WATER QUALITY

Speciation and Availability of Metals in Wetlands

Final Report

Abstract

A direct consequence of anthropogenic activities is the increasing mobilization of metals in surface environments. These metals are now reaching concentrations levels above natural background concentrations in numerous aquatic environments. Among various aquatic systems, wetlands that are located within industrial urban areas are particularly targeted. Within these wetlands, sediments represent the major reservoir for metal sequestration and/or metal remobilization. The fate of metals in sediments depends primarily on the chemical and physical form under which these metals are present. However, as important is the chemical speciation of metals to understand, our means of determining it precisely repose on operationally defined approaches that have many pitfalls.

The goal of this project was to use a direct method for investigating the speciation of metals in wetlands that is based on the use of Synchrotron Radiation. Inasmuch, this approach provides an excellent test-experiment to probe the quality of speciation measurements performed by conventional speciation schemes. In addition, it allows provides the opportunity to obtain spatially distributed information, and better characterize the dynamics of metals in surface sediments.

This research demonstrated a serious pitfall of conventional speciation methods. It showed that the fraction of metals present as metal sulfides can be wrongly assessed as being a fraction associated with iron or manganese oxides. This has important consequences in terms of site management. The mobility and availability of metals is drastically reduced when metal sulfides dominate their speciation. However, it is key to maintain these anoxic conditions to prevent re-oxidation and remobilization under oxygenated conditions. This is usually best achieved by keeping the wetland flooded.

Introduction

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Narrative Report

1. Using X-Ray Absorption Spectroscopy (XAS) to probe the effectiveness of operationally defined metal speciation schemes.

Introduction: XAS offers multiple advantages for determining the speciation of metals in environmental samples. It is a method that is element specific and that can probe all metals of environmental relevance. In addition, it can interrogate a wide range of physical and chemical states: liquids, solids, amorphous precipitates as well as minerals. The primary advantage of XAS is that metal speciation can be determined directly. One just needs to condition the sample and expose it directly to the incident beam. The principle that makes XAS an suitable tool for speciation relies on the linear superposition of spectra. That is, the XAS spectrum of a mixture of various metal species is the linear combination of all XAS spectra of the species present in the sample. Hence:

where XAS(sample) and XAS(i) refer to the x-ray absorption spectra of the sample and the individual components i respectively, and stands for the fraction of the component i in the mixture.

On the other hand, the most common laboratory procedure for determining metal speciation in sediments is based on the selective leaching of metals species using one or more aqueous reagents. Sequential extraction methods use a series of reagents designed to dissolve targeted sediment phases, leaching the associated metals into solution. In theory, each of the different steps is designed for dissolving a specific type of metal precipitate or sorbed phase. These approaches suffer however from several significant drawbacks. First, metal speciation becomes operationally defined, since it depends on a specific reagent and its concentration and the extraction time. Second, the results are prone to artifacts that obscure the true metal speciation. One potential artifact comes from the partial or complete dissolution of sediment phases prior to their targeted extraction step, artificially increasing metal concentrations in the early fractions. These difficulties are particularly acute when working with anoxic sediments, such as those found in wetland systems. In anoxic sediments, the presence of hydrogen sulfide results in the formation of stable, low-solubility metal sulfide phases that significantly reduces the bioavailability of these elements.

In this work, we have examined the speciation of metals in anoxic wetland sediments using two wet chemical extraction techniques, while simultaneously performing XAS analyses to check the accuracy of the extraction results.

Methods

Sediment samples were collected from a shallow wetland, Dead Stick Pond, located in South Chicago, at the southern end of Lake Michigan. Grab samples were collected by hand from the top 10-12 cm of the sediment, placed into plastic specimen cups with minimal headspace, and preserved into airtight containers flushed with nitrogen gas to minimize oxidation.

Sequential Extractions: Zinc speciation was determined using a sequential extraction scheme that is schematically presented in Table 1. It is a five steps method that is widely used, and that was influential in the development of other methods such as the protocol designed by the Commission of the European Community Bureau of Reference. For each sequential extraction, 2-3 g of wet sediment were weighed into a 50 mL centrifuge tube, followed by the reagents for each step. After each extraction step was completed, the samples were centrifuged at 5000 rpm (1900 g) for 12 minutes, and the liquid was filtered through a 0.45 mm nylon filter and collected. Between each reaction step, each sample was rinsed with 8-10 mL of milliQ water, which was centrifuged and then discarded. In order to minimize losses of sulfide phases due to contact with oxygen, all the work through step 4 was carried in a anaerobic chamber, with the exception of the heating stage in step 3. Reagents for step 1,2 and 3, along with the rinse water, were purged with N2 to remove O2, and stored in the anaerobic chamber.

Acid volatile sulfide (AVS) extractions and measurements were performed on Dead Stick Pond sediments following published procedures. AVS was liberated from 5 g of wet sediment using 6 M HCl under a flowing N2 atmosphere. H2S generated in the reaction was trapped in 0.5 M NaOH and total sulfides released were determined by the methylene blue method. The remaining solution in the reaction vessel was filtered through a 0.45 mm filter and stored for analysis of simultaneously extracted metals (SEM). Standard ZnS powder samples were also reacted to determine the recovery efficiency of the apparatus for H2S. A pyrite (FeS2) sample was also reacted to assess the specificity of the method between various iron sulfide phases.

