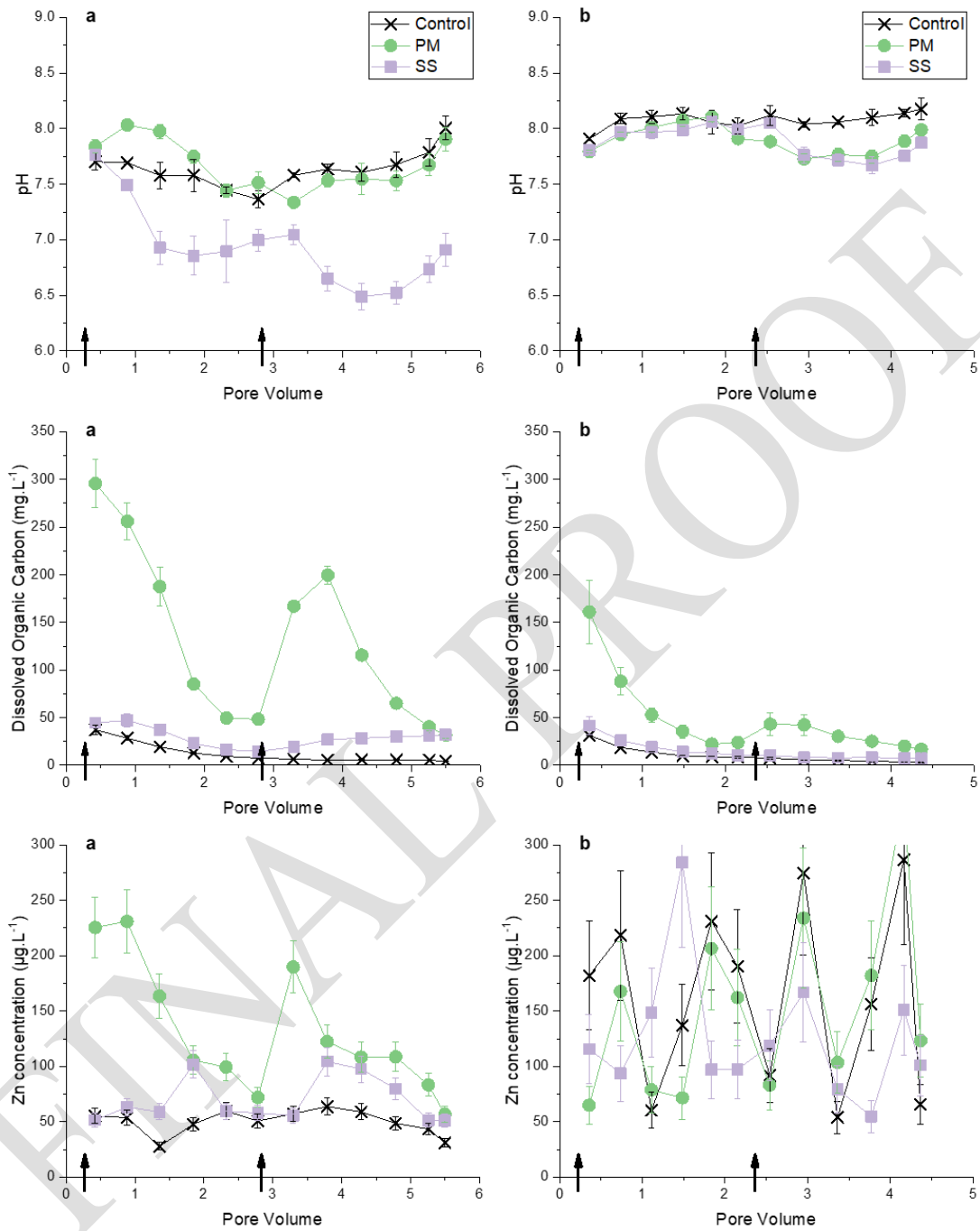
	Amorphous Zn-phosphate	Zn-phytate	Cristalline Zn-phosphate	Zn sorbed on hydroxylapatite	Zn sorbed on hydroxy-Al interlayered montmorillonite	R-factor*
Arenosol + SS		14%		97%		0.050
Fluvisol + PM	75%				14%	0.063
Fluvisol + SS	91%				10%	0.029
PM	96 %		10%			0.030
SS	86 %	15 %				0.037

