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1 Contrasted fate of zinc sulfide nanoparticles in soil 2 revealed by a combination of X-ray absorption 3 spectroscopy, diffusive gradient in thin films and 4 isotope tracing

*Maureen Le Bars**^{a, b, 1}, *Samuel Legros*^c, *Clément Levard*^a, *Claire Chevassus-Rosset*^b,
Mélanie Montes^b, *Marie Tella*^d, *Daniel Borschneck*^a, *Abel Guihou*^a, *Bernard Angeletti*
^a, *Emmanuel Doelsch*^b

5 ^a Aix Marseille Univ, CNRS, IRD, INRAE, Coll France, CEREGE, Aix-en-Provence, France

6 ^b UPR Recyclage et Risque, CIRAD, F-34398 Montpellier, France; Recyclage et Risque, Univ.
7 Montpellier, CIRAD, Montpellier, France

8 ^c UPR Recyclage et Risque, CIRAD, 18524 Dakar, Senegal; Recyclage et Risque, Univ. Montpellier,
9 CIRAD, Montpellier, France

10 ^d CIRAD, US Analyse, F-34398 Montpellier, France. Analyse, Univ Montpellier, CIRAD, Montpellier,
11 France

12 *Corresponding author : maureen.lebars@usys.ethz.ch

13 **Abstract**

14 Incidental zinc sulfide nanoparticles (nano-ZnS) are spread on soils through organic waste (OW)
15 recycling. Here we performed soil incubations with synthetic nano-ZnS (3 nm crystallite size),
16 representative of the form found in OW. We used an original set of techniques to reveal the fate of nano-
17 ZnS in two soils with different properties. ⁶⁸Zn tracing and nano-DGT were combined during soil
18 incubation to discriminate the available natural Zn from the soil, and the available Zn from the dissolved
19 nano-⁶⁸ZnS. This combination was crucial to highlight the dissolution of nano-⁶⁸ZnS as of the third day
20 of incubation. Based on the extended X-ray absorption fine structure, we revealed faster dissolution of
21 nano-ZnS in clayey soil (82% within 1 month) than in sandy soil (2% within 1 month). However, the
22 nano-DGT results showed limited availability of Zn released by nano-ZnS dissolution after 1 month in
23 the clayey soil compared with the sandy soil. These results highlighted: (i) the key role of soil properties
24 for nano-ZnS fate, and (ii) fast dissolution of nano-ZnS in clayey soil. Finally, the higher availability of
25 Zn in the sandy soil despite the lower nano-ZnS dissolution rate is counterintuitive. This study
26 demonstrated that, in addition to nanoparticle dissolution, it is also essential to take the availability of
27 released ions into account when studying the fate of nanoparticles in soil.

¹ Present address: Institute of Biogeochemistry and Pollutant Dynamics, CHN, ETH Zurich, 8092
Zurich, Switzerland

28 **Keywords**

29 Dissolution, availability, clay, sand, speciation

30

31 Introduction

32 Incidental nanoparticles (NPs) are unintentionally formed as a consequence of human activities. We
33 recently illustrated this phenomenon by showing that nanosized zinc sulfide compounds (nano-ZnS) are
34 systematically formed in organic waste (OW) during anaerobic digestion or in liquid OW during storage,
35 thereby boosting nano-ZnS concentrations to up to 1240 mg_{Zn}.kg_{OW}⁻¹.¹ Zn is present in high quantities
36 in OW regardless of the origin: urban, industrial or agricultural (40-4000 mg.kg⁻¹).²⁻⁶ Nano-ZnS are
37 incidentally spread on soils when OW are applied as fertilizer on cropland. Considering the high Zn
38 concentrations in OW, incidental nano-ZnS are released to a substantially greater extent in soils via
39 agricultural recycling than engineered nano-ZnO, for example (predicted concentration in sewage
40 sludge of about 20 mg.kg⁻¹ in Europe, US and Switzerland⁷). Nano-ZnS is also a product of nano-ZnO
41 sulfidation during OW anaerobic treatment.^{8,9} However, the environmental fate of nano-ZnS has been
42 little investigated compared to pristine nano-ZnO, which has been extensively studied over the last 10
43 years.¹⁰⁻¹² Nano-ZnS is a good example of high incidental NP release in the environment that would
44 warrant environmental risk assessment.¹³

45 Only a few studies have focused on nano-ZnS toxicity in soil.¹⁴⁻¹⁶ Oleszczuk *et al.* (2019)¹⁴ documented
46 the toxicity of around 15 nm ZnS generated by nano-ZnO sulfidation. At 250 mg_{Zn}.kg_{OW}⁻¹, nano- ZnS
47 induced 20% *Folsomia candida* mortality and reproduction inhibition in OW-amended soil. Some
48 authors have reported that NP ecotoxicity correlates with the amount of ions released from NP
49 dissolution (e.g. Ag, ZnO).^{11,12,17} Zn-based NP dissolution causes the release of free Zn²⁺ ions that are
50 potentially bioavailable, i.e. freely available to cross an organism's cellular membrane.¹⁸ This fraction
51 can have toxic effects when taken up by living organisms.

52 NPs are considered to be less chemically stable (i.e. dissolve more quickly) than their bulk homologues
53 due to their small size.^{19,20} Nano-ZnS incidentally formed in OW are smaller (3-5 nm^{1,21-23}) than the 15
54 nm nano-ZnS studied by Oleszczuk *et al.* (2019).¹⁴ Their toxicity due to Zn release by NP dissolution
55 could therefore be higher. Findings published so far have shown that nano-ZnS formed in OW dissolve
56 within 2 to 6 months in OW or soil,^{1,8,23} but the kinetics of this process at the day scale has been
57 overlooked and needs further investigation.

58 Besides the nanoparticle size, soil properties can also influence nano-ZnS dissolution and released Zn
59 availability. Voegelin *et al.* (2011)²⁴ revealed different nano-ZnS dissolution kinetics for four soils with
60 different pH, clay and organic carbon content. Numerous studies have highlighted the capacity of
61 phyllosilicates and iron oxides to sorb Zn in soil,^{23,25-29} thereby suggesting that the soil mineralogy can
62 control Zn availability in soils because of the varying affinity with the different mineral surfaces. It
63 would thus be essential to identify the soil properties that could influence nano-ZnS dissolution and
64 released Zn availability so as to better predict the nano-ZnS fate in OW-amended soil.

