Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Transformation of zinc oxide nanoparticles in freshwater sediments under oxic and anoxic conditions

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This file includes 23 pages, 14 figures and 8 tables.

I. Chemical and mineralogical analyses

Acid digestion procedure

The concentrations of major and trace elements of sediment samples (i.e., pristine sediment ; ZnO-NPs_oxic_T3_81d ; Zn^{2+}_oxic_T3_81d ; ZnO-NPs_anoxic_T3_81d ; Zn^{2+}_anoxic_T3_81d) were determined by acid digestion. Especially, 2 ml of a HNO_3 65% and HCl 30% (Suprapur®, Merk) mixture (1:1) was added into 5 ml PTFE vials containing ~50 mg of dry powdered sediment and evaporated after a few hours at 140°C. Subsequently, 3 ml of a HNO_3 65%, HCl 30%, HF 40% (EMSURE®, Merk) mixture (3:1:2) was added into the vials and kept closed at 120°C for 12h. After evaporation, the residues were dissolved in 2 ml HNO_3 65% and evaporated. Then, 2 ml of a HNO_3 65% and H_2O_2 70% (Suprapur®, Merk) mixture (1:1) was added and subsequently evaporated after a few hours. The residues were then dissolved into 3 ml of HNO_3 65%, evaporated, and re-dissolved into 4,5 ml of a 5M HNO_3 solution at 115°C overnight. The final solution were diluted with deionized water and analysed by ICP-OES.

Sequential chemical extractions

Chemical extractions have been performed in triplicates, on the sediments collected at 7 days and 81 days of the incubation experiments. Briefly, about 500 mg of dried sediment was reacted with a 1M $MgCl_2$ solution at pH 7 (1:10 solid:liquid ratio) in 15ml centrifuge tubes. After 1 hour, the samples were centrifuge at 3500g for 10 min and the supernatants were filtered at 0,22 µm and acidified with HNO_3 65%. The carbonate/acid soluble fraction was extracted using a 1M Sodium acetate solution buffered at pH 5 with Acetic acid at a 1:20 solid:liquid ratio, for 6 hours. The samples were then centrifuge at 3500g for 15 min and the supernatants were filtered at 0,22µm and acidified with HNO_3 65%. The remaining solid was reacted with a 0.1 M $Na_4P_2O_7$ solution (1:30 solid:liquid ratio), for 6 hours. The residual fraction was determined by acid digestion using the same procedure as detailed above. Between each extraction steps, the solids were washed with ultra-pure water, centrifuge at 3500g for 10 min and the supernatant was discarded.

Table SI-1. Main characteristics of the sediment used for the incubation experiments.

Elemental composition[a]	
Al_2O_3 (%)	5.4 ± 0.1
CaO (%)	22.8 ± 0.3
Fe_2O_3 (%)	2.0 ± 0.04
K_2O (%)	1.3 ± 0.03
MgO (%)	6.8 ± 0.1
MnO (%)	0.1 ± 0.3
Na_2O (%)	0.6 ± 0.01
P [$mg.kg^{-1}$]	437 ± 1.8
S [$mg.kg^{-1}$]	1600 ± 0.7
Zn [$mg.kg^{-1}$]	40.8 ± 0.8
Mineralogy[b]	
Quartz, Calcite, Dolomite, Chlorite, Mica	
TOC[c] (%)	2.7 ± 0.4
TIC[c] (%)	6.6 ± 0.3

a-Major and minor elements have been determined by acid digestion. Uncertainties on the concentrations correspond to the standard deviation between replicates samples.
b-Mineralogical composition of the sediment was determined by powder XRD (Figure SI-1)
c-TC, TOC and TIC have been determined using a LECO-TOC RC612, multiphase carbon/water analyzer. Uncertainties represent the standard deviation between replicates samples.

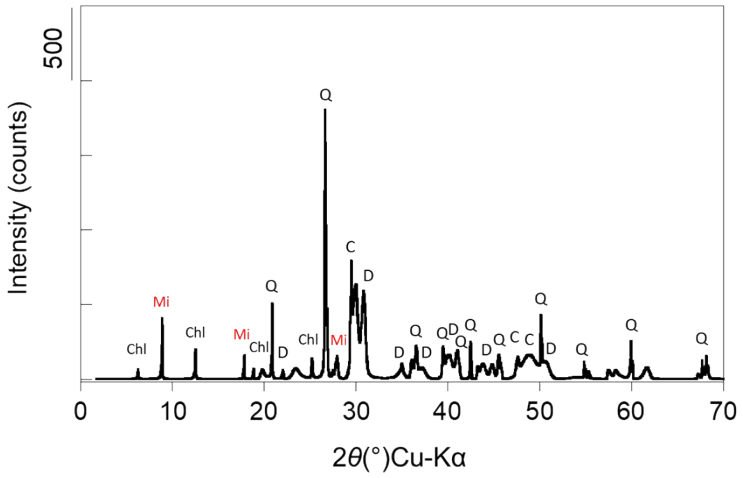

Figure SI-1: X-ray diffraction pattern of the pristine sediment used for the oxic and anoxic incubation experiments. Chl: chlorite ; Mi: mica ; Q: quartz ; D: dolomite ; C: calcite.

II. Incubation experiments

Table SI-2: Description of the incubation experiments and samples nomenclature

Experimental conditions	Zn source	Replicates	Sample
Anoxic condition (N_2 atmosphere)	ZnO NPs	ZnO_anoxic_T1_***t***	liquid (< 0,02µm)
		ZnO_anoxic_T2_***t***	liquid (< 0,02µm)
		ZnO_anoxic_T3_***t***	solid + liquid (centrifugation at 6000g)
	dissolved Zn	Zn^{2+}_anoxic_T1_***t***	liquid (< 0,02µm)
		Zn^{2+}_anoxic_T2_***t***	liquid (< 0,02µm)
		Zn^{2+}_anoxic_T3_***t***	solid + liquid (centrifugation at 6000g)
	--	control_anox_***t***	liquid (<0,02µm)
Oxic condition (Air atmosphere)	ZnO NPs	ZnO_oxic_T1_***t***	liquid (< 0,02µm)
		ZnO_oxic_T2_***t***	liquid (< 0,02µm)
		ZnO_oxic_T3_***t***	solid + liquid (centrifugation at 6000g)
	dissolved Zn	Zn^{2+}_oxic_T1_***t***	liquid (< 0,02µm)
		Zn^{2+}_oxic_T2_***t***	liquid (< 0,02µm)
		Zn^{2+}_oxic_T3_***t***	solid + liquid (centrifugation at 6000g)
	--	control_oxic_***t***	liquid (<0,02µm)

t*= 0, 30min, 3h, 8h,1d,2d,3d,4d, 5d,7d,14d,21d, 28d,40d,53d,81d*

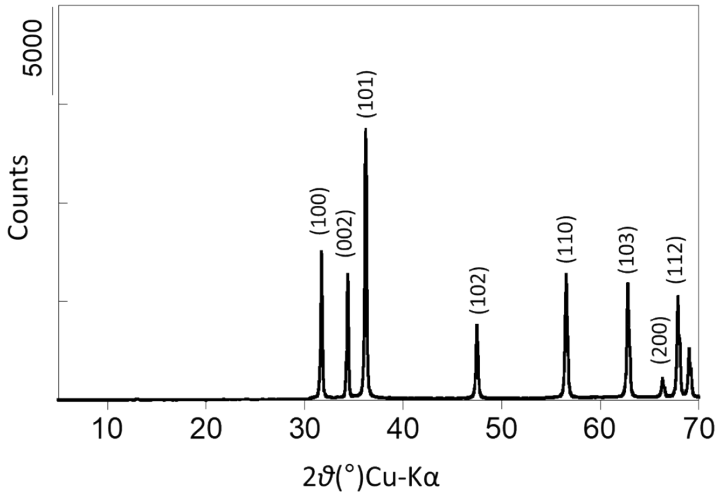

Figure SI-2: X-ray diffraction pattern of the pristine ZnO NPs representative of the hexagonal zincite structure. Under brackets are the (hkl) plans of the zincite structure.

