

# Trace Metal Remobilization from Anoxic Wetland Sediments

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## Introduction

In many wetland systems, conditions exist to allow the formation of very stable, low-solubility metal sulfide precipitate phases. This process could substantially reduce the availability and, therefore, the toxicity of many trace metals — including Pb, Zn, and Cd — to the surrounding ecosystem. However, these sulfide compounds become unstable when exposed to oxygen, either through resuspension of sediment particles or drying up of bulk sediment caused by hydrological changes. Our previous work at Dead Stick Pond, a metal-contaminated wetland pond, has shown that sulfide associations dominate zinc speciation in the anoxic sediments [1]. In this work, we use x-ray absorption fine structure (XAFS) techniques to monitor the changes in zinc speciation in pond sediments as they are reoxidized under laboratory conditions.

## Methods and Materials

Dead Stick Pond is a shallow, 8.1-ha pond located in Chicago, IL, 15 mi south of downtown Chicago and less than a quarter mile east of Lake Calumet. Previous industrial activities in the area have led to elevated concentrations of a number of heavy metals in the pond sediment, including manganese (907 mg/kg) zinc (427 mg/kg), and lead (173 mg/kg). Iron, present in the sediment at 3-5% by weight, heavily influences the chemistry of these other elements.

Sediment samples were collected during the spring and fall of 2001. Grab samples were collected from the top 10 cm of the sediment and stored under N<sub>2</sub> until the beginning of the reoxidation experiments. For these experiments, approximately 60 g of wet sediment was placed into a 50-cm<sup>3</sup> reactor and exposed to flowing, oxygen-saturated water for a period of 2-3 weeks. Water flow through the reactor was carried out under low-flow conditions (<5 mL/h) to avoid entrainment of small sediment particles. Also, a 0.45- $\mu$ m filter at the reactor outlet acted to retain sediments within the reactor. During the experiment, effluent from the reactor was collected and analyzed for trace metals in order to determine the extent of metal release from the sediments. At the conclusion of the experiments, the reactor was opened, and samples for XAFS analysis were collected along the direction of flow. These thin (~3-mm) samples were

covered with x-ray transparent Kapton® tape and frozen in liquid N<sub>2</sub> to prevent reaction before analysis.

X-ray absorption spectroscopy experiments were conducted at the APS at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) facilities. Zinc spectra were collected in fluorescence mode on bending magnet beamline 5-BM by using a solid-state detector because of the low concentrations present in the sample. In order to monitor the progress of the oxidation front in the reactor, iron spectra were also collected for these samples. Iron spectra were collected in continuous XAFS mode [2] from 6920 to 8100 eV in both fluorescence and transmission. Nine scans were taken for each sample, with a collection time of 2 min per scan, and the scans were then averaged to produce a single spectrum.

The determination of zinc speciation in the sediment samples was carried out by comparing the extended XAFS (i.e., EXAFS) data from Dead Stick Pond samples to the spectra of reference standards collected at the same time. The EXAFS spectra are extracted by using AUTOBK [3], and Zn speciation is then determined by performing a spectral decomposition of the sample EXAFS signal by using selected reference standards. Reference standards, chosen on the basis of a chemical analysis of the Dead Stick Pond system, consisted of ZnS, ZnCO<sub>3</sub>, ZnPO<sub>4</sub>, ZnO, and Zn<sup>2+</sup> in aqueous solution and a number of zinc-substituted iron and manganese oxides. Iron XANES spectra were compared to reference Fe(II) and Fe(III) standards to assess the extent of oxidation as a function of distance from the reactor inlet.

## Results

Figure 1 shows the Fe XANES signals for samples taken from a reactor experiment after 2 weeks of oxidation. At the inlet, the XANES signal is much more similar to goethite (FeOOH), an Fe(III) compound; at further distances along the direction of flow, the signal shows an increasing contribution from sulfide compounds and an edge shift corresponding to an increase in the Fe(II)/Fe(III) ratio. At 2 cm from the inlet, the Fe(II)/Fe(III) ratio has reached values similar to those in the unoxidized sediment, where Fe(II)/Fe(III) ratios varied from 2.5 to 3.2. Oxidation fronts were typically found between 0.5 and 1 cm from the inlet after 2 weeks.

