

Coupled Effects of Hydrodynamics and Biogeochemistry on Zn Mobility and Speciation in Highly Contaminated Sediments

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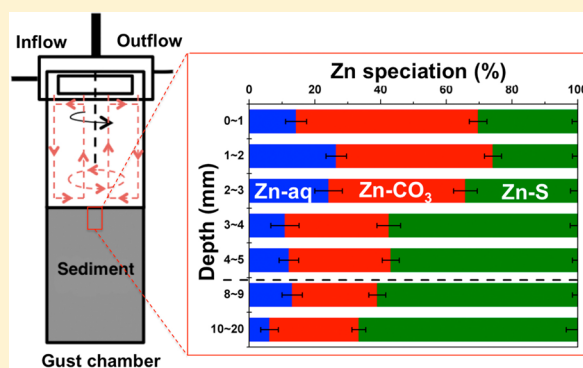
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Supporting Information

ABSTRACT: Porewater transport and diagenetic reactions strongly regulate the mobility of metals in sediments. We executed a series of laboratory experiments in Gust chamber mesocosms to study the effects of hydrodynamics and biogeochemical transformations on the mobility and speciation of Zn in contaminated sediments from Lake DePue, IL. X-ray absorption spectroscopy (XAS) indicated that the oxidation of surficial sediments promoted the formation of more mobile Zn species. Bulk chemical measurements of porewater, overlying water, and sediment also suggested that this process liberated aqueous metals to porewater and facilitated Zn efflux to the overlying water. In addition, sediment resuspension events increased the release of aqueous metals to both surficial porewater and the overlying water column. XAS analysis indicated that resuspension increased dissolution of Zn-sequestering mineral phases. These results show that both steady slow porewater transport and rapid episodic resuspension are important to the release of metal from fine-grained, low-permeability contaminated sediments. Thus, information on metals speciation and mobility under time-varying overlying flow conditions is essential to understanding the long-term behavior of metals in contaminated sediments.



INTRODUCTION

Contamination of aquatic sediment is a major concern worldwide. Approximately 10% of sediments underlying surface waters in the U.S. are substantially contaminated.¹⁻³ Metals and metalloids (e.g., arsenic), PCBs, pesticides, and polycyclic aromatic hydrocarbons are the most frequently reported contaminants in sediments.^{1,4} Metallic contaminants in sediments exhibit high environmental persistence and readily impact benthic organisms.⁵ Benthic organisms take up metals through multiple pathways, including absorption through skin and gills and ingestion of metal-contaminated sediments or food, yielding both acute and chronic toxic effects.⁶ For example, exposure to ppm levels of Zn can damage gills, induce changes in physiology and behavior, and cause death of fishes.⁷

Two-tiered strategies have been suggested for the remediation of contaminated sediment sites.⁸ The first tier of strategies aims to stabilize metals within sediments. Methods for this purpose include sediment amendments and capping. The second tier requires sediments to be dredged and treated *ex situ*. Unless the sediments are heavily contaminated and/or eminently hazardous to human health or biota, *in situ* remediation is generally preferred. Improved methods for comprehensive assessment of the mobility, bioavailability, and

toxicity of metal contaminants in sediments are needed to better evaluate the risks posed by contaminated sediments and design remediation strategies.

Once deposited in sediments, the chemical evolution of metals is strongly influenced by diverse biogeochemical reactions. Sediments are broadly subdivided into oxic, suboxic, and anoxic according to the diagenetic sequence of terminal electron acceptors that regulate the degradation of labile organic matter.^{9,10} The penetration depth of oxygen into sediment reflects the balance between the downward transport of O₂ and its consumption by respiration of benthic organisms and oxidation of reduced mineral phases.⁹ Porewater advection and molecular diffusion control solute transport in surficial sediments, modifying redox gradients and the redistribution of metals between sediment and porewater.¹¹⁻¹³ Sediment resuspension, either natural (storms, tides) or anthropogenic (dredging, construction, ship propeller wash), greatly increases the exposure of sediments to oxygenated overlying water and

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promotes the release of contaminants into the water column.^{14,15} Sediment mixing and reworking by benthic organisms also continually exposes sediment-bound contaminants to the sediment–water interface.^{16,17} Beyond these processes, mobility and bioavailability of metals also strongly depend on their chemical speciation.¹⁸ Metals bind to iron and manganese oxy-hydroxides and organic matter (OM) in oxidized sediment, and the low solubility of many metal oxide and hydroxide minerals limits metals concentration in porewater.¹⁹ In anoxic sediments, the primary mechanism of metal sequestration is normally assumed to be the formation of insoluble metal sulfides.²⁰ Processes such as metabolism of OM, reductive dissolution of Fe and Mn-oxides, and the oxidative dissolution of ZnS release Zn to porewaters.^{21–23}

