

Coupled effects of hydrodynamics and biogeochemistry on Zn mobility and speciation in highly contaminated sediments

Supporting Information

Minwei Xie,^{1,3} Brooke A. Jarrett,¹ Cecile Da Silva-Cadoux,¹ Kyle J. Feters,² G. Allen Burton Jr.,² Jean-François Gaillard,^{1*} Aaron I. Packman^{1*}

¹ Department of Civil and Environmental Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3109, USA

² School of Natural Resources and Environment, University of Michigan, Ann Arbor, Michigan 48109, USA

³ Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu, Sichuan, 610031, China

* Corresponding authors:

Jean-François Gaillard, jf-gaillard@northwestern.edu Tel 847-467-1376; Fax 847-491-4011.

Aaron Packman, a-packman@northwestern.edu Tel: 847-491-9902; Fax: 847-491-4011

This supporting information consists of 27 pages, and includes 11 figures and 6 tables:

Figure S1. Location of Lake DePue and sampling site.

Figure S2. Experimental setup.

Figure S3. Particle size distribution.

Figure S4. Microstructure of sediments obtained by XMT imaging.

Figure S5. Overlying water turbidity.

Figure S6. Dissolved oxygen concentration in sediment column.

Figure S7. The first five components identified by PCA analysis.

Figure S8. Zn K-edge EXAFS spectra of reference compounds and target transformations.

Figure S9. XANES spectra and LCF reconstruction curves of sediment samples.

Figure S10. Correlation between proportions of Zn species derived from EXAFS and XANES spectra.

Figure S11. Zn speciation in sediment beds and resuspended sediment particles determined by LCF of XANES spectra.

Table S1. Bulk characteristics of the Lake DePue sediments used in the experiments.

Table S2. Physicochemical conditions in overlying water at the endpoint of experiments.

Table S3. Depth distribution of SEM and AVS in different treatments.

Table S4. Principal component analysis results.

Table S5. Zn speciation determined by LCF with EXAFS spectra.

Table S6. Zn speciation determined by LCF with XANES spectra.

Site characterization. Metals contamination in Lake DePue has been extensively studied.¹⁻⁴ The site has elevated levels of metals and nutrients because of industrial operations in the last century, including Zn smelting, sulfuric acid production and diammonium phosphate fertilizer production.¹

Sediments in Lake DePue comprise quartz, dolomite and calcite as the only crystalline mineral phases. Zn solid phases primarily showed amorphous structure.¹ Zn speciation in LDP sediments were characterized by means of both analytical electron microscopy method³ and x-ray absorption spectroscopy method.² Zn rich particles existed under significantly different morphologies, ranging from near-spherical colloids to grains intimately associated with biological entities. Zn was shown to be primarily present as: zinc sulfide (ZnS), zinc carbonate (ZnCO₃), zinc bound to hydrous iron oxides (Zn-HFO), zinc phosphate (Zn₃(PO₄)₂) , and also zinc coordinated to water (Zn(aq)). The Zn(aq) coordination environment is representative of Zn coordinated to 6 water molecules and encompasses Zn in solution as well as all the outer-sphere complexes with various environmental surfaces in which Zn retains its solvation shell.



Figure S1. Aerial photograph of Lake DePue indicating the sampling site (Google Earth, Retrieved on March 4, 2013)

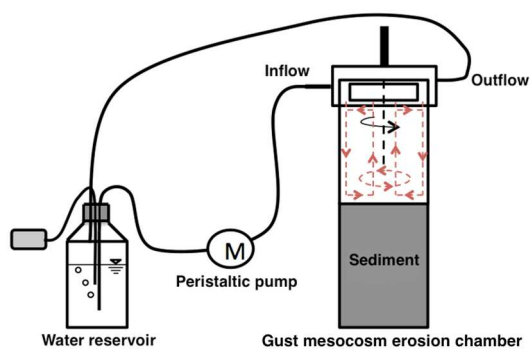


Figure S2. Gust chamber setup. Dashed lines inside the chamber indicate the flow pattern within the chamber.⁵

Table S1. Bulk characteristics of the Lake DePue sediments used in the experiments.

Porosity	49.3%	Permeability (m ²)	2.0±1.2 ×10 ⁻¹⁴
Organic C	3.09%	Zn (mg/kg dry weight)	14,000
Inorganic C	2.65%	Cu (mg/kg dry weight)	410