65 The objective of this study was to determine how soil properties can influence nano-ZnS dissolution
66 kinetics and released Zn availability in soils. Synthesized nano-ZnS representative of nano-ZnS detected
67 in OW were incubated in two different soils with different properties over a 1 month period. The first
68 soil was a silty-clay soil from the island of Réunion (Nitisol) while the second was a sandy-loamy soil
69 from Senegal (Arenosol). We used ^{68}Zn -labelled nano-ZnS to discriminate natural Zn from soil and Zn
70 from nano-ZnS while applying a realistic nano-ZnS input rate ($10 \text{ mg}_{\text{Zn}}.\text{kg}_{\text{soil}}^{-1}$). During this incubation,
71 the availability of ^{68}Zn released by nano- ^{68}ZnS dissolution was evaluated over a time course by
72 measuring the isotopic composition of Zn accumulated on nano-DGT resin (diffusive gradients in thin
73 films [DGT] with 3 kDa dialysis membrane). Then a second incubation with $200 \text{ mg}_{\text{Zn}}.\text{kg}_{\text{soil}}^{-1}$ applied
74 nano-ZnS was carried out to determine Zn speciation changes by X-ray absorption spectroscopy (XAS)
75 after 1 month incubation.

76 Materials and Methods

77 Soils

78 Two soils with different properties were selected for this study (Table 1). Nitisol is a silty-clay soil that
79 was sampled in the 0-20 cm layer at La Mare on the tropical volcanic island of Réunion. Arenosol is a
80 sandy-loamy soil that was sampled in the 0-20 cm layer at Sangalkam (30 km west of Dakar) in Senegal.
81 The sampling procedure has been described previously in Doelsch et al. (2010).³⁰ The soils were
82 analyzed according to the methods described in the supporting data, part I. The mineralogy of both soils
83 was characterized by X-ray diffraction (XRD) after grinding. XRD was performed on a Panalytical
84 X'Pert Pro MPD X-ray diffractometer, with cobalt $\text{K}\alpha$ radiation ($\lambda=1.79\text{Å}$) at 40 kV and 40 mA. An
85 X'Celerator detector was used (a counting time of 5 s per 0.033° step was used for the 2θ $5\text{--}75^\circ$ range).

86 Incubation experiment for *in situ* monitoring of Zn availability

87 The first experiment was designed to determine Zn availability subsequent to release by nano- ^{68}ZnS
88 dissolution in soils over a time course during a 1 month incubation experiment.

89 ^{68}Zn (18.75% naturally abundant) was chosen to synthesize labelled nano-ZnS. Zn oxide enriched in
90 ^{68}Zn (99.16%), i.e. ^{68}ZnO , was purchased from Isoflex. ^{68}ZnO was dissolved at 35 mM concentration in
91 HCl (0.1 M). NaOH was added to this solution to increase its pH from 1.2 to 5.1. Nano- ^{68}ZnS was
92 synthesized by mixing two solutions of dissolved ^{68}Zn and Na_2S . Initial Zn and S concentrations were
93 selected to have an initial S/Zn molar ratio of 0.9 and a final ZnS concentration of 0.014 M. The pH was
94 3.6 after mixing the two solutions. After 5 days of rotative agitation in the dark, the suspension was
95 dialyzed (MWCO = 1 kDa) against ultrapure water to remove excess Na^+ and Cl^- ions. Finally,
96 synthesized nano- ^{68}ZnS were freeze-dried and ground for XRD characterization and incubation
97 experiments. XRD was performed on a Panalytical X'Pert Pro MPD, X-ray diffractometer, with cobalt
98 $\text{K}\alpha$ radiation ($\lambda=1.79\text{Å}$) at 40 kV and 40 mA. An X'Celerator detector was used with a counting time of
99 1400 s per 0.0334° step for the 2θ $20\text{--}75^\circ$ range. The X-ray diffractogram is shown in Figure S1. The

100 crystallite size of synthesized nano-⁶⁸ZnS determined on the (220) peak according to the Scherrer
101 equation was 2.8 nm.³¹

102 To study the nano-ZnS transformation on a day scale, an incubation experiment was carried out in
103 controlled conditions using the two selected soils, according to the incubation set-up applied in Tella et
104 al. (2016).³² The soils were incubated for 28 days, in line with other soil and OW incubation studies
105 focused on heavy metals issues.^{30,33-35} Nano-⁶⁸ZnS was added to soil according to actual fertilizing
106 practice (OW spreading rate: 0.01 kg_{OW}.kg_{soil}⁻¹) and considering OW with 1000 mg.kg_{OW}⁻¹ of Zn as
107 nano-ZnS. A corresponding amount of nano-⁶⁸ZnS (10 mg_{Zn}.kg_{DM soil}⁻¹) was mixed with dried soil (40°C)
108 using a powder mixer (Turbula ® T2F T10B). The mixed soil was distributed into cylindrical PVC
109 microcosms with an internal diameter of 4.4 cm (30 g_{DM soil}/microcosm) containing a nano-DGT (R-
110 LSLM, DGT Research LTD) with four replicates per condition. Soils were packed to reach a density of
111 1.3 g.cm⁻³ and 2.1 g.cm⁻³ for the Nitisol and Arenosol, respectively, which were close measured field
112 densities. Ultrapure water was added to reach a water content of 66% of the maximum water holding
113 capacity (WHC) of the soil. Microcosms were incubated in a closed thermostatic chamber at 28 +/- 1
114 °C with the soil humidity adjustment weekly. Control soils without nano-⁶⁸ZnS were treated similarly.

115 The diffusive gradients in thin films (DGT) measurement provides a calculated Zn concentration
116 representing the diffusion limited, time averaged labile Zn concentrations in the soil. The Zn mass
117 accumulated on DGT resin is correlated with the Zn availability in the soil solution.³⁶ DGT devices have
118 previously been used to quantify a labile form of a range of metals and nutrients in soils.³⁷⁻³⁹³ DGT
119 measurement includes Zn resupplied from the solid phase in response to the disequilibrium caused by
120 depletion of the labile Zn pool at the surface of the device.⁴⁰ Specific nano-DGT devices were used in
121 this study (LSLM-NP from DGT Research Ltd, UK). Their three kDa dialysis membranes mounted in
122 front of the diffusive gel prevent nanoparticle diffusion.^{41,42} The nano-DGT devices were placed in the
123 microcosm at the beginning of the incubation before soil packing and humidification. After 1, 3, 7, 14
124 and 28 days incubation, the resin layer of nano-DGT devices in contact with soil was retrieved with
125 plastic tweezers and eluted in 1 mL of 1 M ultra-pure HNO₃ (Normatom®; VWR Chemicals), in a closed
126 Eppendorf tube for 24 h at 20°C. The eluate was then diluted in a 2% HNO₃ solution for isotopic ratio
127 measurement. In a previous study with the same incubation set-up and the same Nitisol, it was shown
128 that the binding capacity of the DGT binding layer was not saturated after 90 days of incubation.³²