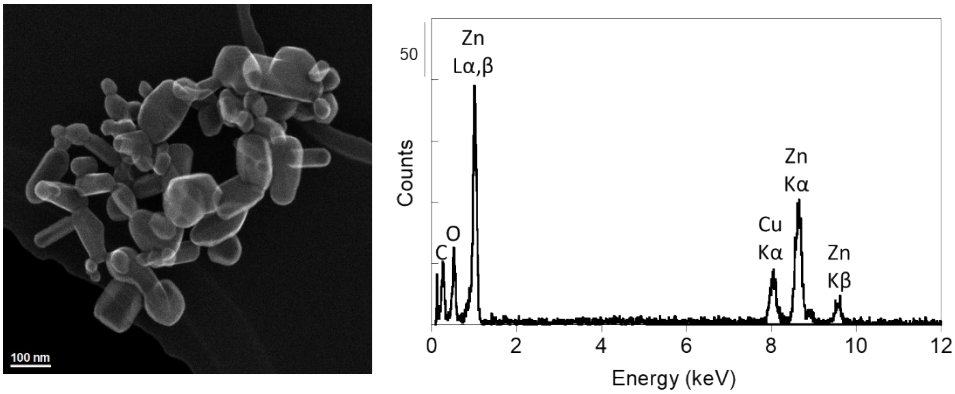

Figure SI-3: STEM micrograph of the pristine ZnO NPs acquired with a secondary detector and the respective EDX spectrum.

III. Model compounds synthesis and characterization

Zn adsorbed onto hectorite SHCa-1 ("Zn-phyllo-like") and Zn adsorbed onto Ca-montmorillonite SCa-3 ("Zn-ads-phyllo")

The hectorite SHCa-1 and Ca-montmorillonite SCa-3 materials were issued from the Source Clay Minerals Repository of the Clay Minerals Society. Zn adsorbed onto hectorite SHCa-1 and Zn adsorbed onto Ca-montmorillonite SCa-3 species were synthetized under N_2 atmosphere in an anaerobic glovebox. 1g of phyllosilicate was placed into a PPE bottle, supplemented with a O_2-free 0.1M $NaNO_3$ solution buffered at pH 7. After 5 hours, a $ZnCl_2$ solution was slowly added. The suspension was mixed for 24 hours using a rotating magnetic bar. The solids were then centrifuge at 5000g for 15 min and dry under vacuum in a desiccator.

The adsorption of Zn onto hectorite is known to result in the formation of Zn polymers at the edges of the hectorite, bridged to surface Mg octahedra and Si tetrahedra, which ressemble Zn-substituted kerolite ($Si_4(Mg_{3-x}Zn_x)O_{10}(OH)_2 \cdot nH_2O$) in which Zn is located in a similar phyllosilicate-like environment (Manceau et al., 2000; Schlegel et al., 2001). Consequently,

the EXAFS spectra of our Zn-hectorite represents Zn in a phyllosilicate-like structural environment and will be called “Zn-phyllo-like”.

Amorphous Zn phosphate

A protocol adapted from Bach et al. (2015) was used to synthetize Amorphous Zn phosphate. In a glass vial, a 10mM KH_2PO_4 solution at a pH adjusted to 11.9 with 5M NaOH was mixed with a 15mM $ZnCl_2$ solution. The precipitate was then immediately centrifuged at 14000 g for 5 min. The solid was washed two times with acetone (>99,8%, VWR) and dried under vacuum in a desiccator.

Crystalline Zinc phosphate identified as Hopeite ($Zn_3(PO_4)_2{\cdot}4H_2O$)

A crystallize Zn phosphate mineral was synthetized following the same protocol as the amorphous zinc phosphate, by mixing a 10mM KH_2PO_4 solution (pH adjusted to 11.9) and a 15mM of $ZnCl_2$. The solution with the precipitate was mixed for 24 hours at room temperature. The precipitate was then centrifuged at 14000 g for 10 min. The solid was washed two times with acetone (>99,8%, VWR) and dried under vacuum in a desiccator.

Zn adsorbed to calcite

Zinc adsorbed to a synthetic calcite was prepared following the protocol described in Elzinga et al. (2002). A synthetic calcite was gently provided by Dr. Naresh Kumar (Wageningen University, Netherlands). In deionized water adjusted to pH 9, 100 mg of calcite was dispersed and after 2 hours 350µL of a 1mM $ZnCl_2$ solution was added. The suspension was mixed during 2 days. The solid was centrifuge at 5000g for 10 min and dried under vacuum.

Zn adsorbed to ferrihydrite

Two-line ferrihydrite was synthetized by titrating a solution of $FeCl_3.6H_2O$ with 1M NaOH to a pH of 7.2-7.3 (Schwertmann & Cornell, 1991). When the pH was stable, within 15 minutes, the suspension was centrifuged at 14000g for 10 min. The solid was washed five times with deionized water to remove residual salts. The freshly prepared ferrihydrite was then dispersed in a solution containing 0.4 mM $Zn(NO_3)_2$ and 0.1M $NaNO_3$, at pH 7.5 for 24 hours. The reacted solid was then centrifuged at 14000g for 10 min and dried under vacuum.

ZnS “nanosized” and Amorphous ZnS

ZnS nanosized was synthesized by mixing $ZnCl_2$ and Na_2S in O_2-free deionized water with a S:Zn ratio of 2:1. The suspension was aged for 10 days at room temperature with constant stirring. The solid was then centrifuged at 6000g for 5 min and washed three times with O_2-free deionized water. The final solid was dried under vacuum in a desiccator and stored in the glovebox. Amorphous ZnS was prepared by mixing $ZnCl_2$ and Na_2S solution at a Zn:S ratio of 1:1. To the opposite of the nanosized ZnS, the precipitate was immediately centrifuged, and washed two times with O_2-free deionized water. The freshly prepared solid was mixed with cellulose for XAS analysis.