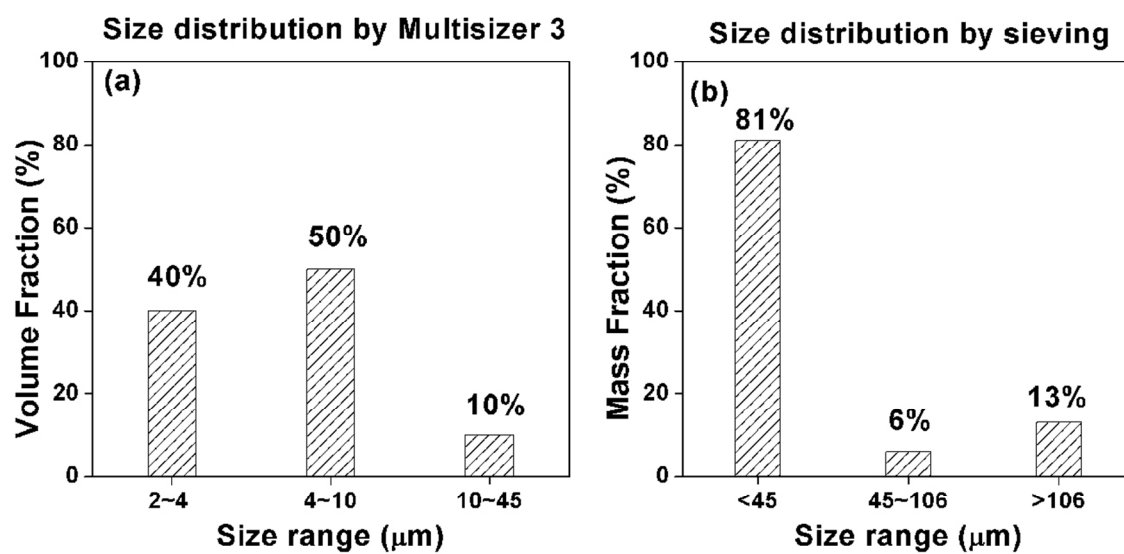


Figure S3. Particle size distribution of Lake DePue sediments.

X-ray Micro-Tomography imaging. Sediment structure was characterized by means of synchrotron X-ray Micro-Tomography (XMT), performed at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) beamline at the Advanced Photon Source, Argonne National Lab. Homogenized sediment was packed into Kapton® tubing (O.D.=1.9 mm, wall thickness=0.025mm) (Cole-Parmer Instrument Co., Vernon Hills, IL), the tube ends were sealed, and then the samples were mounted on a rotating x-y stage and imaged under the X-ray beam at DND-CAT. XMT procedures followed those described in Gaillard *et al.*⁶ The X-ray energy was set using a Si(1,1,1) double crystal mono-chromator to 15 keV and the shadowgrams produced rendered an image with resolution of 2.5 μm . Subcores of intact sediment cores were also imaged by XMT. Microstructure of the sediment subcore was shown in Figure S4. It showed diverse sediment grains ranging in size from 2.5 μm to 125 μm in a much finer matrix. The subcore was enriched in finer particles, which is consistent with the particle size distribution results in Figure S3.

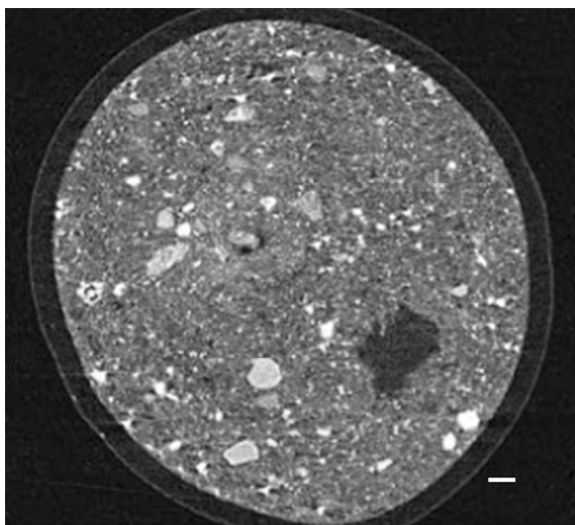


Figure S4. Microstructure of sediments obtained by XMT imaging. Sample shown has an O.D of 1.9 mm, and was obtained by sub-coring an intact sediment core. The white scale bar represents 100 μm .

Physicochemical conditions for the experiments. Physicochemical parameters including temperature, dissolved oxygen (DO), pH and conductivity in overlying water are shown in Table S2. DO in the water was kept at saturation level throughout the course of experiments by bubbling air in the reservoir water using an aquarium pump and DO concentrations were measured with a DO probe (HQ10, Hach). All these parameters remained about constant between the different experiments.

Overlying water was also monitored regularly for total suspended solids with a turbidity meter (2100Q Hach) over the course of experiments (Figure S5). Surficial sediments were mobilized when higher shear stresses were imposed at resuspension. Increased shear caused abrupt increases on overlying water turbidity. Mobilization of sediment particles was highly transient, with turbidity rapidly returned to the pre-resuspension level when resuspension ceased.

Since the Gust chamber head-design prohibits direct oxygen profiling during experiments, we measured the pore water oxygen concentrations in a separate experiment under conditions equivalent to G4 (Figure S6). At the end of experiment, the erosion head of Gust chamber was removed and then dissolved oxygen concentrations in the sediment column were measured with an oxygen microelectrode (OX-50, Unisense) driven by a step motor (Unisense). Measurements were made every 75 μm until the oxygen concentration reached zero. Oxygen was restricted to very small penetration (less than 2mm) (Figure S6).