129 The Zn isotope composition of the nano-DGT eluates was measured with a ICP-MS Nexion 300x
130 (Perkin Elmer) in reaction mode, using helium (0.2 mL.min⁻¹). From the measured ⁶⁸Zn/⁶⁶Zn ratio (R_m),
131 we derived the following equations (demonstration can be found in the supporting data, Part III):

132 1. The $\Delta^{68}\text{Zn}/^{66}\text{Zn}$ in the nano-DGT eluates:

133
$$(\Delta^{68}\text{Zn}/^{66}\text{Zn})_{DGT} = \frac{R_m}{R_{nat}} - \frac{R_{m_{control\ soil\ at\ t=1day}}}{R_{nat}}$$

134 R_{nat} is the natural $^{68}\text{Zn}/^{66}\text{Zn}$ ratio (0.672) verified with a natural Zn solution (Synthetic water EP-L3
 135 (SCP Sciences); $[\text{Zn}] = 0.0425 \text{ mg.kg}^{-1}$, 6 measurements) and the $R_{control \text{ soil at } t=1\text{day}}$ is the measured
 136 $^{68}\text{Zn}/^{66}\text{Zn}$ ratio in each control soil type after 1 day of incubation. Given that the amount of nano- ^{68}ZnS
 137 synthesized with the ^{68}Zn spike added to each soil was similar, the $(\Delta^{68}\text{Zn}/^{66}\text{Zn})_{DGT}$ traces the amount of
 138 Zn released by nano- ^{68}ZnS dissolution and accumulated on the DGT resin and enables us to compare
 139 the results of the two soils.

140 2. The mass balance equation to calculate $m\text{Zn}_{sp}/m\text{Zn}_{tot}$ ratio:

141
$$\frac{m\text{Zn}_{sp}}{m\text{Zn}_{tot}} = \left[1 + \frac{M(\text{Zn}_{nat})}{M(\text{Zn}_{sp})} \times \frac{Ab_{sp}^{66}}{Ab_{nat}^{66}} \times \frac{R_m - R_{sp}}{R_{nat} - R_m} \right]^{-1}$$
 and hence $\frac{m\text{Zn}_{nat}}{m\text{Zn}_{tot}} = 1 - \frac{m\text{Zn}_{sp}}{m\text{Zn}_{tot}}$

142 $m\text{Zn}_{sp}$ and $m\text{Zn}_{tot}$ are the mass of Zn accumulated on the nano-DGT resin, derived from the spike (i.e.
 143 ^{68}Zn solution used to synthesize the nano- ^{68}ZnS) and total Zn (natural Zn and Zn derived from the spike),
 144 respectively. R_{sp} is the $^{68}\text{Zn}/^{66}\text{Zn}$ ratio in the spike ($R_{sp} = 619.8$ from the the Isoflex ^{68}ZnO certificate).
 145 $M(\text{Zn}_{sp})$ and $M(\text{Zn}_{nat})$ are the molar masses (g.mol^{-1}) of Zn used to synthesize nano- ^{68}ZnS and natural
 146 Zn, respectively. Ab_{nat}^{66} and Ab_{sp}^{66} represent the abundance of ^{66}Zn isotopes in natural zinc and spiked
 147 zinc, respectively. Errors on $\Delta^{68}\text{Zn}/^{66}\text{Zn}$ and $m\text{Zn}_{sp}/m\text{Zn}_{tot}$ were estimated lower than 20% and 5%,
 148 respectively. The analytical methods are described in further detail in the supporting data, part III.

149 After retrieving the nano-DGT resin, 1 g of soil was used for microbial activity determination
 150 (supporting data, part IV) and soil pore water was extracted for pH measurement (supporting data, part
 151 V).

152 Statistical tests were performed with XLSTAT software to compare $(\Delta^{68}\text{Zn}/^{66}\text{Zn})_{DGT}$. A Kruskal-Wallis
 153 test (5% significance) was used for the comparison of the samples ($n=10$) according to one parameter
 154 ($(\Delta^{68}\text{Zn}/^{66}\text{Zn})_{DGT}$). The four values obtained from the four replicates were considered for this
 155 comparison. In case of rejection of the null hypothesis ($H_0 =$ all samples from the same population), a
 156 Conover-Iman post-hoc test was used for multiple pair-wise comparison with Bonferroni correction.
 157 The p-values obtained were compared to the corrected Bonferroni significance levels (0.0011) to
 158 determine significant differences.

159 Incubation experiment for characterization of Zn speciation

160 A second experiment was carried out to determine Zn speciation after 1 month incubation using the
 161 selected soils amended with nano-ZnS.

162 Nano-ZnS were synthesized by mixing ZnCl_2 and Na_2S solutions to reach a final ZnS concentration of
 163 0.04 M with a molar ratio S/Zn of 0.5. The suspension pH after mixing was 3.6. After 10 days of rotative
 164 agitation in the dark, the suspension was dialyzed (MWCO = 1kDa) against ultrapure water. Finally,
 165 synthesized nano-ZnS was freeze-dried and ground for XRD characterization and homogeneous mixing
 166 with soil. The XRD parameters were the same as for nano- ^{68}ZnS characterization and the X-ray

167 diffractogram is shown in Figure S2. A crystallite size of 2.5 nm was determined with the Scherrer
168 equation.³¹

169 10 g of both soils were mixed with nano-ZnS at a concentration of 200 mg_{Zn}.kg_{DM soil}⁻¹. We opted for
170 this concentration to be able to determine the speciation of exogenous Zn resulting from the nano-ZnS
171 input in the light of the X-ray absorption spectroscopy detection limit and the natural Zn concentration
172 of the Nitisol (170 mg.kg⁻¹). Soils mixed with nano-ZnS were packed and humidified in the same
173 conditions as in the first incubation. After 1 month, the soils were freeze-dried and ground for XAS
174 characterization.