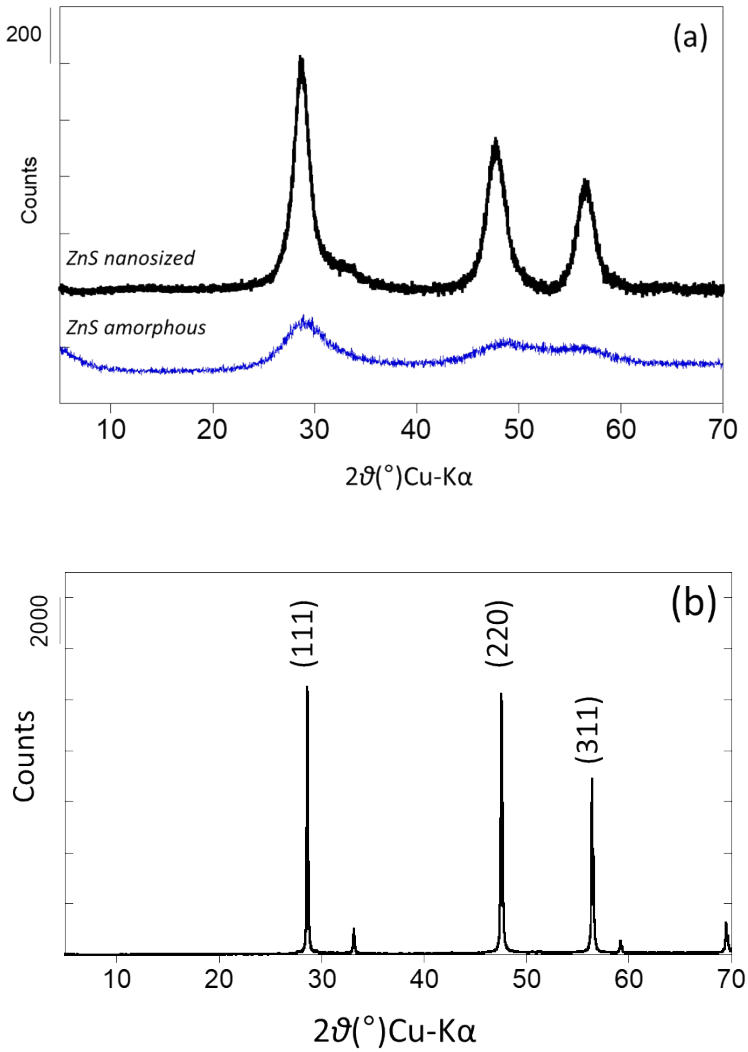

Figure SI-4: X-ray diffraction patterns of (a) the nanosized ZnS, the amorphous ZnS and (b) the natural Sphalerite model compounds used in the present study.

IV. Chemical characteristic measured in the incubation solutions

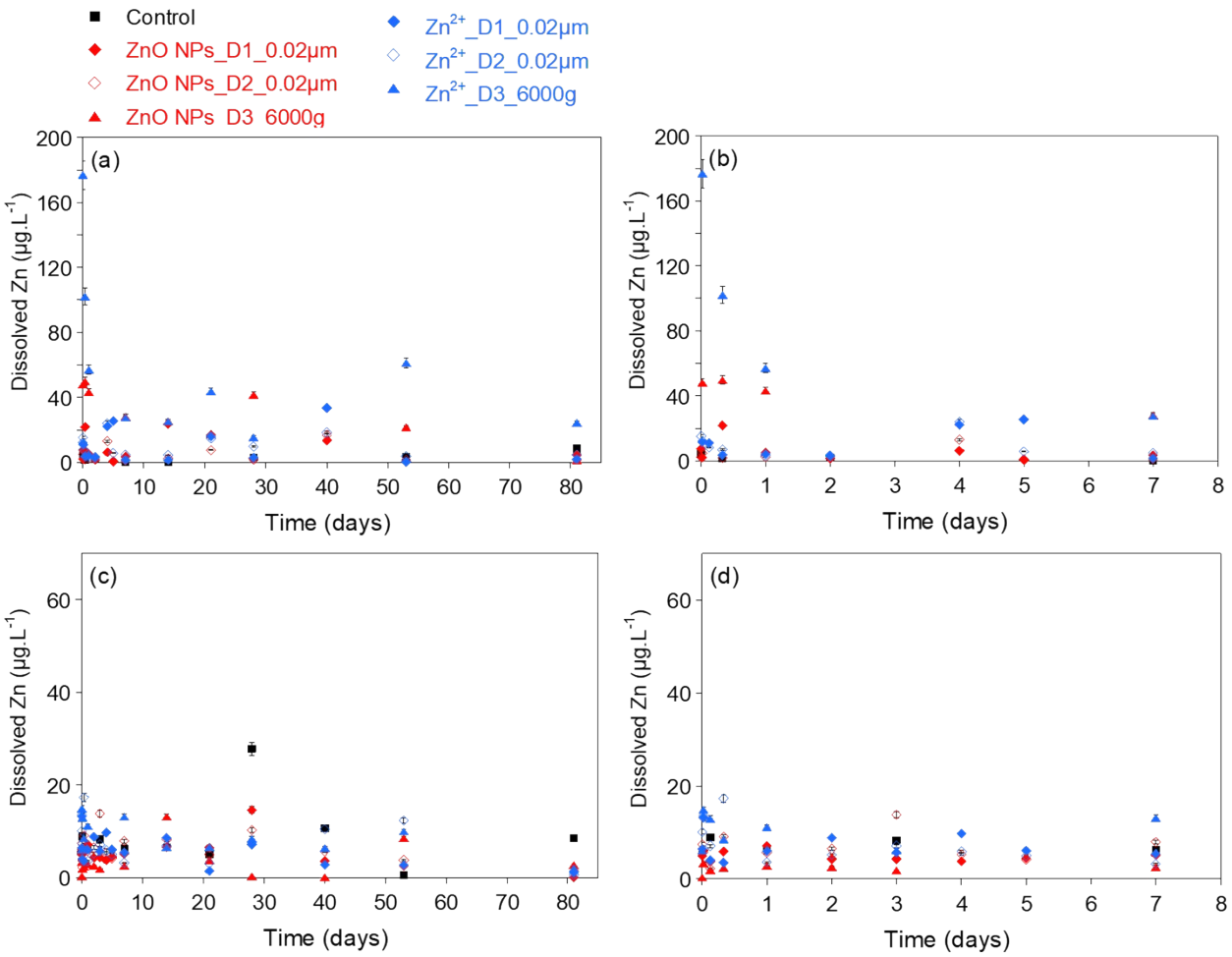

Figure SI-5: Evolution of the dissolved Zn concentrations over the course of the (a,b) oxic and (c,d) anoxic incubation experiments spiked with ZnO NPs (red rhombus and triangles) or dissolved Zn^{2+} (blue rhombus and triangles) and their respective unspiked control experiments (black squares). The detection limit is 0.6 $\mu g.L^{-1}$.

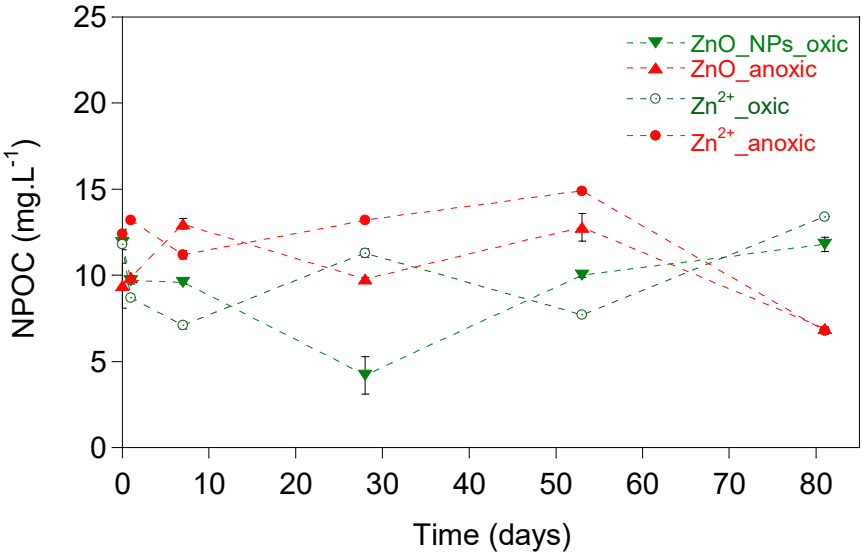

Figure SI-6: Non-purgeable organic carbon (NPOC) concentrations, measured in the incubation solutions over the course of the anoxic (red) and oxic (green) ZnO NPs spiked (triangles) and Zn^{2+} spiked (circles) experiments. Error bars represent the deviation obtained between the triplicate measurements.