Table S2. Physicochemical conditions in overlying water at the endpoint of experiment.

	G1	G2	G3	G4
Temperature (°C)	24.1	24.5	24.3	23.9
Dissolved oxygen (mg/L)	8.25	8.26	8.08	8.21
pH	8.5	8.3	8.1	8.5
Conductivity (μS/cm)	694	404	534	598

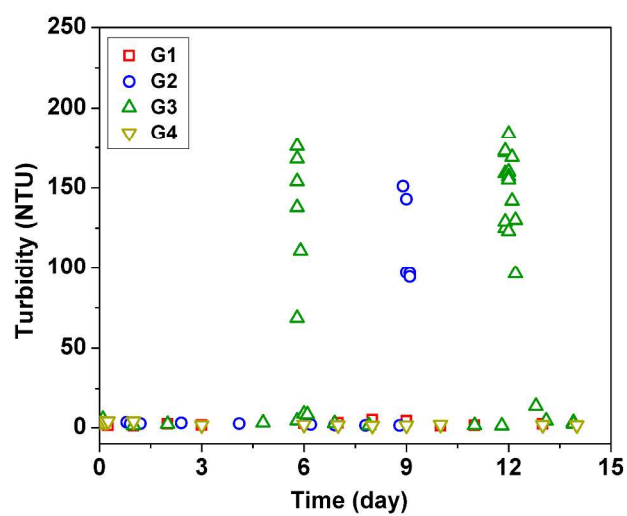


Figure S5. Overlying water turbidity. Sediment resuspension events on day 9 for G2 (blue circles) and day 6, 12 for G3 (olive triangles) caused abrupt increases in turbidity.

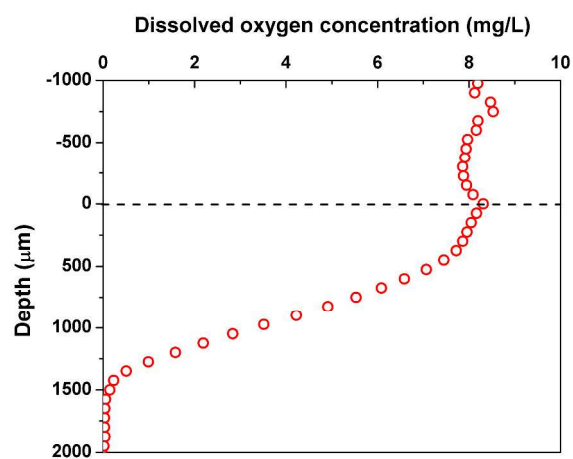


Figure S6. Dissolved oxygen concentration in sediment column.

Table S3. Depth distribution of SEM and AVS in each treatment.

	Depth (cm)	SEM-Cu (μmol/g dry weight)	SEM-Pb (μmol/ g dry weight)	SEM-Cd (μmol/ g dry weight)	SEM-Zn (μmol/ g dry weight)	ΣSEM (μmol/ g dry weight)	AVS (μmol/ g dry weight)
G1	0-1	4.6	1.6	0.8	147	154	49
	1-2	6.4	2.8	1.5	271	281	97
	2-3	4.0	2.3	1.1	216	224	26
	3-4	2.3	2.2	1.0	183	189	24
	4-5	3.3	2.5	1.1	229	236	29
G3	0-0.5	3.6	1.5	0.8	119	126	63
	0.5-1	56	11	3.8	3047	3118	107
	1-1.5	44	8	2.1	1368	1422	115
	1.5-2	84	13	4.6	2150	2251	148
	2-2.5	27	7	2.2	1354	1389	97
	2.5-3	81	13	3.4	2104	2201	131
	3-4	96	14	3.3	2285	2399	42
G4	0-1	3.5	1.2	0.5	94	99	26
	1-2	6.6	2.2	1.0	176	186	81
	2-3	6.1	2.0	0.9	164	173	88
	3-4	5.1	1.7	0.8	136	144	67
	4-5	5.7	1.9	0.8	153	161	67

Principal component analysis (PCA) of sample EXAFS spectra

PCA analysis was performed on the complete set of sample EXAFS spectra (Figure 3) using Athena software to determine the minimum number of components needed to reconstruct sample spectra.

PCA results are shown in Table S4 and the first five abstract components (C1-C5) are shown in Figure S7. The indicator parameter (IND) reached a minimum for three components, suggesting that the first three principal components are necessary to reconstruct sample spectra.^{7,8} Visual inspections of component spectra also suggest three principal components (Figure S7). Component C1 had the highest amplitude among all component spectra, suggesting it represented the primary feature of the sample spectra. C2 was characterized with lower amplitudes but still presented a clear distinction between signal and noise. C3 showed similar noise levels but had amplitude twice the height of the remaining spectra. The remaining component spectra (only C4 and C5 showed) had low signal-to-noise ratios and little meaningful information. C4 and C5 are shown for comparison. Therefore, component C1~C3 were selected for target transformation of reference spectra.