175 Zn K-edge absorption spectra were recorded at the SOLEIL synchrotron (Saclay, France) on the
176 SAMBA beamline. Each spectrum was measured at 10-15 K to prevent sample beam damage. Spectra
177 were measured in fluorescence mode with a Canberra 35-element Ge detector. The spectra were an
178 average of up to 40 scans, depending on noise level. Energy calibration was performed using a metallic
179 Zn reference foil (absorption edge defined at 9659 eV). Normalization and data reduction were
180 performed using Athena software.⁴³

181 Least square linear combination fitting (LCF) was performed for each soil spectrum over a k-range of
182 2.5 - 10.6 Å⁻¹ using Athena software. The library of Zn reference compounds, used to identify Zn species
183 in soils, included reference compounds described elsewhere^{1,22,32,44-47} (Amorphous Zn-phosphate,
184 commercial ZnS, Zn-cysteine, Zn-histidine, Zn-malate, Zn-sorbed to ferrihydrite (Zn-FeO_x), Zn-
185 methionine, Zn-cryptomelane, Zn-phosphate, Zn-phytate, Zn-goethite, Zn-oxalate-hydrate, sphalerite,
186 smithsonite, zincite and Zn hydroxide). The quality of the LCF was evaluated using the residual factor
187 $R = \Sigma(k^3\chi(k)_{exp} - k^3\chi(k)_{fit})^2 / \Sigma(k^3\chi(k)_{exp})^2$. At each step of the fitting, an additional reference
188 spectrum was added if the two conditions were fulfilled: the R factor decreased by 20% or more and the
189 additional reference had a contribution equal to or higher than 10% among Zn species. The uncertainty
190 of this LCF method was estimated at +/- 15%. The sum of fitted fractions (96 and 109% respectively
191 for the Nitisol and Arenosol) were normalized to 100 % for comparison.

192 Results and Discussion

193 Increased Zn availability in the Arenosol exposed to nano-⁶⁸ZnS

194 The ($\Delta^{68}\text{Zn}/^{66}\text{Zn}$)_{DGT} was significantly higher in soils exposed to nano-⁶⁸ZnS than in the control soils,
195 since the third day of exposure in both soils (Figure 1 a, b) and throughout the incubation period. This
196 difference indicated that a significant fraction of ⁶⁸Zn accumulated in the nano-DGT resin originated
197 from nano-⁶⁸ZnS dissolution, regardless of the soil type. The time-course pattern was similar for the two
198 soils: there was a rapid increase of the ($\Delta^{68}\text{Zn}/^{66}\text{Zn}$)_{DGT} during the three first days of incubation and a
199 second phase characterized by a slight increase.

200 The same nano-⁶⁸ZnS mass was applied to both soils, representing 6 and 30% of the total Zn in the
201 Nitisol and Arenosol microcosms, respectively (Figure 2 a). However, ⁶⁸Zn released by nano-⁶⁸ZnS
202 dissolution accounted for 50% and 75% of the total Zn accumulated on nano-DGT resin in the Nitisol
203 and Arenosol, respectively (Figure 2 b). This highlights the chemical instability⁴⁸ of nano-⁶⁸ZnS and
204 their higher potential to release available Zn compared to naturally occurring Zn.

205 The ($\Delta^{68}\text{Zn}/^{66}\text{Zn}$)_{DGT} was significantly greater in the Arenosol than in the Nitisol from the third day of
206 incubation (Figure 1 c). The higher ($\Delta^{68}\text{Zn}/^{66}\text{Zn}$)_{DGT} noted for the Arenosol compared to that of the
207 Nitisol could be explained by an increased dissolution of applied nano-⁶⁸ZnS and/or higher availability
208 of released ⁶⁸Zn.

209 The difference in the nano-⁶⁸ZnS chemical stability in these two soils could not be revealed by the
210 ($\Delta^{68}\text{Zn}/^{66}\text{Zn}$)_{DGT} alone. Indeed, we could not determine whether the lower ($\Delta^{68}\text{Zn}/^{66}\text{Zn}$)_{DGT} for the Nitisol
211 was due to a lower dissolution of nano-⁶⁸ZnS and/or lower availability of released ⁶⁸Zn. Extended X-ray
212 absorption fine structure (EXAFS) characterization of soils after nano-ZnS application appeared to be a
213 suitable method for evaluating nano-ZnS stability in soils.

214 Zn speciation reveals nano-ZnS dissolution in the Nitisol

215 A significantly different fate of nano-ZnS in the two soils was highlighted by contrasted EXAFS spectra
216 1 month after nano-ZnS application (Figure 3). The Arenosol + nano-ZnS spectrum was similar to the
217 nano-ZnS reference spectrum with structured oscillations (e.g. 6.5, 7.5 and 9.1 Å⁻¹), whereas the Nitisol
218 + nano-ZnS spectrum had smoother oscillations with few structured features similar to the Zn-kaolinite
219 and Zn-iron oxide (Zn-FeOx) reference compounds. Linear combination fitting (LCF) of the Nitisol +
220 nano-ZnS spectrum involved a combination of four references (36% Zn-kaolinite, 39 % Zn-FeOx, 15 %
221 Zn-cryptomelane, 10 % nano-ZnS). At the beginning of the incubation period, 2 mg of Zn as nano-ZnS
222 were applied on the Nitisol, representing 54% of the total zinc in soil (T0 in Figure 4). However, after
223 1 month incubation, the nano-ZnS fraction only represented 10% of the total zinc. This decrease revealed
224 the dissolution of 1.6 mg of nano-ZnS in the Nitisol, i.e. 82% of the applied nano-ZnS. Conversely, the
225 Arenosol + nano-ZnS spectrum were fitted with nano-ZnS (88%) and Zn bound to an undefined soil
226 compound (12%) after 1 month incubation (using Zn-kaolinite, Zn-phosphate or Zn-iron oxide reference

227 spectra gave the same quality of fit). Originally, the 2 mg of applied nano-ZnS represented 90% of the
228 total zinc in the Arenosol exposed to nano-ZnS (T0 on Figure 4). The final speciation after 1 month
229 incubation revealed the dissolution of 0.04 mg of Zn as nano-ZnS, i.e. 2% of the nano-ZnS dissolved
230 (Figure 4). This comparison revealed that there was more dissolution of applied nano-ZnS in the Nitisol
231 than in the Arenosol.

232 The full picture: when nanoparticle dissolution does not mean increased availability 233 in soils

234 *Evidence of fast 3 nm nano-ZnS dissolution*

235 The nano-⁶⁸ZnS dissolution pattern starting during the third day of soil incubation (Figure 1 a and b),
236 highlighted faster dissolution than has been observed to date. In a previous field study, we had shown
237 that nano-ZnS (~ 3 nm crystallite size), which accounted for 100% of speciation in pig slurry, was not
238 detected in a clayey soil 6 months after pig slurry amendment,²³ but no measurements of Zn speciation
239 in amended soil were performed at shorter times. Here, by combining nano-DGT and ⁶⁸Zn tracing, we
240 were able to monitor nano-ZnS dissolution at a day scale. Fast nano-ZnS dissolution was detected for
241 both soils, regardless of their properties.