While many of these processes have been extensively studied, interactions between them are not clearly understood. In particular, the coupled effects of sediment resuspension and biogeochemistry on metals speciation, mobility, and net remobilization to the water column are poorly understood. This information is essential to understanding the release of metals from contaminated sites that are subject to episodic disruptive events, such as storms, flooding, or dredging. The goal of this study was to improve understanding of the underlying mechanisms that control the mobility of metals in hydrodynamically disrupted sedimentary systems, focusing particularly on interactions between sediment resuspension and metal speciation that control metal mobility. We performed experiments under controlled hydrodynamic forcing in Gust chamber mesocosms with sediment cores and homogenized sediments collected from a Zn-contaminated sediment site. We compared metals chemistry in porewaters, overlying waters, bed sediments, and resuspended sediment particles with and without sediment resuspension to determine how resuspension controls metal mobility.

MATERIALS AND METHODS

Sediment Source. Laboratory experiments were performed with Zn-contaminated sediments from Lake DePue, a shallow backwater lake of the Illinois River located in north-central Illinois (Figure S1, Supporting Information). Lake DePue has an average surface area of 212 ha with 18.2 km of shoreline. Lake DePue has received substantial metal contamination from industries, particularly Zn smelting, since the early 1900s. Zn has been found in Lake DePue sediments at concentrations ranging from 304 to 42 300 mg/kg.²⁴ Zn in lake sediments has been shown to be associated with P close to the contamination source and becomes more predominately associated with S farther from the source.^{25,26}

Sediment Collection. Experiments were performed on both intact sediment cores and homogenized sediments. Sediments were collected from Lake DePue in September 2011 at the location shown in Figure S1, Supporting Information. Three cores (diameter = 10 cm and length = 45 cm, polycarbonate) were hand driven into sediment to a depth of 35 cm carefully to minimize the disturbance of the sediment–water interface, leaving 10 cm headspace of overlying water. Following insertion into the sediment, the upper part of each core was sealed with a piston, carefully retrieved, and closed from below with another piston. Sediments for homogenized experiments were collected from the same location to a depth of 15 cm. Sediment samples were immediately transported to the laboratory and refrigerated at 4 °C until used in laboratory experiments.

Sediment Characterization. Bulk sediment properties (porosity, particle size distribution (PSD), permeability, total metals) were measured on homogenized sediment samples. Porosity was determined by drying 3 cm³ sediment samples at 70 °C for 48 h and converting the weight loss to water volume fraction. The sediment grain size distribution was determined by wet-sieving at 45 and 106 μm and measuring the dry weight. In addition, smaller particles were sized using a Beckman Coulter Multisizer 3 (Fullerton, CA).²⁷ Permeability was measured in a constant-head permeameter with a test section of 2.5 cm diameter and 5 cm length (Chromatography column, Omnifit Ltd.). Total bulk sediment metal concentrations were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Vista-MPX, Varian) after microwave-assisted acid digestion following USEPA method 3051A. Total organic carbon was measured with a Costech ECS 4010 elemental analyzer (Costech Analytical Technologies Inc., Valencia, CA) after acidifying 80 mg of dried and powdered sediment with 1.5 mL of 4 M HCl to remove inorganic carbon.

Experimental Setup. The Gust chambers (Green Eyes LLC, Cambridge, MD, USA) (Figure S2, Supporting Information) use a combination of a spinning disk and central suction to generate nearly uniform shear stress across the sediment–water interface. All parts of the Gust chamber in contact with sediments and water were made of polycarbonate to minimize metal contamination. Overlying water was recirculated by means of a peristaltic pump to a 500 mL HDPE water reservoir (Nalgene). Shear stresses from 0.01 to 0.45 Pa were achieved by varying the rotation rate of the spinning disk and the recirculation flow rate. Oxygenated artificially reconstituted fresh water (ARFW), composed of 5 g of CaSO₄, 5 g of CaCl₂, 3 g of MgSO₄, 9.6 g of NaHCO₃, and 0.4 g of KCl in 100 L of milli-Q water (Millipore),²⁸ was recirculated throughout the experiment.