V. PCA and LCF-EXAFS Fitting results at the Zn K-edge

PCA analysis was performed using the set of 27 k^3-weighted EXAFS spectra collected from the oxic and anoxic incubated samples. The result indicated that the samples can be adequately reconstructed using the four first spectral components, representing 78% of the total experimental variance. This indicates that more than four Zn species contribute to the experimental signal and that some of these species might have similar EXAFS spectra. The first four components were used for target transformation in order to evaluate the suitability of each model compounds to describe the experimental data. SPOIL values obtained from the TT are reported in Table SI-3.

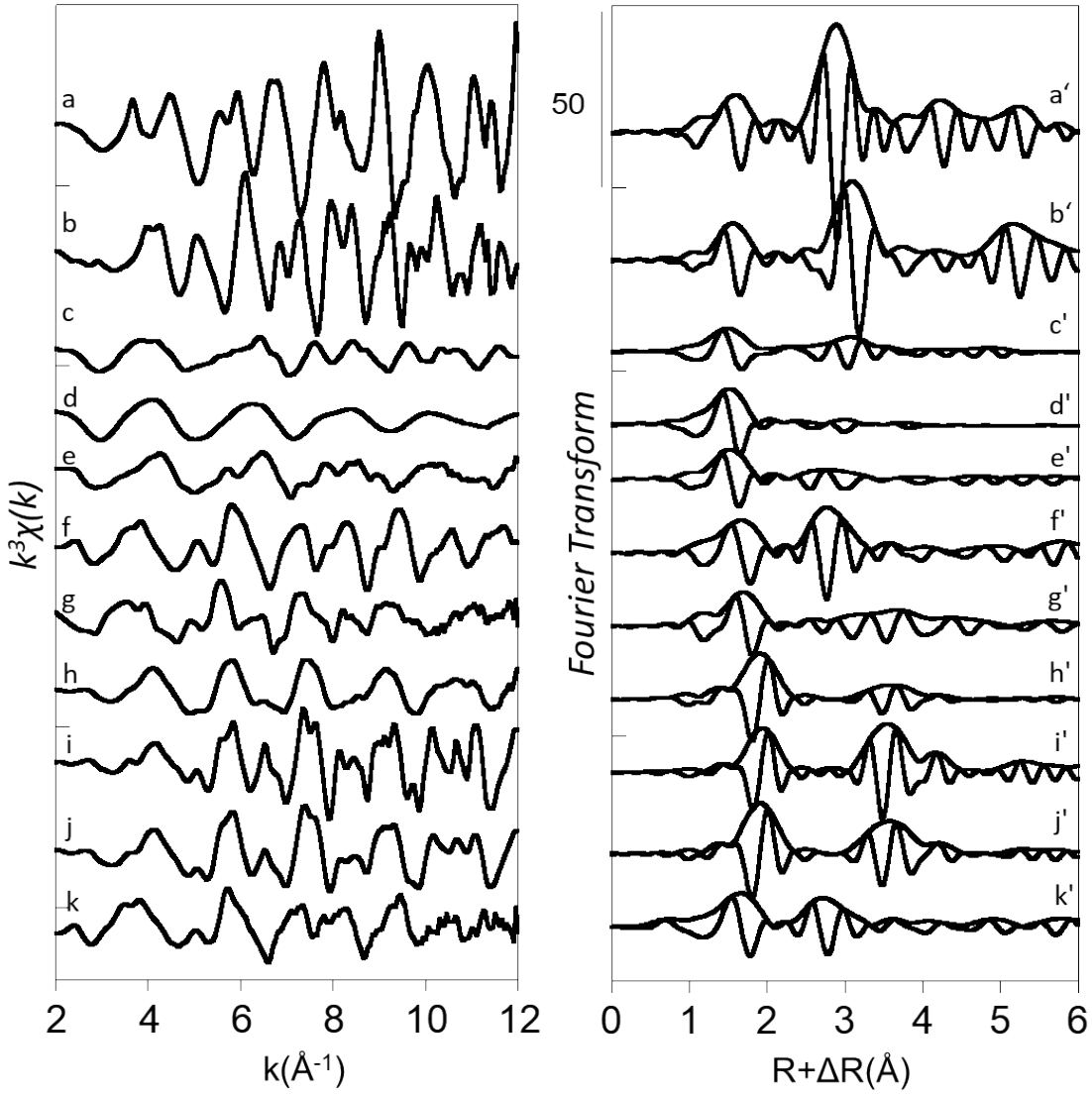

Figure SI-7: Unfiltered k^3-weighted EXAFS spectra (left) and corresponding Fast Fourier Transforms magnitude and imaginary parts (right) of the set of crystalline and amorphous Zn-bearing minerals recorded and used as model compounds in this study. (a,a') pristine ZnO NPs ; (b,b') Franklinite $ZnFe^{3+}{}_2O_4$ (c,c') Hopeite $Zn_3(PO_4)_2{\cdot}4H_2O$ (d,d') Amorphous Zn-phosphate (e,e')Hemimorphite $Zn_4Si_2O_7(OH)_2$ (f,f') fraipontite $(Zn, Al)_3[(Si, Al)_2O_5](OH)_4$ (g,g') Zn-rich calcite $CaCO_3$ (h,h') amorphous ZnS (i,i') sphalerite ZnS (j,j') nanosized ZnS (k,k') hendriksite $KZn_3(Si_3Al)O_{10}(OH)_2$