Target transformation for reference spectra

Target analysis was performed by reconstructing each reference spectrum (3 to 10 Å⁻¹) individually with the three abstract principal components (C1-C3) to identify reference standards for linear combination fitting (LCF). Normalized sum-square residual (NSS) values of each spectra reconstruction were used as the primary criterion for assessing the quality of target transformation. Prospective reference EXAFS spectra were also visually

assessed to ensure they were significantly distinct from each other, which is a requisite for proper selection of reference compounds.⁹

13 reference compounds were investigated and the results are shown in Figure S8.

Among all reference compounds, Zn(aq), ZnS, and Zn₅(CO₃)₂(OH)₆ had the smallest NSS values. Also, their EXAFS spectra showed significantly different oscillation structures. The spectrum of Zn₅(CO₃)₂(OH)₆ had a small oscillation near $\sim 7.0 \text{ \AA}^{-1}$ and wider separation of the first two peaks. The ZnS spectrum was characterized with small peaks either on the shoulder of a large peak or between two oscillations. Therefore, Zn(aq), ZnS and Zn₅(CO₃)₂(OH)₆ were selected as references to decompose the sample spectra.

LCF for EXAFS and XANES spectra

Least-squares LCF with the three reference standards were performed on EXAFS spectra (3 to 10 $\text{\AA}^{-1}$). The EXAFS spectra and fitted curves are displayed in Figure 3. Proportions of each Zn species and the associated uncertainties are shown in Figure 4 and Table S5. Residuals of the fits were calculated, as the sum of squares of residuals normalized to sum of squares of experimental data, R factor (Table S5). Reconstructed curves fit the original EXAFS spectra very well. Almost all R values were < 0.1 , with the only exception for sample G3_44min due to high levels of noise in the sample spectrum (Figure 3).

LCF was also performed on XANES data (-20 to 100 eV above absorption edge) with the same reference spectra. XANES spectra and reconstructed curves are shown in Figure S9. Proportions of Zn species and associated uncertainties obtained from LCF of XANES spectra are also shown in Table S6. The percentages of each Zn species derived from

XANES spectra correlated well with those calculated from EXAFS spectra (Figure S10). All points distributed close to the diagonal line $y=x$, indicating that both methods yielded equivalent results. Zn speciation (XANES) in both sediment beds and suspended particles showed similar trends (Figure S11). The fraction of Zn-CO₃ decreased with depth in the sediment bed while the fraction of Zn-S increased with depth. The Zn-CO₃ fraction in resuspended sediment decreased with time, while Zn-aq fraction increased with time and Zn-S fraction remained approximately constant through the course of sediment resuspension.

Table S4. Principal component analysis results

Component #	Eigenvalue	IND ($\times 10^{-5}$)
C1	18.25	7.079
C2	1.08	5.029
C3	0.21	4.818
C4	0.10	4.965
C5	0.08	5.180
C6	0.05	5.581
C7	0.04	6.066

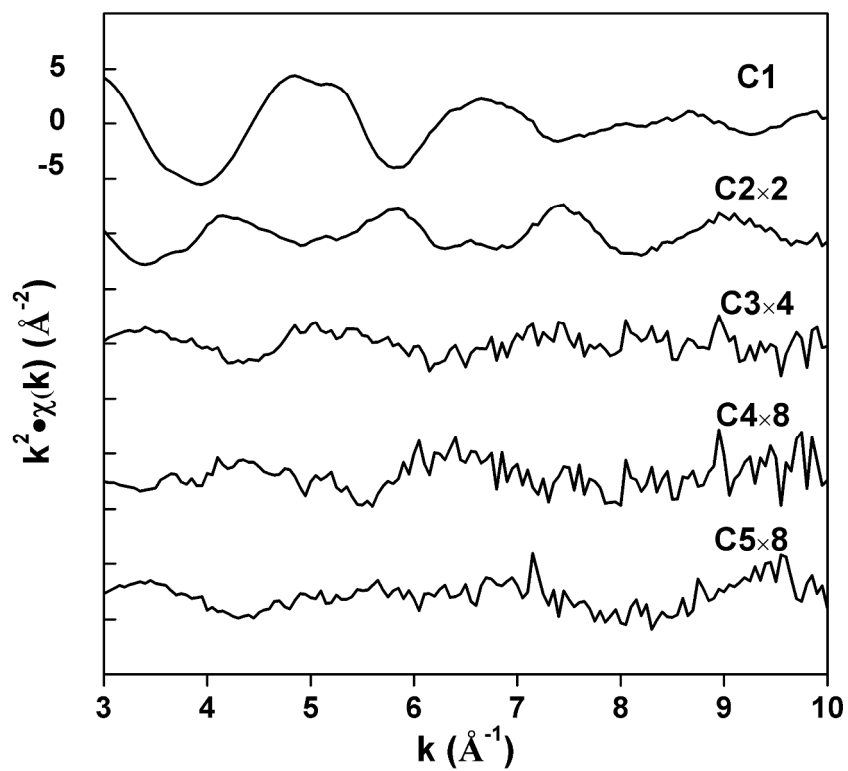


Figure S7. The first five components identified by PCA analysis. Amplitudes of C2, C3, C4 and C5 were multiplied by 2, 4, 8, and 8 respectively for clarity.

