Assessing Zinc Speciation and Availability in Wetland Sediments

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Introduction

In most wetland systems, metal compounds accumulate in the sediment. The presence of anoxic conditions and hydrogen sulfide in these sediments can result in the creation of very stable, low solubility MeS precipitate phases. This process could substantially reduce the availability, and therefore toxicity, of these metals to the surrounding ecosystem. At the same time, however, the potential also exists for significant uptake of potentially toxic metals into existing vegetation, leading to accumulation throughout the food web. The extent of sequestration into the sediment versus bioaccumulation can only be assessed by determining metal speciation under typical wetland conditions. This work uses a Quick-XAFS technique to allow determination of metal speciation in a non-destructive manner, even at relatively low concentrations in a complex natural system.

Methods and Matrials

Dead Stick Pond is a shallow, 8.1 ha pond located in Chicago, IL, 15 miles south of downtown Chicago and less than a quarter mile east of Lake Calumet. The pond is located in a heavily industrial part of Chicago and may have been used to receive dredging spoils from the nearby Calumet River. The pH and alkalinity are both high (8.1- 9.0 and 2- 6 meq/l during the study period, respectively), due to the high proportion of steel slag waste in the surrounding area. This slag waste has also led to elevated concentrations of a number of heavy metals in the pond sediment, including manganese (932 ppm) zinc (95 ppm), and lead (36 ppm). Iron, present in the sediment at 3-5% by weight, heavily influences the chemistry of these other heavy metals.

The speciation of zinc in Dead Stick Pond sediment samples was investigated using x-ray absorption spectroscopy (EXAFS + XANES). Sediment cores were collected by hand using clear PVC tubes 1.5 ft. in length in November of 1999 and June and September of 2000. Subcores were retrieved using 60 ml polypropylene syringes, which were then sectioned to provide samples at the required depths. These thin (~3 mm) sections were covered with x-ray transparent Kapton tape and frozen in liquid N_2 to prevent reaction before analysis.

X-ray absorption spectrophotometry experiments were conducted at the Advanced Photon Source at Argonne National Laboratory, at the DuPont-Northwestern-Dow Collaborative Access Team facilities. Spectra were collected in fluorescence mode on the 5-BM bending magnet beamline using a Lytle cell filled with Ar gas. Zinc spectra were collected in Quick-XAFS mode[1] from 9470 to 10400 eV, a range of approximately 200 eV below to 700 eV above the K_α fluorescence edge. Nine scans were taken for each sample with a collection time of 75 seconds per scan, and the scans were then averaged to produce a single spectrum. Earlier experiments have shown that, even at the relatively low concentrations of zinc present in these samples, the Quick-XAFS mode provides better spectra compared to the conventional method.[2]

The determination of zinc speciation in the sediment samples was carried out by comparison of the extended x-ray absorbance fine structure (EXAFS) data of the Dead Stick Pond sampled to spectra of reference standards collected under identical conditions.[3] Extraction of the EXAFS spectra is performed using AUTOBK,[4] and Zn speciation is then determined by performing a spectral decomposition of the sample EXAFS signal using selected reference standards. Reference standards, chosen based on the chemical analysis of the Dead Stick Pond system, consisted of ZnS, $ZnCO_3$, $ZnPO_4$, ZnO, Zn^{2+} in aqueous solution, and a number of zinc substituted iron and manganese oxides. Experimental errors obtained through the Quick-XAS method were carried through the fitting steps using a Monte Carlo method.

Results

Quick-XAS results from all core samples indicate that sulfide associations dominate zinc speciation in the sediments, representing 50-80% of the total zinc present in the core samples. These data are supported by the presence of free sulfide in sediment pore waters beginning 7-10 cm below the sediment-water interface. Among the other reference compounds, only $ZnCO_3$ and the aqueous zinc standard consistently contributed significantly to fitting the sample spectra. Carbonate phases in this sediment are most likely formed due to oversaturation in the surface waters, a result of the high alkalinity seen during dryer seasons. The $Zn_{(aq)}$ standard corresponds to zinc bound in outer shell complexes, and in this case primarily represents zinc that is adsorbed to the surface of clay particles in the sediment.[3]

Discussion

Given the low solubility of zinc sulfide ($K_{sp}=10^{-11}$), the bioavailability of the sulfide associated zinc should be minimal at equilibrium conditions. The aqueous or loosely bound zinc, which accounts for up to 30% of the total in some samples, is expected to be more easily available to plants and biota present in Dead Stick Pond. Samples taken from Phragmites (common reed) plants grown in and around Dead Stick Pond indicate elevated concentrations of zinc, primarily in the roots. The accuracy of the EXAFS fitting, was limited by a high signal to noise ratio in the data, a result of the low concentration of Zn (~400 ppm) compared to iron.

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