242 3 nm nano-ZnS dissolved more quickly (e.g. 82 % after 1 month in the Nitisol, Figure 4) compared to
243 larger ZnS particles. Indeed, Voegelin *et al.* (2011)²⁴ assessed the dissolution of commercial ZnS (25-
244 40 nm) in four different soils. The fastest dissolution rate was observed for a loamy soil in which 76%
245 of nano-ZnS had dissolved within 2 years. For 63 μm sphalerite crystals, dissolution rates in soils were
246 even slower: 0.6 to 1.2% within 1 year.⁴⁹ Moreover, in our previous study, we had shown the dissolution
247 of nano-ZnS (3 nm) formed in OW within 2 months of composting.¹ Therefore, the fast dissolution of
248 nano-ZnS of around 3 nm size could be explained by the nanosize of these compounds. Indeed, structural
249 changes induced by the < 20 nm size could affect the NP chemical stability.¹⁹ More specifically, 3.4 nm
250 nano-ZnS exhibited a significant lattice contraction compared to their bulk homologues.⁵⁰ Lattice
251 contraction is interpreted as being the result of the hydrostatic pressure exerted by surface stress within
252 a continuum elastic model.⁵¹ We hypothesize that particles with lattice contraction are more reactive
253 than larger particles due to increased surface stress.

254 *Enhancement of nano-ZnS dissolution in clayey soils*

255 After 1 month incubation in the Arenosol, only 2% of 3 nm nano-ZnS compounds were dissolved as
256 compared to 82% observed for the Nitisol. Several assumptions could explain these discrepancies.

257 First, the mineralogical compositions of the Nitisol and Arenosol sharply contrasted (Figure 5). Quartz
258 mainly accounted for the Arenosol mineralogy whereas the Nitisol contained a more diversified
259 mineralogy with the presence of clays (kaolinite and halloysite), iron and aluminum oxy-hydroxide
260 (magnetite, hematite, goethite, ilmenite and gibbsite). Those minerals have been identified in the
261 literature for their capacity to sorb Zn.^{23,25-29} In the case of the Nitisol, our XAS results have shown that
262 Zn released by nano-ZnS dissolution is sorbed on iron oxides (ferrihydrite), clays (kaolinite), and

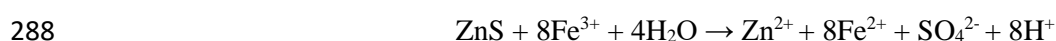
263 potassium manganese oxide (cryptomelane). Similarly, Formentini *et al.* (2017)²³ observed that Zn
264 released by 3 nm nano-ZnS dissolution was complexed with organic matter and sorbed to kaolinite and
265 iron oxides. These minerals are thus suspected to have an impact on nano-ZnS dissolution in Nitisol.
266 Indeed, in a simpler system with only nano-ZnS and water, Zn partitioning could reach equilibrium with
267 a given percentage of Zn in water and nano-ZnS. In a more complex soil system, waterborne Zn could
268 be sorbed on other solid surfaces in the soil (the minerals mentioned above). This sorption would
269 decrease the waterborne Zn concentration and induce more nano-ZnS dissolution.⁵² Such promoted
270 dissolution was not observed for larger particles: Voegelin *et al.* (2011)²⁴ observed only ~7% dissolution
271 of 25-40 nm nano-ZnS after 2 years for a clayey soil (47%, including kaolinite). We consider that both
272 the nano-scale and the soil mineralogy could drive the fate of ZnS in soil.

273 Nano-ZnS dissolution could also have been induced by the ligand competition mechanism in the Nitisol.
274 Indeed, ligand-mediated dissolution has already been reported for several nanoparticles. Siy *et al.*
275 (2010)⁵³ showed an increase in CdSe NPs dissolution in the presence of organic ligands (stearic acid,
276 oleic acid, octadecylamine). EDTA is a strong complexing agent that enhances Ag-NP dissolution.⁵⁴
277 Moreover, it was shown that CuS or HgS nanoparticles did not dissolve in oxic conditions without
278 natural organic matter.⁵⁵⁻⁵⁷ For ZnS, according to Zhang *et al.* (2010)⁵⁸ based on thermodynamic models,
279 small nano-ZnS compounds cannot dissolve without EDTA complexation in solution at pH 9-10. In the
280 Nitisol, organic ligands were more abundant than in the Arenosol, as shown by the C_{org} content of the
281 two soils (2.3 and 0.76%, respectively (Table 1)). As natural organic matter is known to bind trace
282 metals, including Zn,⁵⁹ Zn complexation with organic matter could also have contributed to nano-ZnS
283 dissolution in the Nitisol.

284 Biotic or abiotic sulfur oxidation could have enhanced nano-ZnS dissolution in the Nitisol. Indeed, ZnS
285 can be dissolved by sulfur oxidation in the presence of O₂⁶⁰ or via Fe³⁺ reduction:⁶¹



287 or



289 Heidel *et al.* (2011)⁶⁰ showed that sphalerite dissolution occurred through O₂-induced sulfur oxidation
290 during the first days. Then Fe²⁺ released by sphalerite dissolution was oxidized by O₂ and resulted in
291 sphalerite oxidation by Fe³⁺. *Thiobacillus ferrooxidans* bacteria were shown to enhance ZnS dissolution
292 by Fe²⁺ oxidation into Fe³⁺ combined with removal of the S⁰ layer formed at the ZnS surface, thereby
293 hindering the rate of Fe³⁺ diffusion.⁶² Some bacteria like *Acidithiobacillus thiooxidans* can directly
294 oxidize sulfur,⁶³ but *T. ferrooxidans* and *A. thiooxidans* have not been previously detected in agricultural
295 soils,^{64,65} probably because the pH in these soils is not within their optimal pH range (1.3-4.5).⁶⁶
296 Neutrophilic sulfur-oxidizing *Thiobacillus* bacteria have been detected in agricultural soils, including *T.*

297 *thioparus*, *T. denitrificans* and/or *T. plumbophilus*.^{64,65} In addition, ZnS dissolution could occur in
298 bacterial biofilms that form in soils, as shown by Desmau *et al.* (2020)⁶⁷ for CdSe/ZnS quantum dots in
299 *Shewanella oneidensis* biofilms. Our results did not show a significant difference between total
300 bacterial activity in the Nitisol and Arenosol (supporting data, Part IV). However, this does not exclude
301 the possibility that some specific biological activity not detected by the total bacterial activity
302 measurement, such as iron/sulfur oxidation, was higher in the Nitisol than in the Arenosol.