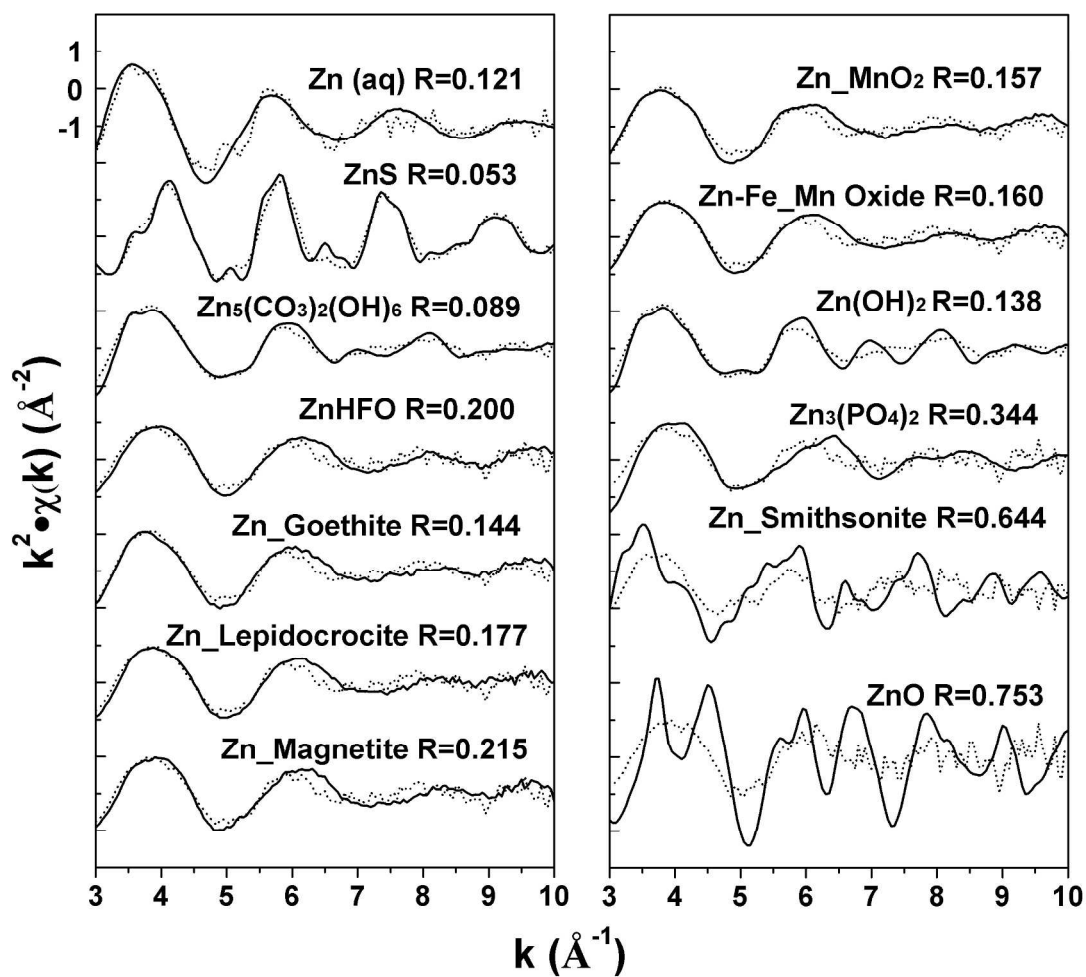


Figure S8. Zn K-edge EXAFS spectra (full lines), target transformations (dotted lines), and NSS values of 13 reference compounds. $R = \frac{\sum_i [k^2 \chi(k_i)_{\text{data}} - k^3 \chi(k_i)_{\text{fit}}]^2}{\sum_i [k^2 \chi(k_i)_{\text{data}}]^2}$.