Hydrodynamic Conditions and Sediment Resuspension. The Gust chambers support controlled investigations of sediment resuspension.^{29,30} We characterized the critical shear for resuspension of Lake DePue sediment by increasing the stirring and the recirculation rates in a stepwise fashion while recording the turbidity of the overlying water. The critical shear stress was 0.36 Pa. Metals efflux and speciation were then observed in Gust chambers with intact cores and homogenized sediments and with and without periods of episodic resuspension, as detailed in Table 1.

Experimental Procedure. Before each experiment, all parts of the Gust chamber, including tubing and reservoir container, were cleaned by soaking in 10% HNO₃ (v/v) for 24 h followed by soaking and rinsing twice with Milli-Q water. For

Table 1. Conditions for Gust Chamber Experiments^a

	duration (days)	periods of sediment resuspension		sediment structure
G1	14.2	–		intact core
G2	9.0	4 h on day 9	–	intact core
G3	14.2	0.3 h on day 6	4 h on day 12	intact core
G4	14.7	–		homogenized

^aAll experiments were conducted under a baseline hydrodynamic shear of 0.19 Pa (50% of the shear required for resuspension). Experiments G2 and G3 were also subject to episodic resuspension. Experiment G2 was disassembled immediately after resuspension on day 9, while experiment G3 was disassembled on day 14, 2 days after the sediment resuspension event on day 12.

experiments with homogenized sediment structure, 800 mL of sediments was homogenized with a plastic utensil and then packed into the Gust chamber to form a 10 cm sediment bed with a flat surface, leaving 10 cm of headspace for overlying water. ARFW was then introduced slowly to avoid disturbing the sediment–water interface (SWI). The Gust chamber erosion head was placed on the core, with the inlet and outlet ports connected to the recirculation system using tygon tubing (VWR International, USA) and a peristaltic pump (Masterflex, Cole Parmer). Sediments were allowed to consolidate overnight, and then, the experiments were initiated by rotating the stirring disk at a constant speed and recirculating the water at a constant rate. For experiments performed on intact sediment cores, the overlying water brought with the core from the field was slowly replaced with ARFW and then the Gust chamber erosion head was fit directly onto the cores. Experiments were run continuously for 9–15 days, as noted in Table 1. In experiments G2 and G3, episodic periods of resuspension were imposed by increasing the shear above the critical value for the defined period noted in Table 1 and then returning to the baseline condition. In experiment G2, the Gust chamber was disassembled on day 9, immediately after the resuspension event, to observe transient changes in metals speciation caused by resuspension. In experiment G3, two periods of resuspension were imposed, and then, the shear was returned to the baseline level for the remainder of the two-week experiment.

Sampling and Analysis. At the end of each experiment, sediment subcores were obtained using 60 mL modified plastic syringes. Four subcores of each experiment were transferred to an anaerobic chamber (3% H₂ and 97% N₂) (Coy laboratory products Inc., USA). Two subcores were then sectioned at 1 cm intervals and centrifuged at 3414g for 20 min to extract porewater (Legend RT plus, Thermo Scientific). The supernatant was then filtered through a 0.2 μm nylon filter (VWR International, USA), acidified with concentrated, trace-metal grade HNO₃ (Sigma-Aldrich, USA) to pH < 2, and stored at 4 °C until analyzed by ICP-AES. Another subcore was sectioned at 1 cm intervals and stored at –20 °C for analysis of acid volatile sulfides (AVS) and simultaneously extracted metals (SEM). The last core was sectioned at 1 mm intervals over the first centimeter of sediment and then at 1–2 cm intervals over the remainder of the core for analysis of metals speciation by X-ray absorption spectroscopy (XAS). These samples were smeared on filter paper, sandwiched between two layers of Kapton tape, and stored under N₂ atmosphere frozen at –80 °C until analysis. Resuspended particles from experiment G3 were also analyzed by XAS. Eight mL of overlying water was filtered using a 0.2 μm isopore polycarbonate membrane filter (Millipore, MA, USA). The filters were then sandwiched between two layers of Kapton tape and then handled as described above.

AVS and SEM were determined by the 1 M cold HCl extraction and 0.5 M NaOH trap technique.³¹ S^{2–} was measured by colorimetry with a UV–visible spectrophotometer (Spectronic 20, Spectronic Instrument) after the addition of a mixed diamine reagent. Metal concentrations in the extractant were measured using ICP-AES.