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

670

671

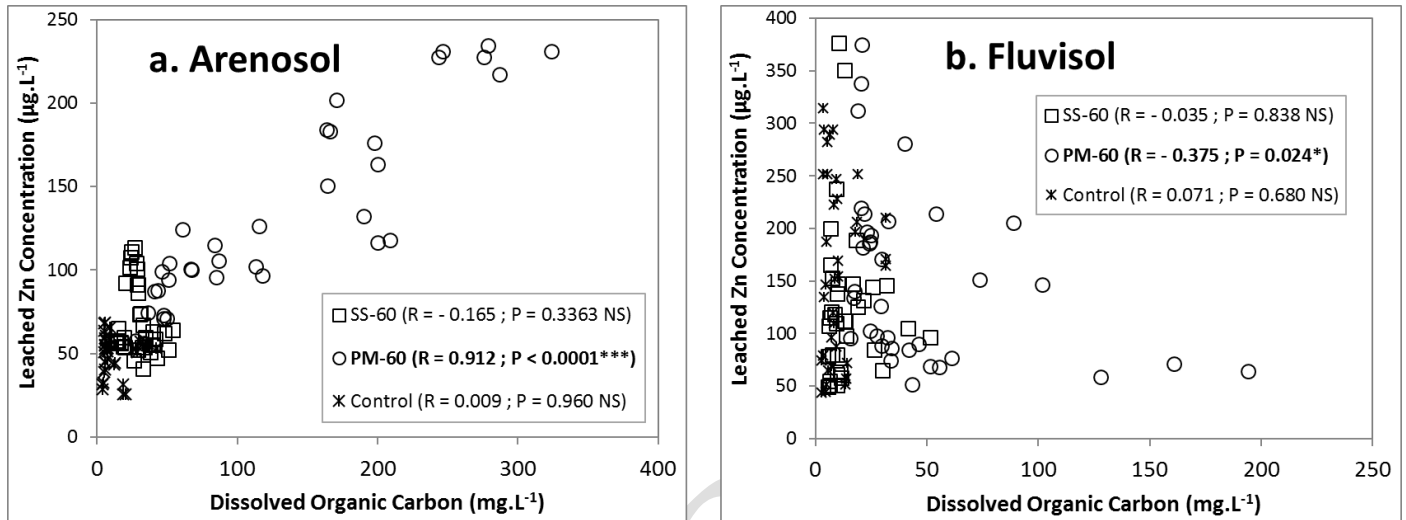
672 **SI 6 variations in pH, DOC and Zn in the drained water at the soil column outlets.**



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

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

679



680  
681

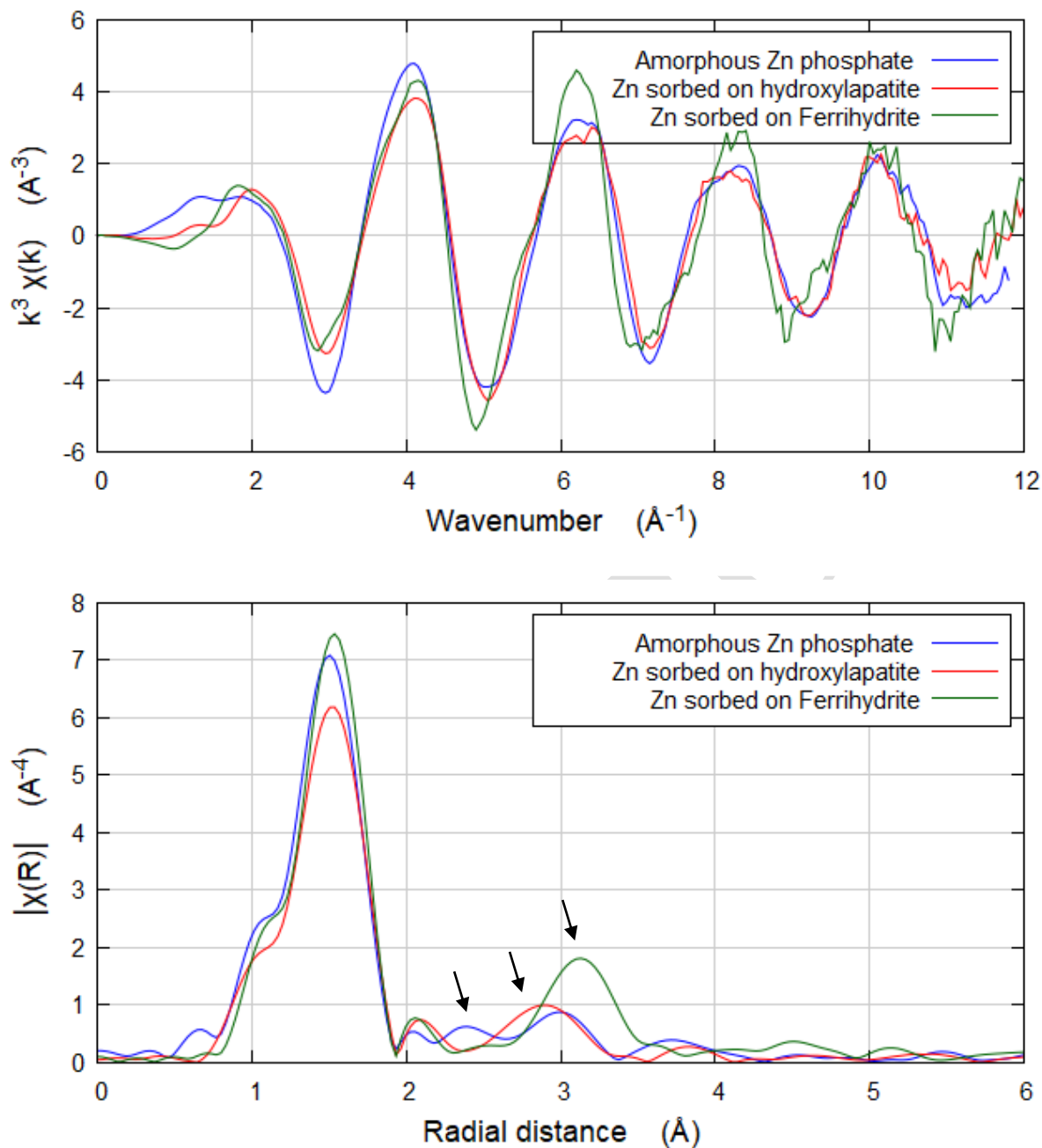
682 Figure SI 7: Zn concentration as a function of dissolved organic carbon in drained water at the  
683 column outlets of the Arenosol (a) and Fluvisol (b). R corresponds to the Pearson linear correlation  
684 coefficient; NS = not significant; Significance level: \* =  $p < 0.05$ , and \*\*\* = 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

685

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

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

695



696

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

700

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