Table S5. Zn speciation determined by LCF with EXAFS spectra

Sample	Zn-S (%)	Zn-CO ₃ (%)	Zn-aq (%)	R [*] (×10 ⁻²)
G2_0-1mm	9.6±1.9	72.1±3.1	18.4±3.6	6.59
G2_1-2mm	12.9±1.6	59.8±2.5	27.2±3.0	4.91
G2_2-4mm	39.3±1.7	50.4±2.8	10.3±3.3	5.00
G2_8-9mm	52.8±2.1	31.9±3.3	15.4±3.9	5.59
G2_10-20mm	56.9±1.6	31.0±2.5	12.1±3.0	3.73
G3_0-1mm	30.3±1.7	55.4±2.7	14.3±3.2	4.96
G3_1-2mm	25.8±1.6	47.7±2.6	26.5±3.1	5.01
G3_2-3mm	34.2±2.2	41.6±3.6	24.2±4.2	8.59
G3_3-4mm	57.5±2.3	31.6±3.6	10.9±4.3	6.98
G3_4-5mm	56.9±1.6	31.0±2.6	12.1±3.0	3.80
G3_8-9mm	61.0±1.6	25.9±2.6	13.1±3.1	3.62
G3_10-20mm	66.7±3.5	27.2±2.1	6.2±2.7	5.25
G3_t=42min	6.8±3.6	82.7±5.8	10.4±6.8	21.60
G3_t=62min	9.0±2.1	73.5±3.3	17.4±3.9	8.32
G3_t=122min	13.4±1.8	71.0±2.8	15.6±3.4	6.44
G3_t=217min	11.5±2.0	73.4±3.2	15.1±3.7	7.75
G3_t=249min	9.9±1.9	76.0±3.0	14.1±3.6	6.92
G3_t=283min	11.5±1.9	72.6±3.1	15.9±3.6	7.31
G3_t=544min	11.1±2.1	59.9±3.3	29.0±3.9	7.32
G3_t=1369min	9.4±1.9	70.0±3.1	20.6±3.6	6.85

$$*R = \sum_i [k^2 \chi(k_i)_{\text{exp}} - k^3 \chi(k_i)_{\text{reconstr}}]^2 / \sum_i [k^2 \chi(k_i)_{\text{exp}}]^2$$

Table S6. Zn speciation determined by LCF with XANES spectra.

Sample	Zn-S (%)	Zn-CO ₃ (%)	Zn-aq (%)	R [*] (×10 ⁻³)
G2_0-1mm	14.3±2.2	64.0±5.1	21.7±6.6	2.9
G2_1-2mm	23.1±1.6	56.5±3.7	20.3±5.4	1.7
G2_2-4mm	46.4±1.3	38.5±3.0	15.0±4.9	1.1
G2_8-9mm	63.1±2.2	19.0±5.2	17.8±6.6	3.4
G2_10-20mm	69.9±1.3	16.3±2.9	13.7±4.8	1.2
G3_0-1mm	39.4±1.5	44.0±3.4	16.6±5.2	1.5
G3_1-2mm	35.1±1.3	49.0±3.1	16.0±4.9	1.2
G3_2-3mm	48.2±1.8	35.7±4.2	16.1±5.8	2.3
G3_3-4mm	62.4±1.3	24.0±3.0	13.6±4.8	1.1
G3_4-5mm	69.9±1.2	16.7±2.8	13.4±4.7	1.1
G3_8-9mm	71.4±1.3	15.7±3.1	12.9±4.9	1.3
G3_10-20mm	68.3±2.7	16.8±6.3	14.9±7.7	4.7
G3_t=42min	16.5±4.0	72.0±9.1	11.6±10.6	9.7
G3_t=62min	19.9±2.0	65.0±4.7	15.1±6.2	2.7
G3_t=122min	22.1±1.8	63.8±4.2	14.1±5.8	2.1
G3_t=217min	20.9±2.7	62.6±6.2	16.5±7.6	4.5
G3_t=249min	16.3±4.0	60.2±6.9	23.5±5.6	10.3
G3_t=283min	19.9±1.9	65.0±4.3	15.1±5.9	2.3
G3_t=544min	12.8±4.2	57.8±7.3	29.4±5.9	11.0
G3_t=1369min	11.0±4.2	64.5±7.3	24.6±5.9	11.0

$$* R = \sum_i [k^2 \chi(k_i)_{\text{exp}} - k^3 \chi(k_i)_{\text{reconstr}}]^2 / \sum_i [k^2 \chi(k_i)_{\text{exp}}]^2$$