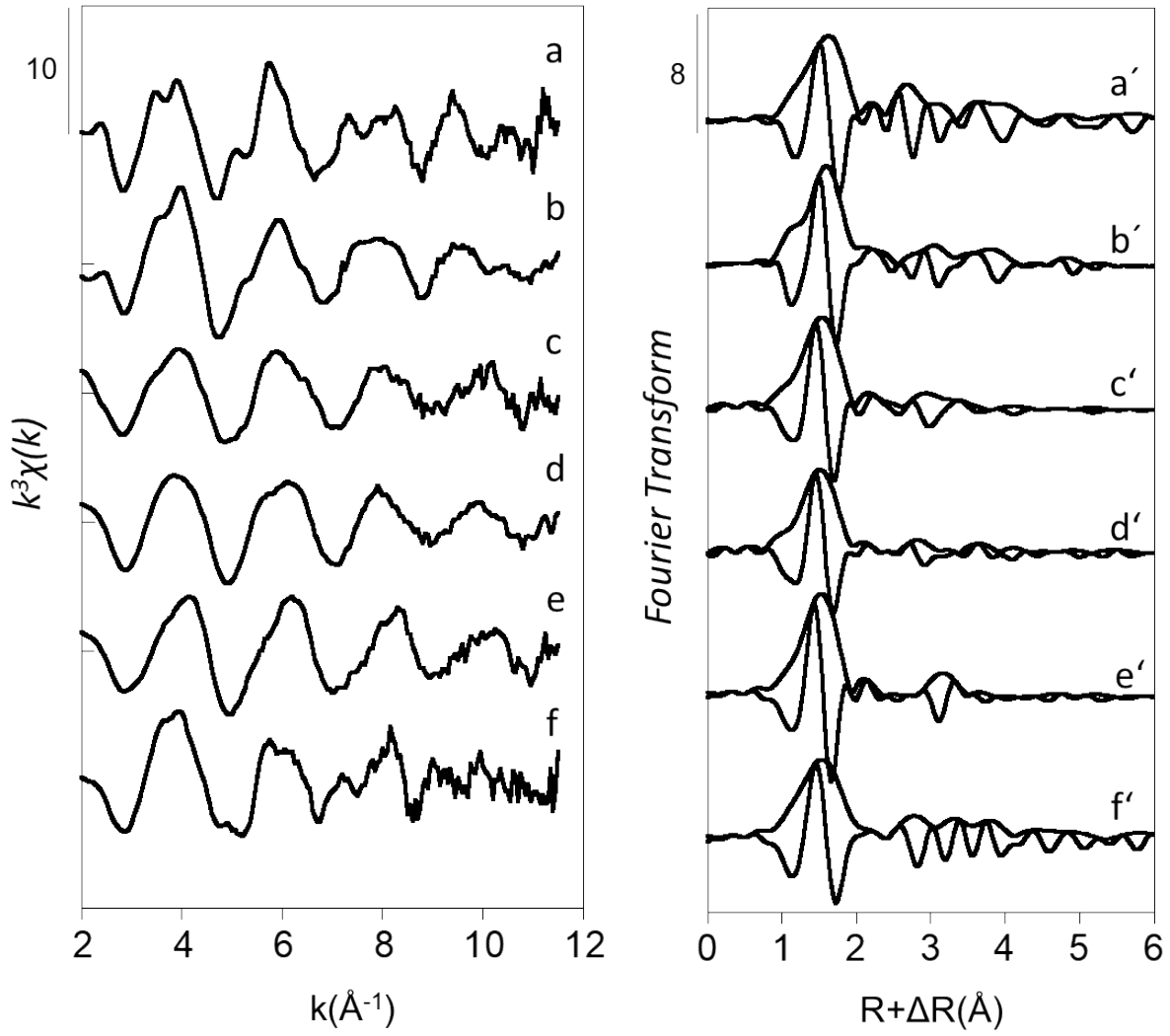

Figure SI-8: Unfiltered k^3-weighted EXAFS spectra (left) and corresponding Fast Fourier Transforms magnitude and imaginary parts (right) of the set of adsorbed Zn model compounds analysed in this study. (a,a') "Zn-phyllo-like" (2302 mg.kg^{-1}) ; (b,b') Zn adsorbed to montmorillonite (1471 mg.kg^{-1}) (c,c') Zn bound to humic acid (d,d') Zn-acetate dihydrate (e,e') Zn adsorbed to ferrihydrite (f,f') Zn adsorbed to synthetic calcite. The spectra for Zn-phytate, Zn-malate, Zn-citrate are described in Sarret et al., 2004;2009).

Table SI-3: SPOIL values obtained from the target transform analysis for EXAFS spectra of each model compounds.

Model compounds	**SPOIL values**
ZnO_NP	1.6
ZnS_nano	3.1
ZnS_amorph	3.6
Sphalerite	8.6
Zn-rich calcite	8.5
Zn-phyllo-like (Zn-hect)	3.0
Zn-ads-phyllo (Zn-mont)	3.8
fraipontite	3.2
hendriksite	2.3
Zn-CaCO3	6.7
Hopeite	2.7
Zn-Fh	2.6
Zn acetate dihydrate	2.2
Zn-HA	1.8
Zn-phytate	2.3
Zn-malate	6.3
Zn-citrate	9.1
ZnPO4_amorph	2.2
hemimorphite	2.2
Franklinite	26.1

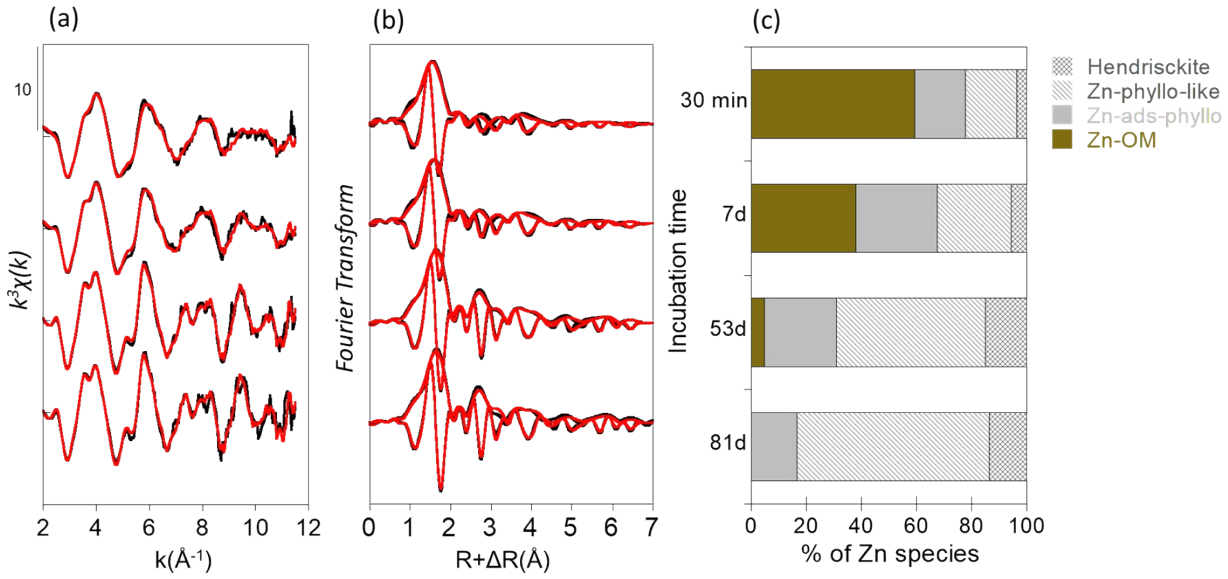

Figure SI-9: (a) EXAFS spectra (black) and reconstructed spectra (red) based on LCF results of the oxic incubated samples spiked with dissolved Zn^{2+} (Zn^{2+}_oxic_T3_t samples). (b) Fourier Transform Magnitude and Imaginary parts of the experimental (black) and the reconstructed spectra (red). (c) LCF-proportions of the fitting components for each experimental spectrum. For the LCF analyses, Zn-ads-phyllo, representing Zn adsorbed onto montmorillonite (grey), Zn-OM, representing Zn-organic compounds (Zn-acetate dihydrate and Zn-phytate, brown), and Zn-phyllo-like (striped light grey) and Hendricksite (framed grey) representing structural Zn in phyllosilicate, were used as fitting components. Fractions of the fitting components were normalized to 100%. Non-normalized results and uncertainties are provided in Table SI-4.