The ICP-AES was calibrated by using single-element standards (Zn, Cu, 1000 mg L^{–1}) (Sigma-Aldrich, USA) added to Milli-Q water to span the concentration range of each metal in the experimental samples. Standards were reanalyzed after every ten experimental samples to correct for drift.

XAS was performed at the Zn K-edge on sediment samples and reference phases using the bending magnet beamline of the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT), Sector 5 of the Advanced Photon Source, Argonne National Lab. A Si (111) double crystal monochromator was used to vary the X-ray energy from –100 to +600 eV above the Zn K-edge (9658.6 eV). Sample spectra were collected in fluorescence mode using either a silicon drift detector (Vortex-ME4) or a 13 element HP-Ge solid state detector (Canberra) while reference spectra were collected in transmission mode. The intensity of the incoming beam (I_0) as well as the transmitted beams (I_{T1} and I_{T2}) was measured using Oxford ionization chambers with path lengths of 29.6 cm. The energy scale of the monochromator was calibrated to 9658.6 eV using the first derivative of the absorption threshold of a Zn foil that was simultaneously measured during data acquisition.

The chemical speciation of Zn in bed and resuspended sediments was assessed directly using XAS based on the decomposition of observed spectra as the sum of its components. Mathematically:

$$\text{FIT} = \sum_i f_i \times \text{REF}_i$$

where FIT is the reconstructed sample spectrum for a mixture of compounds and f_i is the fraction corresponding to the reference compound spectrum REF_{*i*}.

Extended X-ray absorption fine structure (EXAFS) data were processed and analyzed with the Athena software³² to determine the distribution of Zn major chemical species in bulk sediment samples.^{33–35} Briefly, EXAFS spectra were first normalized to an edge step of 1, and the EXAFS were extracted using a smooth background function ($\mu_0(E)$) as calculated by the AUTOBK algorithm, integrated into Athena, imputing the same set of parameters for the entire observed spectra.³⁶ Principal component analysis (PCA) was performed on k^2 -weighted EXAFS spectra (k ranging from 3 to 10 Å^{–1}) of the 20 sediment samples analyzed to determine the minimum number of statistically relevant components necessary to reproduce the observed spectra. Target transformation (TT) analysis was then carried out on a library of 13 reference spectra (with $3 < k < 10$ Å^{–1}) with the identified principal components to select reference compound EXAFS for spectral decomposition. Finally, Zn speciation in the sediment samples was determined by least-squares linear combination fitting (LCF) of the EXAFS using the basis set defined by the selected reference compounds. PCA, TT, and LCF calculations are described in detail in the Supporting Information.

RESULTS

Sediment Characteristics. Measurements of bulk sediment properties are reported in Supporting Information. Bulk sediment characteristics are reported in Table S1, Supporting Information, the sediment particle size distribution in Figure S3, Supporting Information, and sediment microstructure in Figure S4, Supporting Information. The sediment was composed primarily of very fine particles (~80% of particles with diameter <10 μm) and contained, on average, 3% organic carbon. Consequently, the sediment had a very low permeability, $2.0 \pm 1.2 \times 10^{-14}$ m². The bulk sediment Zn concentration was very high, on the order of 1.4% by mass, which is consistent with prior assessments of metals contamination in Lake DePue.^{24,26,37}

Zn Concentration in Porewater. Porewater Zn concentrations in experiments with and without sediment resuspension are shown in Figure 1. Zn concentrations in porewater

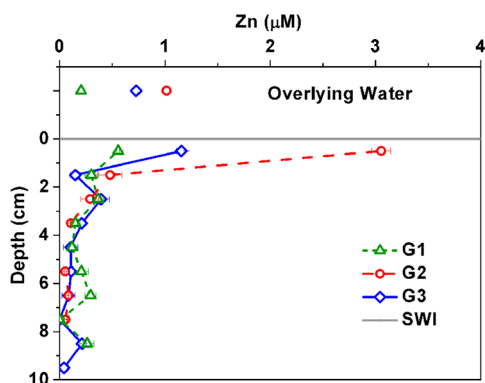


Figure 1. Zn concentrations in porewater. G3 was sampled 2 days after resuspension; G2 was sampled immediately after resuspension, and there was no resuspension in G1. Error bars represent ± 1 standard deviation of three measurements.

from experiment G1 (without resuspension) provide a frame of reference for experiments G2 and G3 (with resuspension). Results from experiments G2 and G3 reflect measurements of porewater Zn concentrations at different times after resuspension: immediately after resuspension and 2 days later.