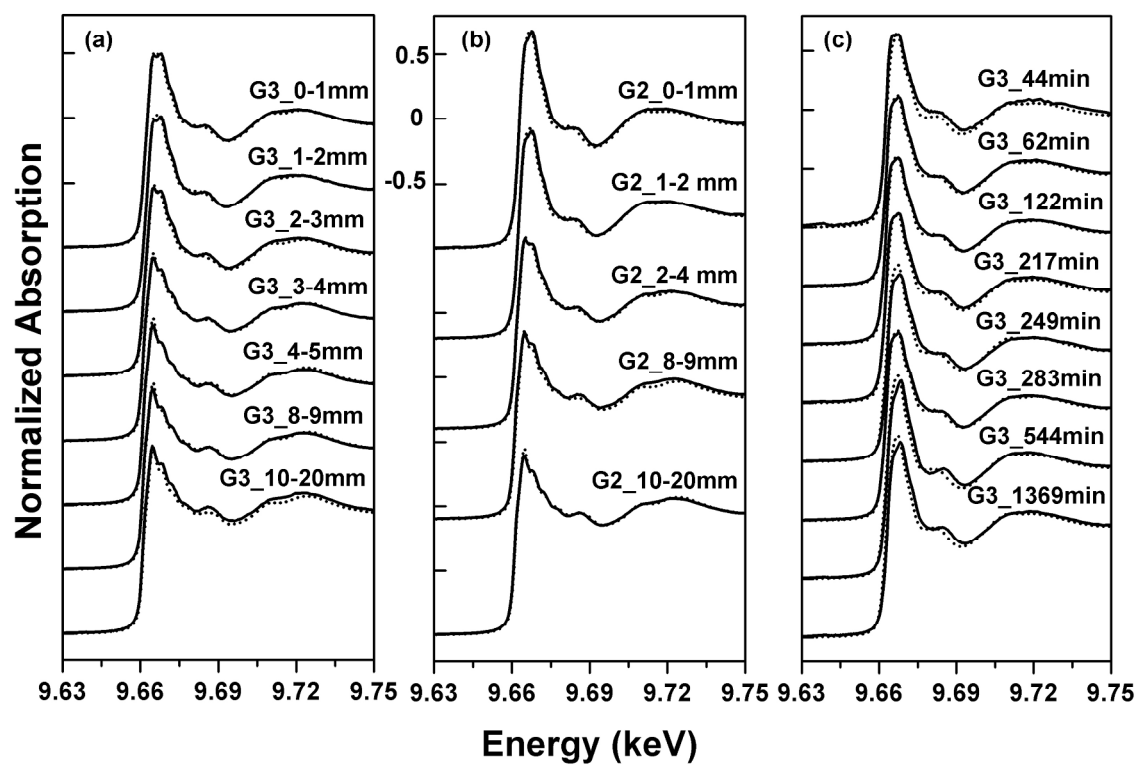


Figure S9. XANES spectra (full lines) and reconstructed curves (dotted lines) of sediment samples.

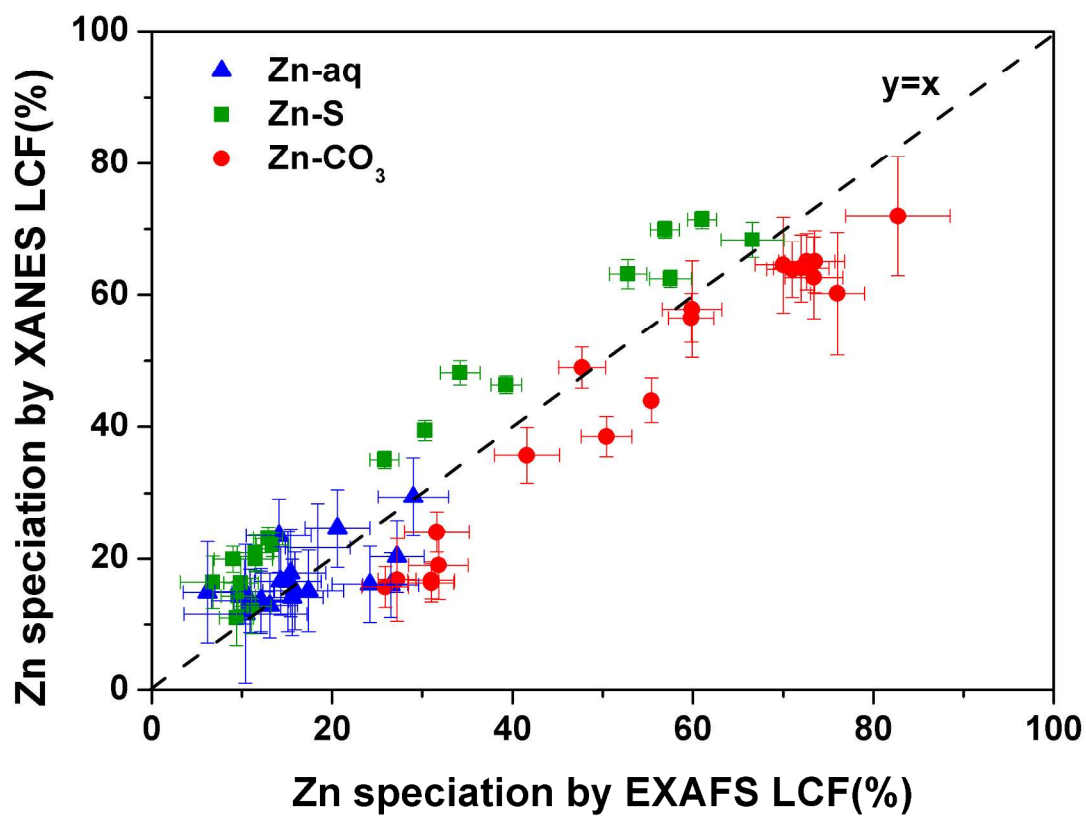


Figure S10. Correlation between percentages of Zn species determined by LCF from EXAFS and XANES spectra.