303 *Clayey soil properties limit Zn availability*

304 ⁶⁸Zn released by nano-⁶⁸ZnS dissolution had a contrasted fate depending on the soil type. As the XAS
305 results revealed faster dissolution in the Nitisol than in the Arenosol, we would expect that more ⁶⁸Zn
306 accumulated on the nano-DGT resin in the Nitisol, and therefore a higher ($\Delta^{68}\text{Zn}/^{66}\text{Zn}$)_{DGT}. The fact that
307 the opposite trend was observed suggests that the availability of Zn released by nano-ZnS dissolution
308 was strongly dependent on the soil properties. Indeed, Zn availability depends on its physicochemical
309 affinity for the different soil constituents. In particular, cation exchange reactions, specific adsorption
310 processes, surface precipitation on mineral surfaces or complexation with soil organic matter are
311 possible reactions that have been widely described to affect metal retention in soils.⁶⁸ These processes
312 are governed by the pH, which plays a key role in trace element partitioning between solid and solution
313 phases in soil.^{69,70} However, at t=28 days, the pH levels were quite similar, i.e. 4.7 and 5.1 for the Nitisol
314 and the Arenosol, respectively (supporting data, Part V). Therefore, we assumed that factors other than
315 pH control Zn availability in these soils. Several authors have argued that Nitisol has a stronger retention
316 capacity than Arenosol.

317 The cationic exchange capacity (CEC) is an overall indicator of the soil capacity to sorb cations,
318 including Zn²⁺, through cation exchange reactions. The CECs of the Nitisol and Arenosol were 11.6 and
319 7.1 cmol.kg⁻¹, respectively. The higher CEC value for the Nitisol could be explained by its higher clay
320 fraction (42.7%) compared to that in the Arenosol (10.2%). Isomorphous substitution of cations in clays
321 causes a pH-independent negative charge favoring cationic adsorption (e.g. Al³⁺ substitutes for Si⁴⁺ in
322 the tetrahedral sheet causing a negative charge).⁷¹ The clay fraction has been identified as the principal
323 driver of Zn retention in soils based on investigations on the solid/solution partitioning coefficient (K_d)
324 in various conditions and through statistical analysis of large soil datasets.⁷²

325 Specific (pH dependent) adsorption phenomena can also occur. A number of spectroscopic studies have
326 documented the formation of specific inner-sphere complexes on the surface of iron oxides and clays
327 identified in Nitisol (hematite, kaolinite, goethite). Zn was found to bind to hematite through a
328 mononuclear inner-sphere complex at pH 5.5.⁷³ Nachtegaal and Sparks showed that Zn formed a bi-
329 dentate inner-sphere sorption complex on the goethite surface at pH 5.⁷⁴ In the same study, they found
330 that Zn formed a monodentate inner-sphere sorption complex at the kaolinite surface with Zn binding
331 to Al-OH edge groups. Similar results were obtained for Zn sorbed on kaolinite at pH 5.5.⁷⁵ In all of the
332 above-cited studies, no surface precipitation was observed, which usually occurs at higher pH and

333 surface coverage.⁷⁴ Conversely, for quartz, the main Arenosol constituent, a combined isotopic and
334 spectroscopic study revealed that, below pH 7, Zn predominantly formed outer-sphere sorption
335 complexes on the quartz surface.⁷⁶ Outer-sphere complexes, contrary to inner-sphere complexes, are
336 reversible.

337 Complexation with organic matter can also reduce Zn availability in soil as the organic carbon
338 concentration is higher in Nitisol (2.3%) than in Arenosol (0.76%). Indeed, Formentini *et al.* (2017)²³
339 showed that Zn applied to a clayey soil via pig slurry spreading was no longer present in the initial nano-
340 ZnS form, and 41% of this exogenous Zn was bound to organic molecules. Through a statistical analysis
341 of the findings of over 302 soil studies, Sauvé *et al.* (2000)⁷⁰ highlighted that soil organic matter (SOM)
342 was a major factor affecting Zn solid/solution partitioning in soil, where a high SOM content was found
343 to decrease available Zn in soil.⁷⁰ Furthermore, several studies have highlighted the formation of inner
344 sphere complexes between Zn and SOM.⁷⁷⁻⁷⁹

345 The tortuosity of the diffusion pathway could also explain a lower diffusion of available ⁶⁸Zn to nano-
346 DGT resin in Nitisol.⁸⁰ Indeed, solute transport in soil is controlled by the soil texture, water content and
347 dry bulk density.⁸¹ Particularly, for a same water content, it was shown that Cl⁻ diffusivity was favored
348 in sandy soils compared to clayey soils.⁸² According to the models developed to predict solute
349 diffusivity,^{83,84} the relative solute diffusivity coefficient in Arenosol was estimated to be around 1.5-fold
350 higher than in Nitisol based on their different clay and organic matter content, volumetric water content
351 and dry bulk density (see supporting data, Part VI).

352 Environmental implications

353 These results are surprising and could have led to opposite conclusions on the environmental
354 implications if presented independently. Indeed, we were expecting that: (i) high nano-ZnS dissolution
355 would be associated with high Zn availability, and (ii) low nano-ZnS dissolution would be associated
356 with low Zn availability. Indeed, Sekine *et al.* (2015)⁴¹ demonstrated that nano-Ag₂S had high chemical
357 stability in soil (highlighted by XAS) while Ag had a low availability (highlighted with nano-DGT).
358 Combining XAS, nano-DGT and isotope tracing was essential in drawing the key conclusion of this
359 study, i.e. high NP dissolution does not necessarily means high element availability and vice versa.

360 Our results provide new keys for understanding the fate of Zn in soils. We obtained evidence that, in a
361 clayey soil, most nano-ZnS were dissolved whereas most of the released Zn was quickly immobilized.
362 Nano-ZnS application on such soils would therefore have little impact on Zn availability in the short
363 term. Yet, while nano-ZnS dissolution is much slower in a sandy soil, the released Zn would be more
364 available. Application of nano-ZnS on such soils could thus have a significant impact with respect to Zn
365 availability and toxicity. These results must be complemented by further studies to identify the long-
366 term impact of OW recycling on Zn contamination in soils. The stability of Zn associated with the
367 identified bearing phase in Nitisol (clay, iron oxide, manganese/potassium oxide) should be evaluated

368 over a longer term under varying climate conditions. Indeed, Tella *et al.* (2016)³² showed that Zn-FeOx
369 speciation in organic waste was correlated with Zn availability in OW-amended soil. This result was
370 explained by soil acidification following organic matter mineralization, which would induce Zn
371 desorption from iron oxide. This mechanism should be considered with regard to the fate of Zn sorbed
372 on iron oxide in Nitisol. On the other hand, after 11 years of repeated pig slurry amendment, Zn was
373 found to accumulate in the top 30 cm of a clayey soil, and was sorbed on clay, iron oxide and organic
374 matter.²³ These findings suggest that Zn bearing phases and the small granulometry composing the
375 Nitisol would also limit Zn transfer to deeper soil layers in a longer term.