Dissolved Zn concentrations at depths greater than 1 cm were uniform for all three treatments, suggesting that Zn solubility remained constant with depth. Porewater Zn concentrations near the top of the core, i.e., within the first centimeter, were significantly higher than those observed at depth and those in the overlying water, suggesting that diagenetic processes change the solubility of Zn resulting in its mobilization near the sediment–water interface, making the sediment a source of Zn to the overlying water. Resuspension increased porewater Zn concentration in the first centimeter of the sediments, and these concentrations decreased following cessation of sediment transport. In experiment G2, which was subcored immediately after resuspension, the Zn concentration in the porewater within the first centimeter of sediment was $3.04 \mu\text{M}$, much greater than the surficial porewater concentration in experiment G3, $1.15 \mu\text{M}$, which was sampled

2 days after resuspension. Both of these porewater Zn concentrations were much higher than those observed in experiment G1, $0.55 \mu\text{M}$, which had no resuspension.

SEM and AVS. SEM and AVS results are presented in Figure 2. Extracted Zn, Cu, Pb, and Cd concentrations are reported in Table S3 (Supporting Information). Zn was the primary metal present in the sediments: Zn was more than 95% of the total SEM (ΣSEM) for all samples. The AVS profile for experiment G4, with homogenized sediment structure, showed lower concentrations in the surficial sediment and relatively constant concentrations at depth, suggesting oxidation of surficial sediment by diffusion of oxygen from the overlying water.³⁸ The SEM/AVS molar ratios were all >1 , indicating that a significant fraction of metals is bound to other ligands other than volatile sulfides. This condition is generally interpreted to mean that metals toxicity is likely.³⁹ The maximum SEM/AVS ratio was observed at the SWI, suggesting higher likelihood of metal toxicity to epibenthic organisms.

AVS profiles for experiments G1 and G3, with intact sediment structure, showed higher concentrations at a depth of 1–2 cm than in both surficial and deeper sediment, suggesting that sulfide production was the greatest at this depth. Lower AVS concentrations in the surficial sediment also suggest oxidation from oxygen diffusion from the overlying water. The SEM/AVS ratio varied dramatically between the two cores, with an average of 6.1 and 20.9 for G1 and G3, respectively, suggesting that there is significant spatial variability in sediment metal toxicity at this site.

Zn Speciation. EXAFS spectra and their LCF results for all sediment samples are shown in Figure 3. In both experiments G2 and G3, the first two oscillations shifted toward higher k values with depth, while two other oscillations in the region $k = 7\text{--}10 \text{ \AA}^{-1}$ became more evident (Figure 3a,b), suggesting changes in the average coordination environment of Zn.

PCA analysis of the entire data set revealed three major principal components which were identified by target transformation as $\text{Zn}(\text{aq})\text{--Zn-aq}$, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6\text{--Zn-CO}_3$, and ZnS--Zn--S (see Supporting Information). The percentage of each Zn species in sediment samples and associated uncertainties determined by LCF are reported in Table S5, Supporting Information, and the resulting reconstructed curves are displayed in Figure 3.

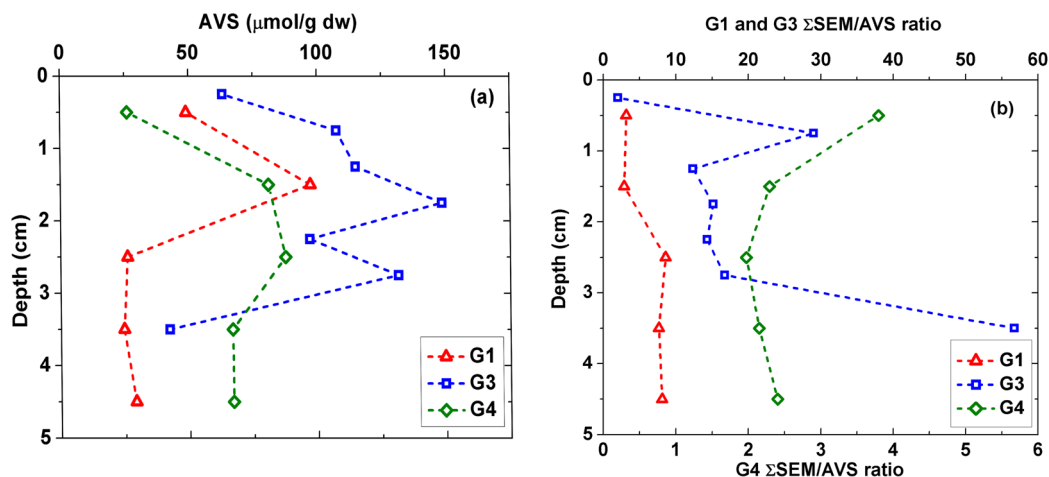


Figure 2. Profiles of AVS and SEM/AVS ratio in homogeneous sediments (G4) and intact sediment cores (G1 and G3).