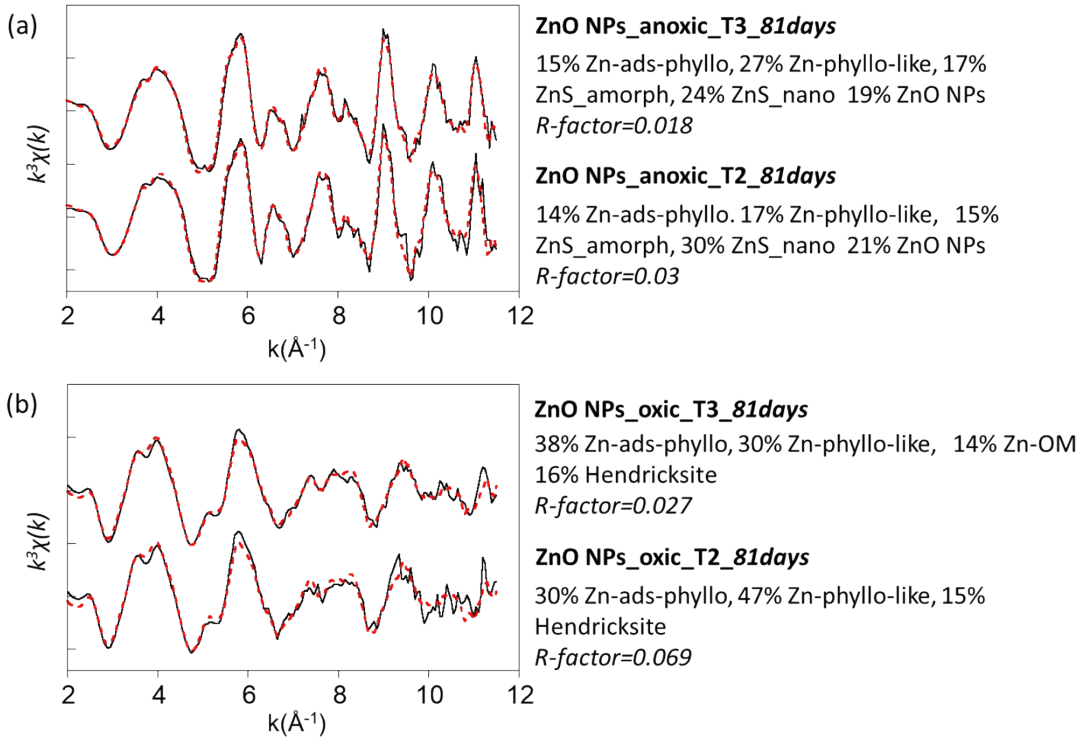

Figure SI-10: EXAFS spectra (black) and reconstructed spectra (red-dotted line) based on LCF results of the (a) anoxic incubated replicate samples spiked with ZnO NPs collected at the end of the incubation experiment (81 days) and (b) oxic incubated replicate samples spiked with ZnO NPs collected at the end of the incubation experiment.

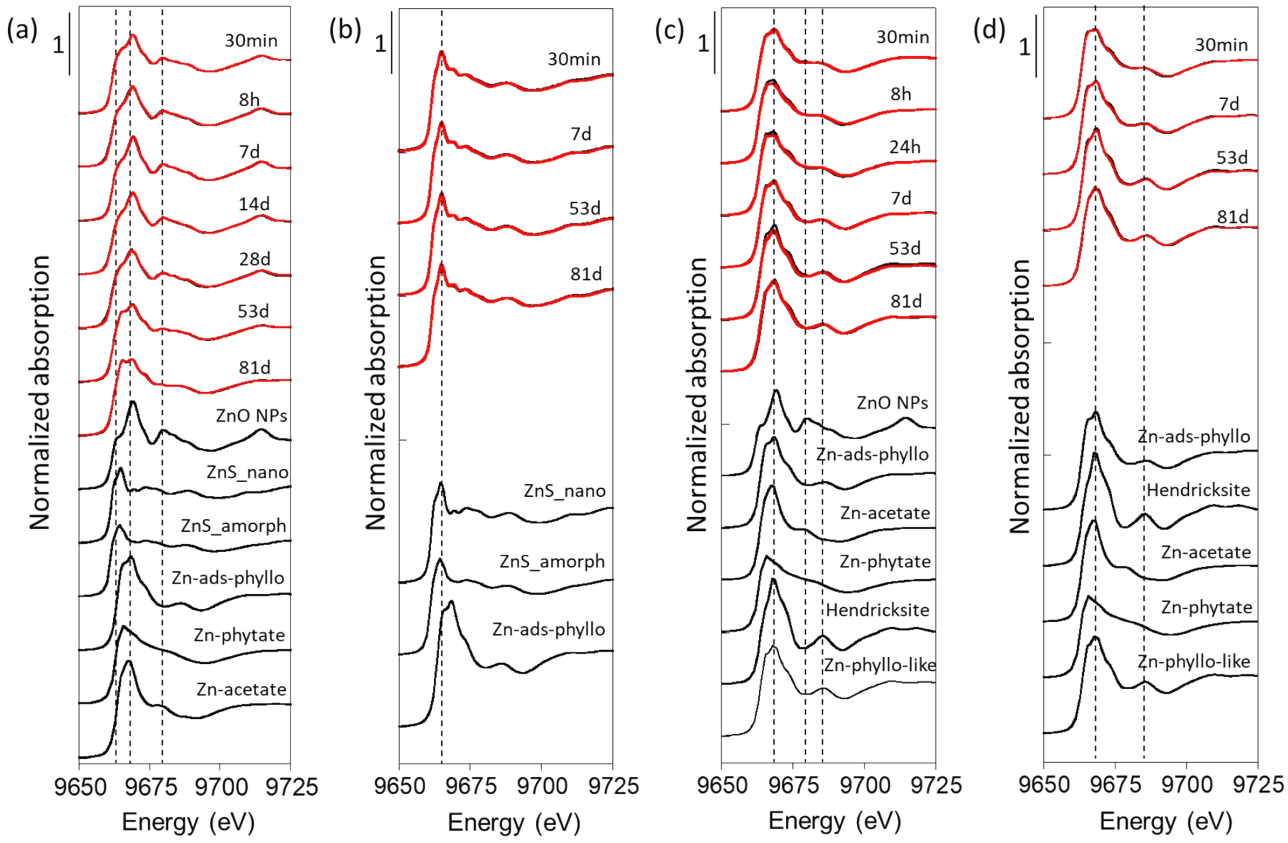

Figure SI-11: XANES spectra (black) and reconstructed spectra (red) based on LCF results of (a,b) the anoxic incubated samples spiked with (a) ZnO NPs and (b) dissolved Zn^{2+} and (c,d) the oxic incubated samples spiked with (c) ZnO NPs and (d) dissolved Zn^{2+}. The XANES spectra of the model compounds used for the LCF analyses are also displayed. Non-normalized fractions of the fitting components and uncertainties are provided in Tables SI-6 and SI-7.