376 When nano-ZnS are formed in OW, organic matter composing OW can interact with the nano-ZnS
377 surface. Likewise, OW-borne nano-ZnS are potentially biogenic due to the presence of sulfate-reducing
378 bacteria,¹³ and could therefore be closely associated with extracellular proteins⁸⁵ that in turn could
379 change the nano-ZnS properties. Indeed, it was shown that organic molecules with a thiol group had an
380 influence on nano-ZnS aggregation properties.^{86,87} It is also possible that these molecules influence the
381 size and structure properties, as water molecule surface interactions with 3 nm nano-ZnS can increase
382 their crystallinity.⁸⁸ According to the mechanisms highlighted by our study, systems with higher
383 complexity should now be studied, e.g. the fate of nano-ZnS in soils, using nano-ZnS precipitated in the
384 presence of organic matter or directly precipitated in OW. Organic matter application by OW recycling
385 on soils can alter the physicochemical conditions in soil (e.g. pH variation due to organic compound
386 mineralization³²), thereby changing the Zn adsorption behavior and fate. Furthermore, the presence of
387 plants in the soil is expected to influence the nano-ZnS fate. Indeed, Panfili *et al.* (2015)⁸⁹ showed that
388 a higher proportion of ZnS was detected in unvegetated sediment (26-49% of total Zn) compared to
389 vegetated sediment (0-11% of total Zn), suggesting that the physicochemical changes due to the
390 presence of plants had induced ZnS dissolution.

391 Conclusion

392 In conclusion, a combination of two factors govern the Zn fate in cropland soils, i.e. Zn speciation and
393 soil properties. We previously showed that the OW treatment choice (anaerobic digestion vs.
394 composting) controlled Zn speciation in OW¹ and that Zn speciation in OW was a key factor controlling
395 the environmental fate of this element in OW-amended soils.⁹⁰ The present study revealed another key
396 parameter to consider when evaluating environmental impact of OW recycling regarding Zn
397 contamination, i.e. the amended soil properties. Further research is required to identify the parameters
398 controlling nano-ZnS dissolution and released Zn availability. For example, a dissolution study in
399 aqueous solution with a different chemical composition would be of interest to identify the principal
400 factors driving nano-ZnS dissolution in soils. According to our results with these two different soils,
401 several hypotheses could be put forward to explain the faster nano-ZnS dissolution in the Nitisol and
402 the higher availability in the Arenosol: (1) Zn affinity for Nitisol minerals, (2) Zn complexation with

403 organic molecules (3)(a)biotic sulfur oxidation favored in Nitisol, and (4) higher Zn diffusivity in
404 Arenosol.

405

406 Conflicts of interest

407 There are no conflicts to declare.

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418

419 Table 1 : Soil properties. Concentrations are expressed on a dry matter (DM) basis.

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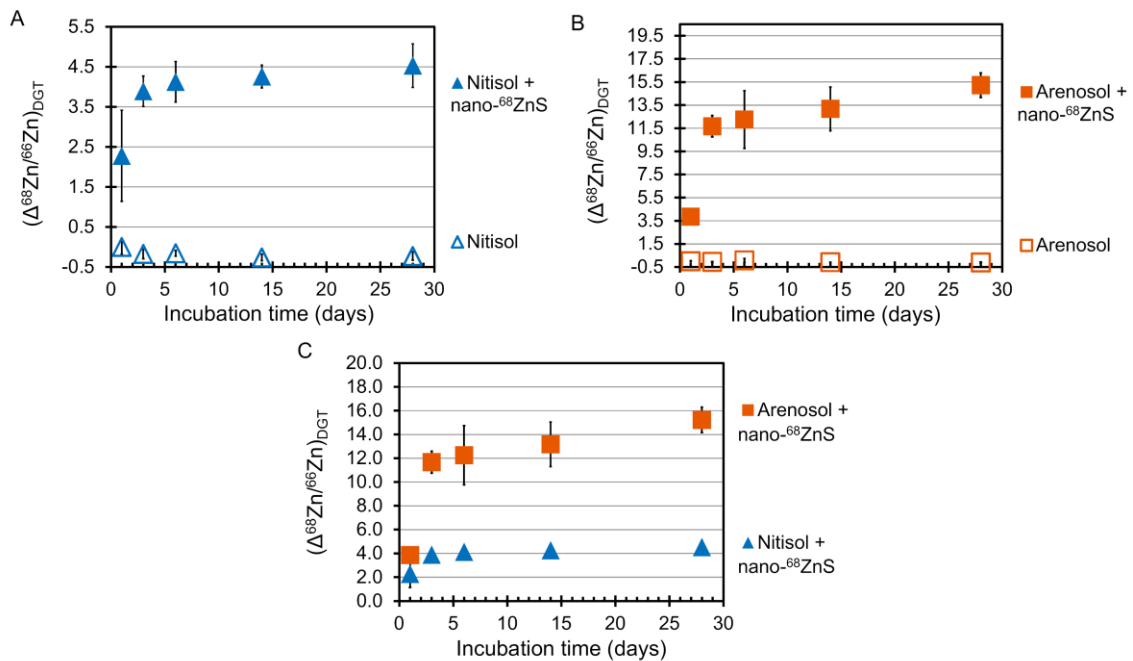
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Parameters		Nitisol	Arenosol
Granulometric composition	Clay (%)	42.7	10.2
	Silt (%)	46.5	11.5
	Sand (%)	10.8	78.3
[C _{org}] %		2.3	0.76
[Zn] _{total} mg.kg ⁻¹		170	19
CEC ¹ cmol(+).kg ⁻¹		11.6	7.1
pH in water		6.5	6.8
Max WHC ² (L.kg ⁻¹)		0.46	0.26