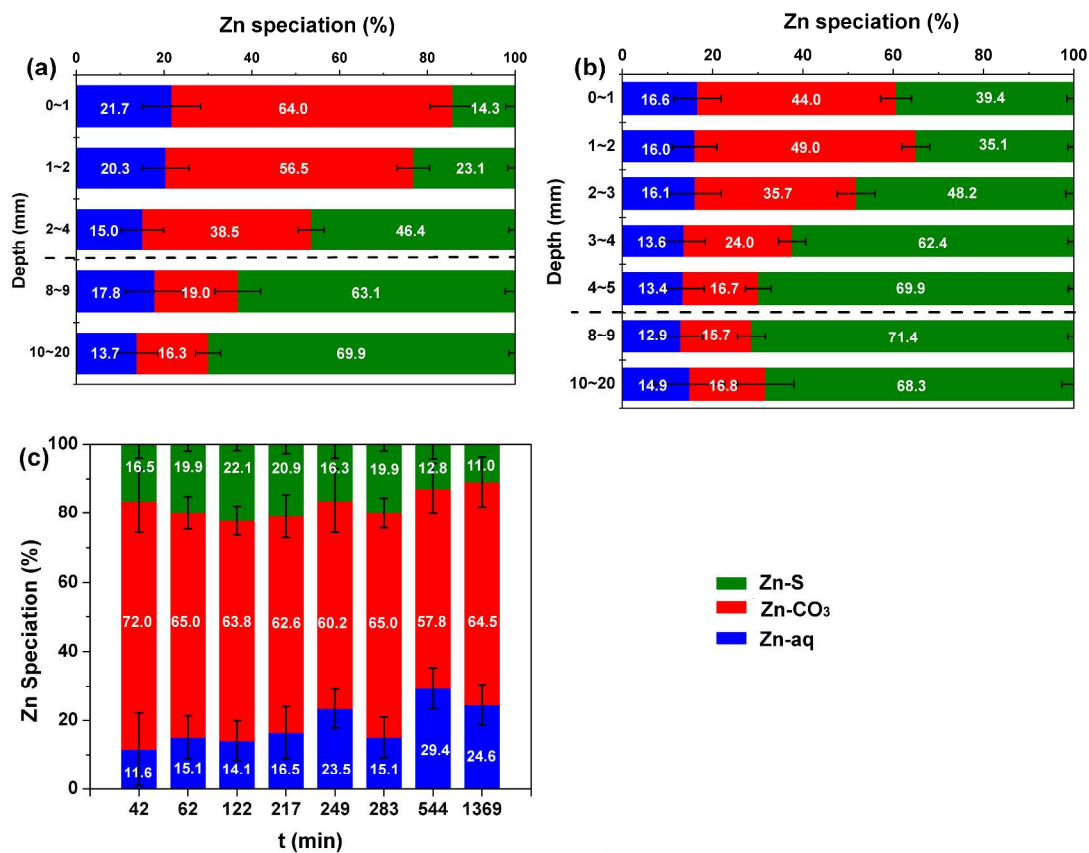


Figure S11. Zn speciation in sediment beds and resuspended sediment particles determined by LCF of XANES spectra.

References:

1. Webb, S. M. The Chemistry of Zinc-Microbe Interactions in the Sediments of Lake DePue, IL. Ph.D. Dissertation. Northwestern University, 2001; <http://www-ssrl.slac.stanford.edu/~swebb/thesis.html>.
2. Webb, S.; Gaillard, J.-F., Zinc Speciation in Contaminated Sediments: Quantitative Determination of Zinc Coordination by X-ray Absorption Spectroscopy. *Aquatic Geochemistry* **2014**, 1-18; DOI 10.1007/s10498-014-9243-x.
3. Webb, S. M.; Leppard, G. G.; Gaillard, J. F., Zinc speciation in a contaminated aquatic environment: characterization of environmental particles by analytical electron microscopy. *Environmental science & technology* **2000**, 34, (10), 1926-1933.
4. Gaillard, J. F.; Webb, S. M.; Quintana, J. P. G., Quick X-ray absorption spectroscopy for determining metal speciation in environmental samples. *Journal of Synchrotron Radiation* **2001**, 8, 928-930.
5. Green Eyes Environmental Observing Systems Website; http://gescience.com/erosion_microcosm.html
6. Gaillard, J. F.; Chen, C.; Stonedahl, S. H.; Lau, B. L. T.; Keane, D. T.; Packman, A. I., Imaging of colloidal deposits in granular porous media by X-ray difference microtomography. *Geophysical Research Letters* **2007**, 34, (18).
7. Scheinost, A. C.; Kretzschmar, R.; Pfister, S.; Roberts, D. R., Combining selective sequential extractions, X-ray absorption spectroscopy, and principal component analysis for quantitative zinc speciation in soil. *Environmental science & technology* **2002**, 36, (23), 5021-5028.
8. Malinowski, E. R., Determination of the number of factors and the experimental error in a data matrix. *Analytical Chemistry* **1977**, 49, (4), 612-617.
9. Da Silva-Cadoux, C.; Zanella, L.; Gaillard, J.-F., Selecting reference compounds for determining chemical speciation by X-ray absorption spectroscopy. *Journal of Analytical Atomic Spectrometry* **2012**, 27, (6), 957-965.