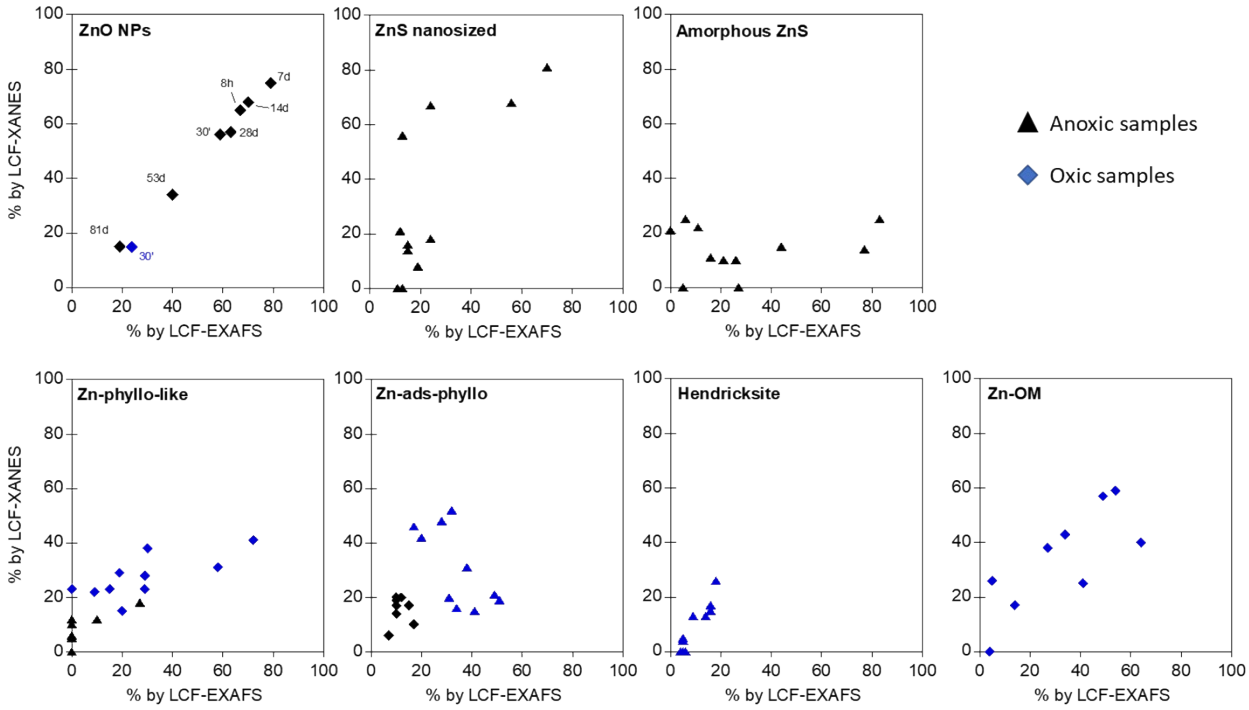

Figure SI-12: Fractions obtained by LCF-XANES versus the fractions obtained by LCF-EXAFS for each model compound used in the LCF procedures. The diamonds represent the fractions obtained on the samples from the ZnO NPs spiked anoxic (black) and oxic (blue) experiments. The triangles diamonds represent the fractions obtained on the samples from the Zn^{2+} spiked anoxic (black) and oxic (blue) experiments.

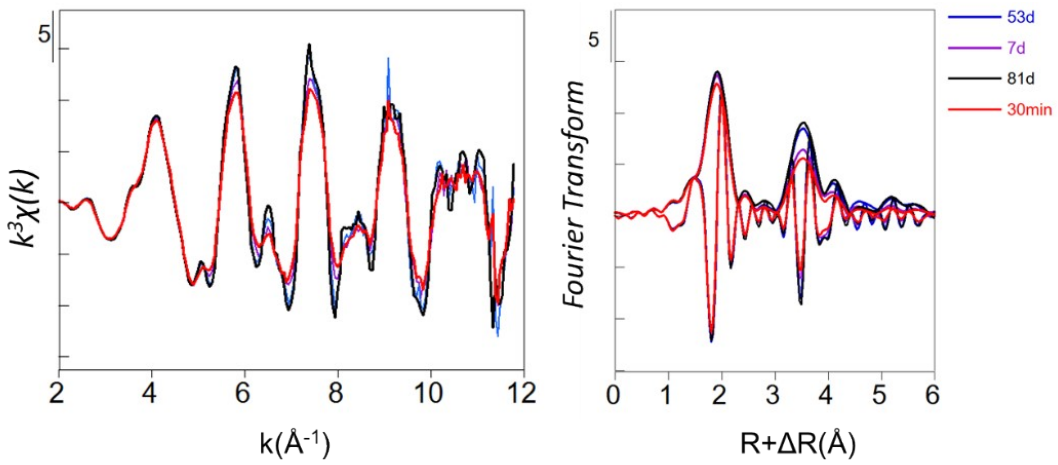

Figure SI-13: Superposed k^3-weighted EXAFS spectra and their respective fourier transforms of the anoxic Zn^{2+} spiked incubated samples.

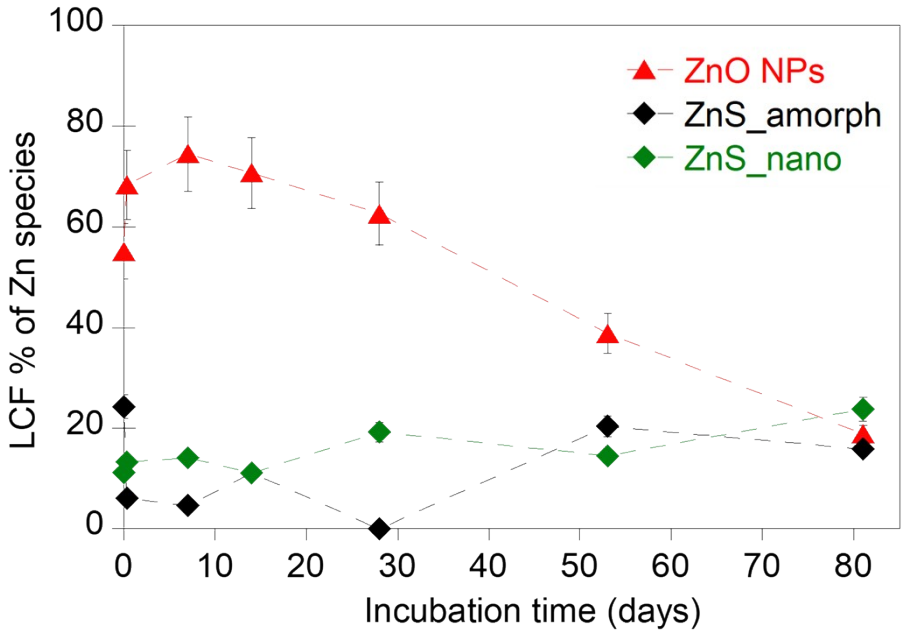

Figure SI-14: LCF proportions of the fitting components ZnO-NPs (red triangle), ZnS_amorph (black rhombus) and ZnS_nano (green rhombus) as well as the proportions of the pool of ZnS phases (ZnS_amorph + ZnS_nano, green square) determined over the course of the anoxic ZnO-NPs spiked experiment. The error bars represent the 10% uncertaineties of the LCF procedure.

Table SI-4: Results of LCF analyses of the Zn K-edge EXAFS spectra of oxic incubated sediment samples spiked with either ZnO NPs or Zn^{2+}. Results are expressed in percentage of the fitting components corresponding to the experimental spectra of the pristine ZnO NPs, the Zn-phytate, the Zn-acetate dihydrate, the Zn-montmorillonite (Zn-phyllo) and the Hendricksite model compounds. Uncertainties on the fitting components are given under bracket. Corresponding experimental spectra and fit curves are displayed in Figures 1 and SI-9.