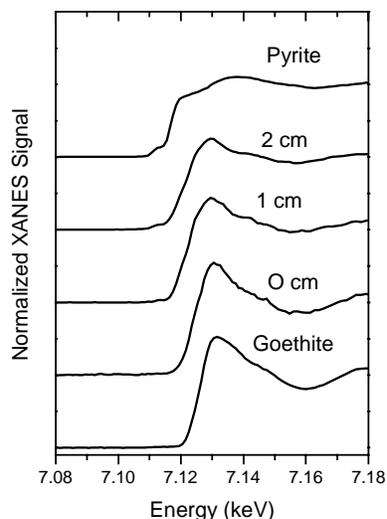


FIG. 1. Fe XANES signals for samples at varying depths from the reactor inlet.

EXAFS analysis at the Zn edge indicates that significant changes occur in zinc speciation across the oxidation front. In samples oxidized during November 2001, the zinc speciation prior to oxidation is primarily divided between only two phases: ZnS and ZnCO<sub>3</sub> species. In the oxidized region, however, the fraction of zinc associated with sulfide phases is substantially decreased (Table 1), and a third phase, hydrated zinc (Zn(H<sub>2</sub>O)<sub>6</sub>), is also present. This shift is consistent with a metal sulfide oxidation model, in which the dissolution of ZnS compounds results in the release of dissolved Zn<sup>2+</sup> from the sediment phase. The carbonate fraction, by contrast, appears unaffected by the presence of oxygen.

Reactor effluent samples consistently showed little release of trace metals from the reactor over the course of the experiments. Dissolved concentrations of Fe and all trace metals were highest in the first 24 h, while sediment pore waters are flushed from the reactor. After this period, Zn and Pb were not detected in the effluent at concentrations above 1 µg/L.

## Discussion

The Zn<sup>2+</sup><sub>(aq)</sub> standard used in our reference set corresponds to a hydrated zinc ion, Zn(H<sub>2</sub>O)<sub>6</sub>, and cannot distinguish between Zn<sub>(aq)</sub> and zinc adsorbed to particle surfaces in outer-sphere complexes [4]. Given the low concentrations of dissolved Zn present in the reactor

Table 1. Speciation of Zn in low-flow reactor as a function of distance along the flow path. All values are given in % of total Zn as determined by EXAFS spectral deconvolution.

Distance (cm)	% of total Zn		
	ZnS	ZnCO <sub>3</sub>	Zn(H <sub>2</sub> O) <sub>6</sub>
0	25	38	27
1	55	31	<5
2	58	35	<5
4	65	27	<5
Initial sediment	63	31	<5

effluent, it is likely that zinc released into solution during sulfide phase dissolution is, in fact, re-adsorbed onto the sediments, either onto iron oxide phases or clay particles. Since the bioavailability of both aqueous and loosely adsorbed Zn phases is much higher than that of zinc sulfides, reoxidation will increase the availability of Zn to plants and biota in Dead Stick Pond and other similar anoxic systems.

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## References

- [1] E. F. Peltier, S. M. Webb, and J.-F. Gaillard, *Adv. Environ. Res.* (in press).
- [2] J. P. G. Quintana, *Synchrotron Rad. Instrum., AIP Conf. Proc.* **521**, 194-197 (2000).
- [3] M. Newville, P. Livins, Y. Yacoby, R. A. Stern, and J. J. Rehr, *Phys. Rev. B* **47**, 14126-14131 (1993).
- [4] J.-F. Gaillard, S. Webb, and J. P. G. Quintana, *J. Synch. Rad.* **8**, 928-930 (2001).