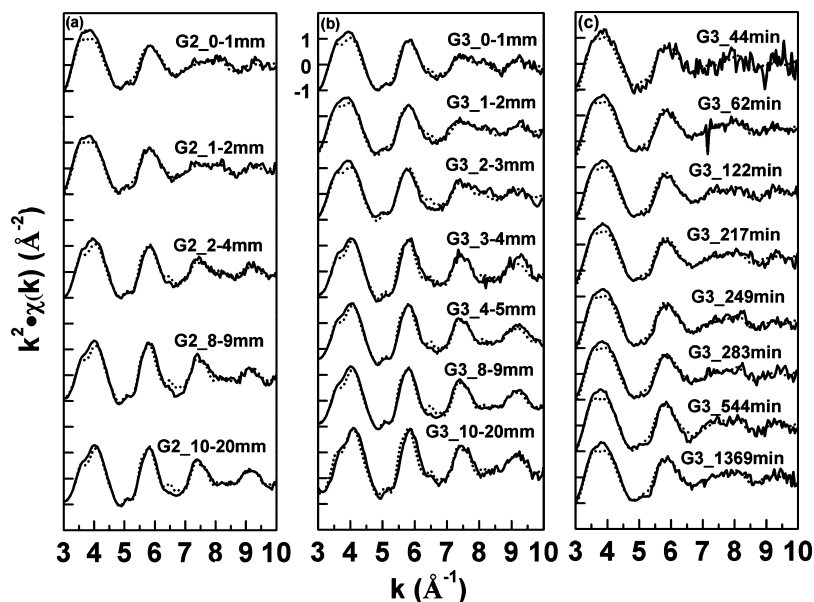


Figure 3. EXAFS spectra (full lines) and LCF reconstructed curves (dotted lines) for sediment samples in experiments G2 and G3. (a) Sediment core from experiment G2. (b) Sediment core obtained from experiment G3. (c) Resuspended sediments from experiment G3.