Experiment spiked with ZnO NPs	ZnO NPs	Zn-phytate	Zn-acetate dihydrate	Zn-ads-phyllo	Zn-phyllo-like	Hendricksite	Sum	R-factor *10^{-2}*	Chi^2_R *10^{-1}*
30 minutes	25 (0)	18 (2)	16 (5)	41 (5)	-	5 (1)	105	1.4	1.7
8 hours	4 (1)	25 (2)	29 (6)	34 (6)	9 (6)	5 (2)	106	5.3	2.7
24 hours	-	14 (3)	35 (6)	31 (6)	15 (6)	5 (2)	102	6.1	3.1
7 days	-	15 (2)	12 (4)	49 (4)	19 (4)	9 (1)	104	2.5	1.5
53 days	-	5 (0)	-	51 (4)	29 (2)	18 (1)	103	2.5	1.9
81 days	-	-	14 (4)	38 (4)	30 (4)	16 (1)	98	2.7	1.8
Experiment spiked with Zn^{2+}									
30 minutes	-	33 (3)	31 (5)	20 (6)	20 (7)	4 (2)	108	3.6	1.8
7 days	-	19 (3)	22 (5)	32 (6)	29 (7)	6 (2)	108	3.1	1.8
53 days	-	4 (3)	-	28 (6)	58 (7)	16 (2)	106	2.4	2.0
81 days	-	-	-	17 (2)	72 (4)	14 (2)	103	4.3	3.7

Table SI-5: Results of LCF analyses of the Zn K-edge EXAFS spectra of the anoxic incubated sediment samples spiked with either ZnO NPs or Zn^{2+}. Results are expressed in percentage of the fitting components corresponding to the experimental spectra of the pristine ZnO NPs, the Zn-phytate, the Zn-acetate dihydrate, the Zn-montmorillonite (Zn-phyllo), Amorphous ZnS (ZnS_amorph) and Nanosized ZnS (ZnS_nano) model compounds. Uncertainties on the fitting components are given under bracket. Corresponding experimental spectra and fit curves are displayed in Figures 4 and 5.

Experiment spiked with ZnO NPs	ZnO NPs	Zn-phytate	Zn-acetate dihydrate	Zn-ads-phyllo	Zn-phyllo-like	Amorphous ZnS	Nanosized ZnS	Sum	R-factor *10^{-2}*	Chi^2_R *10^{-1}*
30 minutes	59 (1)	-	-	10 (2)	-	26 (3)	12 (2)	107	0.6	2.3
8 hours	67 (1	-	-	12 (3)	-	6 (5)	13 (4)	98	1.3	6.4
7 days	79 (1)	-	-	7 (2)	-	5 (4)	15 (3)	106	0.5	3.2
14 days	70 (1)	-	-	7 (2)	-	11 (4)	11 (3)	99	0.7	3.6
28 days	63 (1)	-	-	18 (4)	-	-	19 (2)	100	3.4	15
53 days	40 (0)	-	-	17 (4)	10 (4)	21 (3)	15 (2)	103	0.9	2.0
81 days	19 (0)	-	-	15 (4)	27 (4)	17 (3)	24 (2)	101	1.8	1.8
Experiment spiked with Zn^{2+}										
30 minutes		-	-	12 (2)		83 (3)	13 (2)	107	1.4	*2.5*
7 days		-	-	10 (2)		77(3)	24 (2)	*110*	*1.4*	*2.9*
53 days		-	-	10 (2)		44 (4)	56 (3)	110	1.4	*3.3*
81 days		-	-	10 (2)		27 (3)	70 (2)	*107*	1.0	2.6

Table SI-6: Results of LCF analyses of the Zn K-edge XANES spectra of oxic incubated sediment samples spiked with either ZnO NPs or dissolved Zn^{2+}. Results are expressed in percentage of the fitting components ZnO NPs, Zn-phytate, Zn-acetate dihydrate, Zn-montmorillonite and Hendricksite. Uncertainties on the fitting components are given under bracket. Corresponding experimental spectra and fit curves are displayed in Figure SI-11.

Experiment spiked with ZnO NPs	ZnO NPs	Zn-phytate	Zn-acetate dihydrate	Zn-ads-phyllo	Zn-phyllo-like	Hendricksite	Sum	R-factor *10^{-3}*	Chi^2_R *10^{-3}*
30 minutes	16 (1)	43 (2)	-	15 (4)	23 (5)	5 (2)	101	0.5	0.09
8 hours	-	59 (3)	-	16 (7)	22 (8)	4 (4)	101	0.4	0.08
24 hours	-	57 (4)	-	20 (9)	23 (11)	-	101	0.8	0.2
7 days	-	38 (3)	-	21 (7)	29 (7)	13 (3)	101	1.3	0.2
53 days	-	26 (4)	-	19 (9)	28 (11)	26 (5)	99	2.6	0.5
81 days	-	17 (4)	-	31 (13)	38 (12)	15 (5)	101	0.7	0.1
Experiment spiked with Zn^{2+}									
30 minutes		40 (2)	-	42 (5)	15 (3)	-	100	0.9	0.2
7 days		25 (2)	-	52 (5)	23 (2)	-	100	0.8	0.2
53 days		-	-	48 (5)	31 (3)	17 (3)	100	0.9	0.2
81 days		-	-	46 (12)	40 (6)	13 (5)	100	1.3	0.4

Table SI-7 : : Results of LCF analyses of the Zn K-edge XANES spectra of anoxic incubated sediment samples spiked with either ZnO NPs or dissolved Zn^{2+}. Results are expressed in percentage of the fitting components ZnO NPs, Zn-phytate, Zn-acetate dihydrate, ZnS_nano, ZnS_amorph and Zn-montmorillonite. Uncertainties on the fitting components are given under bracket. Corresponding experimental spectra and fit curves are displayed in Figure SI-11.

Experiment spiked with ZnO NPs	ZnO NPs	Zn-phytate	Zn-acetate dihydrate	Zn-ads-phyllo	Zn-phyllo-like	Amorpphous ZnS	Nanosized ZnS	Sum	R-factor *10^{-3}*	Chi^2_R *10^{-3}*
30 minutes	56 (0)	-	-	14 (2)	-	10 (2)	21 (2)	101	0.1	0.02
8 hours	65 (1)	-	-	-	10 (1)	25 (5)	-	101	0.5	0.09
7 days	75 (1)	-	-	-	12 (0)	-	14 (3)	100	0.4	0.08
14 days	68 (1)	-	-	6 (4)	5 (5)	22 (4)	-	101	0.2	0.04
28 days	57 (2)	-	9 (3)	-	6 (3)	21 (10)	08 (11)	100	1.0	0.2
53 days	34 (1)	18 (1)	-	10 (4)	12 (4)	10 (3)	16 (3)	100	0.2	0.05
81 days	15 (1)	21 (1)	-	17 (5)	18 (4)	11 (3)	18 (3)	100	0.3	0.05
Experiment spiked with Zn^{2+}										
30 minutes		-	-	20 (0)		25 (3)	56 (3)	101	0.6	0.08
7 days		-	-	19 (0)		14 (3)	67 (3)	100	0.7	0.09
53 days		-	-	17 (0)		15 (3)	68 (3)	100	0.6	0.08
81 days		-	-	20 (0)		-	81 (3)	101	0.6	0.08

Table SI-8: Total amount of available sulfide deducted from the sulfide concentration measured in the incubation solutions and total amount of sulfide consumed by the precipitation of ZnS in regard to LCF results. The volume of incubation solution and mass of dry solid were estimated from the volume and mass removed after sampling. Calculations were done considering sulfide concentrations and Zn concentration in the T3 batch.

Time range (days)	**Volume incubation solution (ml)**	**Total amount of available sulfide (µmoles)** [a]	**% ZnS formed by LCF** (±10%)	**Mass dry sediment (g)**	**Total amount of sulfide consumed according to LCF analyses (µmoles)** [b]
t= 0 to 28	190	65 ± 3	24	30	35.8 ± 15
t= 28 to 81	136	**19 ± 1**	15	24	**18 ± 12**

[a] Uncertaineties correspond to the 5 % error on sulfide concentration

[b] Uncertaineties correspond to the 10% errors on the LCF procedures

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