428 The analytical methods are described in the supporting data, part I.

429 1. CEC : cation exchange capacity ; 2. WHC : water holding capacity



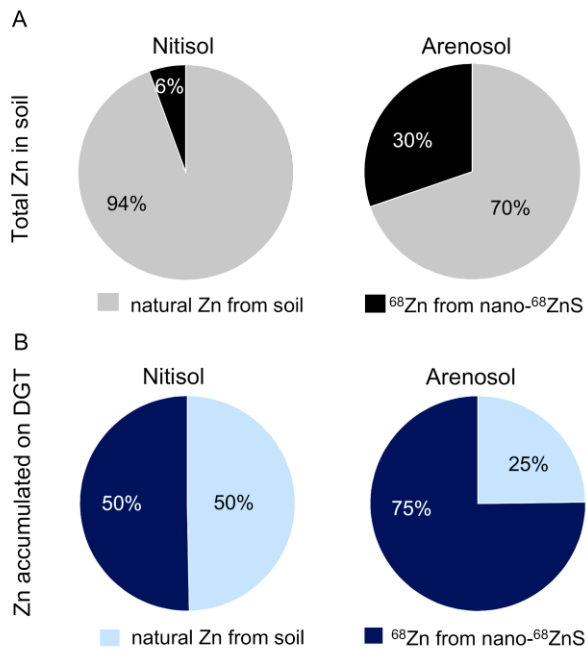
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431 Figure 1 : Isotopic composition of Zn accumulated on nano-DGT resin ($\Delta^{68}\text{Zn}/^{66}\text{Zn})_{\text{DGT}}$ during soil incubation.

432 Comparison of the Nitisol exposed to nano-⁶⁸ZnS and the control Nitisol (A), comparison of the Arenosol exposed

433 to nano-⁶⁸ZnS and the control Arenosol (B) and comparison of the two soils exposed to nano-⁶⁸ZnS (C). Error bars

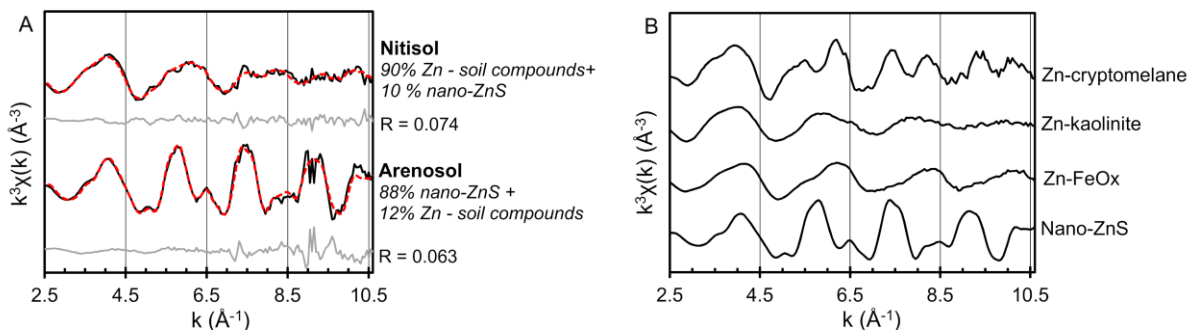
434 represent the standard deviation of the four replicates.



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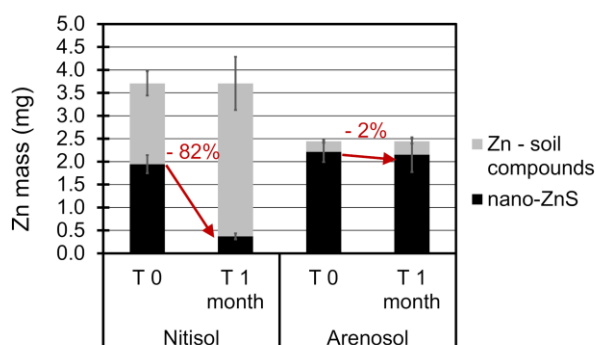
436 Figure 2 : A) Total zinc in the two soils with respective proportion of naturally occurring Zn and ^{68}Zn from nano-
 437 ^{68}ZnS , B) Zinc accumulated on nano-DGT for the two soils with respective proportion of naturally occurring Zn
 438 and ^{68}Zn from nano- ^{68}ZnS ($m\text{Zn}_{\text{nat}}/m\text{Zn}_{\text{tot}}$ and $m\text{Zn}_{\text{sp}}/m\text{Zn}_{\text{tot}}$).

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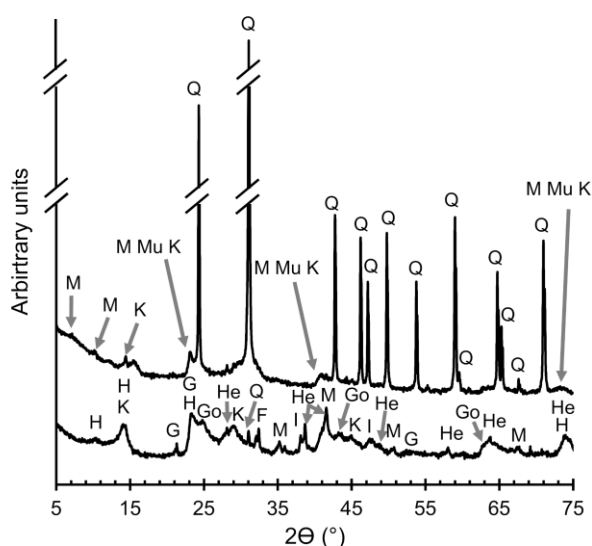
441 Figure 3 : Zn K-edge extended X-ray absorption fine structure spectroscopy of (A) soils spiked with nano-ZnS
 442 after 1 month incubation (black), best linear combination fitting (red) and fit residue (grey) with R the calculated
 443 residual factor of the fit. (B) Zn reference compounds selected by linear combination fitting of the soils.



444

445 Figure 4 : Zn mass in each soil shown as applied nano-ZnS or Zn bound to soil compounds for both soils at the
 446 initial and final incubation times, calculated from the known $[Zn]_{soil}$ and mass of applied nano-ZnS for the initial
 447 time, and from the XAS speciation results after 1 month exposure. Error bars include the error of the ICP-MS
 448 measurement (15%) and the soil/nano-ZnS weighting (0.1 mg) for T0 and T1 month, and LCF error (15%) for T
 449 1 month.

450



451

452 Figure 5: X-ray diffractogram ($\lambda=1.789 \text{ \AA}$) of the Nitisol (bottom) and Arenosol (top) with mineral phase
 453 identification (M: montmorillonite; Mu: muscovite; K: kaolinite; Q: quartz; H: halloysite; G: gibbsite; M:
 454 magnetite/maghemite; I: ilmenite; He: hematite; Go: goethite; F: feldspar).

455

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