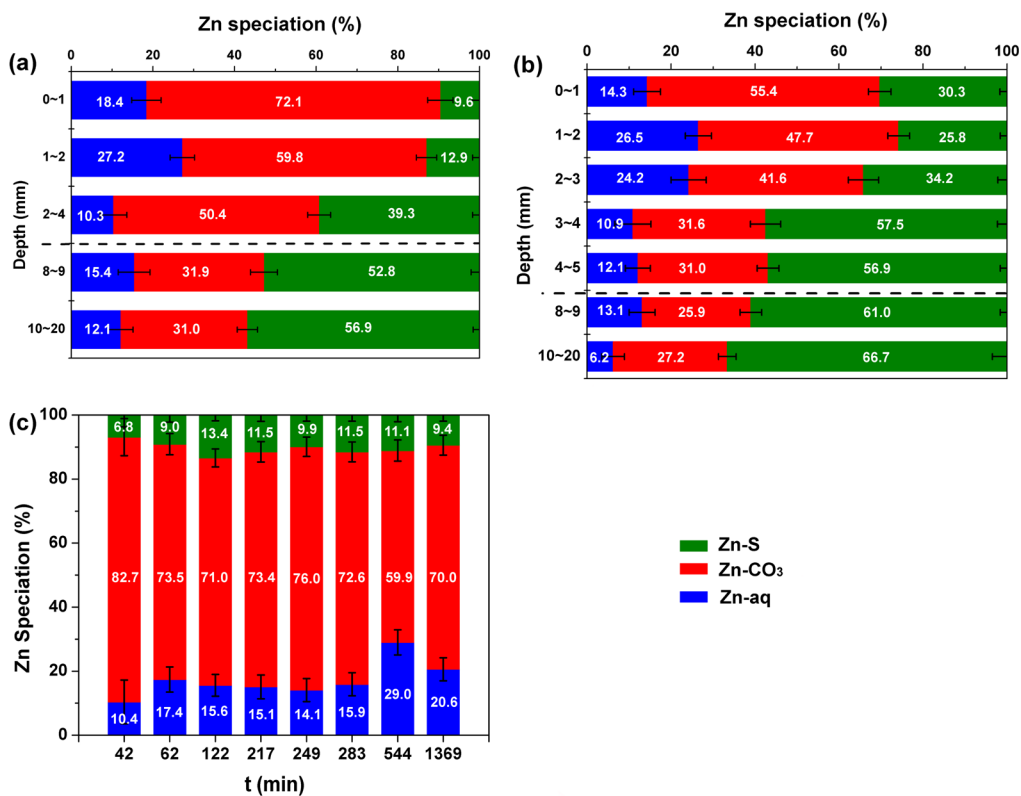


Figure 4. (a) Zn speciation in sediment core from experiment G2, obtained immediately after a resuspension event. (b) Zn speciation in sediment core of experiment G3, obtained 2 days after a resuspension event. (c) Temporal evolution of Zn speciation in resuspended sediments in the water column from experiment G3. $t = 0$ corresponds to the initiation of resuspension.

Cores from experiments G2 and G3 showed similar speciation profiles (Figure 4a,b). Zn was primarily associated with sulfide at a depth below 1 cm). The fraction of Zn-S increased with depth whereas Zn-CO₃ decreased, evidencing a change in Zn coordination as a result of the biogenic formation of sulfides. Experiment G2, sampled immediately after a resuspension event, showed greater abundance of Zn-CO₃

and Zn-aq in surficial sediments than experiment G3, sampled 2 days after a resuspension, indicating that resuspension led to repartitioning of Zn between oxidized and reduced phases, and liberated Zn(aq) near the SWI. This observation is consistent with the porewater concentration profiles shown in Figure 1.

Resuspension events scoured surficial sediments to a depth of just 1–2 mm. Zn-aq, Zn-CO₃, and Zn-S were identified in

resuspended particles from experiment G3 (Figure 4c). During the period of resuspension, the Zn–S fraction in the resuspended material increased for 2 h and then slowly decreased, suggesting that a balance was achieved between suspension of the sediment bed and deposition of suspended particles. The Zn–aq fraction increased significantly over the first 2 h, indicating ongoing erosion of surficial sediments. After 2 h, the Zn–aq fraction continued to increase slowly while Zn–S and Zn–CO₃ fractions slowly decreased, suggesting Zn was released from dissolution of these two phases. Experiment G3 also showed that a significant proportion of Zn–S persisted as a function of time in the suspended particles. This indicates that the ZnS phase was not significantly oxidized in the presence of dissolved oxygen, as observed previously.⁴⁰

DISCUSSION

The mobility and bioavailability of metals in sediments are affected by the solubility of the metal species present.⁴¹ Using XAS, we identified a mixture of three Zn species in bed sediments and resuspended particles: Zn–aq, Zn–CO₃, and Zn–S.⁴² The Zn–aq fraction represents the most labile form of Zn since it encompasses the hexa-coordinated Zn aqua ion as well as weak outer-sphere Zn surface complexes.⁴² Throughout the sediment cores, the solubility of Zn in the porewaters was primarily controlled by the presence of the more soluble Zn–CO₃ coexisting with less soluble Zn–S species.

XAS analysis of sediment subcores revealed that Zn sulfide species increased with depth in the sediments. AVS followed similar patterns, as Zn sulfides were the primary components of AVS, resulting in high SEM/AVS ratios near the sediment surface. Lower surficial AVS concentrations have been observed in many other studies, and toxicity is anticipated when the SEM/AVS ratio exceeds one.^{38,43,44} Here, the combination of XAS, O₂, SEM, and AVS profiles suggests that oxidation reactions near the SWI dissolved binding phases and released weakly bound Zn–aq to porewater and the water column.

While release of contaminants from fine sediments is normally assumed to occur primarily by diffusion, we observed that transient releases induced by sediment remobilization were critical to overall efflux of metals from the sediments. The Lake DePue sediment was extremely fine grained and had a very low permeability, in the regime where porewater flow is expected to be negligible and diffusion is the dominant mechanism of solute transport.¹² However, episodic resuspension greatly increased concentrations of Zn both in surficial porewater and overlying water. These elevated concentrations were highly transient and decreased to near preresuspension levels within 2 days of the cessation of sediment resuspension. XAS analysis also indicated that resuspension led to repartitioning between Zn–aq, Zn–CO₃, and Zn–S phases in both sediment cores and resuspended particles. This suggests that resuspension liberated weakly bound Zn–aq to the overlying water and enhanced dissolution of Zn-sequestering mineral phases, resulting in increased metals mobility and efflux from the sediments. This process is expected to contribute to substantial net Zn release from the sediments in fine-grained natural systems subject to episodic sediment transport.

It is recognized that sediments are extremely complex systems and the fate of metals in sediments varies greatly with sediment properties. The sediments used in this study have very high Zn (~220 μmol/g) and sulfide (25–150 μmol/g) concentrations owing to discharge of waters resulting from the leaching of Zn smelter tailings. Such high concentrations are

quite typical of sites with sediments contaminated by mining and smelting activities.^{45–47} Mines and smelting plants processing ores of massive metal-sulfide deposits often give rise to contaminated sediment deposits with chemistry similar to that found in Lake DePue.^{48–51} In other contaminated sites with higher sulfide and lower Zn concentrations, Zn speciation and mobility also greatly depend on fate of other redox-sensitive metals like Fe and Mn. However, FeS and MnS are readily oxidized whereas the oxidation of ZnS is slow.¹⁴

Implications for Assessment of Contaminated Sites.

The results of the present study focus on both steady slow porewater transport and rapid sediment resuspension to assess the mobilization and release of metals from highly contaminated sediments. Some of these findings are also broadly applicable to many other types of sediment since the development of conceptual models for critical processes and exposure pathways is essential to support risk assessments and remediation designs for contaminated sediment sites. Successful remediation designs require projection of how specific interventions/events will affect contaminant efflux and effects and therefore must be targeted to specific mechanisms of contaminant mobility, bioavailability, and toxicity. Site models are often limited by difficulty in obtaining information in the field, particularly in large and complex sites. Low sampling densities, infrequent sediment sampling, and incomplete characterization of contaminant phases often restrict interpretations of controlling physical and chemical processes. Effects of spatial and temporal variability are particularly difficult to assess, especially when contaminant dynamics are influenced by changing hydrodynamic or sedimentary conditions.

Ex situ testing provides specific information useful for assessing key processes that control metals bioavailability, efflux, and effects in contaminated sediments. By providing the ability to impose a wide range of controlled hydrodynamic conditions on sediments, the Gust chamber system supports direct evaluations of metals redistribution and transformation processes.

In the Lake DePue sediments we tested here, Gust chamber experiments revealed important outcomes of both spatial and temporal variability. SEM and AVS measurements are commonly used to predict toxicity of metal-contaminated sediments, but their exact meaning is unclear because they rely on bulk extraction methods that are prone to artifacts and consequently may not necessarily reflect the *in situ* metals speciation and associated sediment toxicity.^{14,52–54} Here, the bulk sediment SEM/AVS ratio did not yield sufficient information to assess the processes that regulate metal mobility. Direct sediment sampling under steady and unsteady hydrodynamic forcing in the Gust system enabled more detailed assessments of interactions between porewater transport, sediment resuspension, and contaminant mobilization. XAS measurements provided direct and detailed characterization of spatial patterns in metals chemistry within the sediments and temporal variability associated with resuspension. The XAS characterization was essential to demonstrate that changes in Zn speciation modulated contaminant release.

By analyzing a large number of sediment cores, the methods employed here can readily be used to assess spatial patterns in metals speciation at contaminated sites. The primary limitation on this method is that relatively high metals concentrations are required for XAS analysis, but this limitation is not expected to be severe in many metals-contaminated sediments. The Gust

system can also be employed with more conventional metals characterization methods, at the expense of capability to discriminate metals speciation in detail. This approach makes it more difficult to evaluate relationships between hydrodynamic conditions, chemical transformations, and contaminant bioavailability but retains the advantage of enabling evaluations of contaminant efflux and toxicity under a range of imposed overlying flows. Initial investigations of contaminant mobilization in porewater, dissolved and particulate efflux to the water column, and toxicity to epibenthic organisms can readily be explored in initial experiments, with more detailed analytical methods employed as needed to identify critical controls on contaminant sequestration and bioavailability. For site assessments, these methods provide an additional set of tools that can be deployed to improve conceptual models of contaminant dynamics and effects integrating physical, chemical, and biological processes.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional explanations, tables, and figures as noted in the text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00416.

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Notes

The authors declare no competing financial interest.

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