Liquid supernatants from the sediment sequential extractions were analyzed for concentrations of Fe, Mn, Pb and Zn. Fe, Mn and Zn concentrations were measured using Flame Atomic Absorption Spectroscopy at dilutions ranging from 1- 10% of the original solution concentrations. Standard solutions run at the same time showed no interferences from the reagents present it the supernatants. A Zeeman Graphite Furnace unit was also used to determine Pb concentrations in some samples. SEM from the AVS experiments were analyzed using ICP-AES. Metals analyzed for included Fe, Zn, Pb, Cd, Cu, Cr, Ni and Sn. Total extractable concentrations of Fe, Mn, Zn and Pb in the sediments were determined by microwave assisted digestions using a 2:1 mixture of HNO3 and HCl.

X-ray Absorption Spectroscopy: X-ray absorption spectroscopy experiments were carried out on Dead Stick Pond to determine the speciation of Zn (and, in some cases, Fe) prior to chemical extraction. XAS data for sediment samples and reference Zn phases were collected at the DuPont-Northwestern-Dow Collaborative Access Team, Advanced Photon Source, Argonne National Laboratory. Spectra were collected on a bending magnet beamline using a Continuous-XAS (C-XAS) mode. Ion chambers were used to record incident and transmitted intensity, and a Lytle cell filled with Ar gas was used to monitor fluorescence. For each sample, data were typically recorded from 150 eV below to approximately 8000 eV above the Ka edge of the metal of interest, with 9 scans taken and averaged for each sample. Due to the low concentrations of Zn in some sediments, fluorescence data from these samples were collected using a solid state detector in conventional step scanning mode.

The determination of zinc speciation in the sediment samples was carried out by comparison of the Extended X-ray Absorption Fine Structure (EXAFS) data of the Dead Stick Pond sample to spectra of reference standards collected under identical conditions. Zinc speciation is then determined by performing a spectral decomposition of the sample EXAFS signal using a quadratic linear programming method. This spectral decomposition minimizes the difference between a set of basis spectra made up of selected reference standards, subject to two constraints: the fractional multipliers of the reference standards must add to one, and no component may have a negative contribution. At each step in this processing method, the standard deviation, or error, was calculated from the previous step by use of a Monte Carlo method.

Results: XAS results show that Zn speciation in sediments is dominated by metal sulfide phases (~60%), with significant contributions from only two other phases, hydrated zinc (Zn(H2O)62+) and zinc carbonate hydroxide. An example of a spectral decomposition is presented in Figure 1.

Figure 1: Zinc speciation in Dead Stick Pond sediments prior to chemical extraction. The figure shows the k weighted c-transformed data for the sample S2, along with the best fit of the reference spectra (58% ZnS, 32 % ZnCO3*Zn(OH)2)

Results of the AVS experiments carried out at the two locations, S1 and S2 are shown in Table 2. These results show that AVS concentrations in the sediments are very high. The only simultaneously extracted metals found at significant concentrations were Zn, Pb, Ni, Sn and Cr; their combined concentrations at both

S1 and S2 are much lower than the AVS concentrations. From a bioavailability standpoint, the metals at this site should be almost entirely sequestered into low availability solid phases. Extracted Zn concentrations (on a dry mass basis) are 77% of the total "extractable" zinc at S1, and 68% of the total found at S2. Based on the XAS speciation of Zn in the sediment prior to reaction, these Zn values are higher than would be expected solely from dissolution of sulfide phases.

The results of the sequential extraction are presented in Figure 2. The total amount of Zn solubilized in the sequential extraction process was 92% and 68 % of the total extractable Zn at sites S1 and S2, respectively. This indicates that a significant portion of the zinc at site S2 may be present in relatively recalcitrant mineral phases. Sequential extraction results for Zn speciation patterns at both S1 and S2 are significantly different from those expected from the XAS information. At both S1 and S2, sequential extraction results show carbonate phases accounting for 10% or less of the extracted zinc, while sulfide phases account for a further 10%. The largest concentration of Zn is found in the F3 fraction, the fraction theoretically associated with reducible Fe and Mn oxide phases. The lack of sulfides seems improbable, given the high concentration of AVS and strong zinc speciation into sulfide phases.

Iron speciation, as determined by the sequential extraction method, shows that more than half of the Fe is present either as organic and sulfide bound phases, or in the residual sediment. Overall, comparison of these values with the XAS speciation data can be difficult, since it is not immediately apparent from the EXAFS spectra what iron oxide phases are easily reducible and which are well crystallized. The sulfide and organic fraction, at about 30% in both samples, is significantly lower than the overall iron sulfide percentages determined by XAS.

Figure 2: Trace Metal Phases by Sequential Extraction.

This is likely due to the early oxidation of some of the more amorphous iron monosulfides, similar to the effect seen with zinc. Published results with model iron sulfide phases indicate that the sequential extraction method is significantly less selective for iron monosulfides than for well-crystallized pyrite.

Discussion: The sequential extraction experiments show a significantly different picture of trace metal speciation in the Dead Stick Pond sediments than is presented by either AVS extraction or X-ray absorption spectroscopy. The lack of selectivity of the sequential extraction method with regard to sulfide phases, particularly more amorphous, poorly crystalline phases, was noted early in the development of the sequential extraction procedure, but is sometimes ignored in application of the process to anoxic sediments. The partial oxidation of metal sulfide species in steps prior to the targeted sulfide phase extraction (F4) indicates that this method should be used very cautiously in systems where significant speciation of metals into these phases is expected. The impact will be especially severe in sediments with freshly formed metal sulfides, such as wetland sediments, since these sediments seem most prone to early oxidation and solubilization. The apparent culprit in the early solubilization of metals from sulfide phases appears to be the hydroxylamine hydrochloride reagent used in the reduction of iron and manganese oxides (the F3 fraction), where our results showed the greatest release of zinc in this fraction. Other researchers have noted a negative correlation between the strength of hydroxylamine hydrochloride used in the extraction process and the fraction of metals associated with sulfide phases, and thermodynamic calculations allow for the possibility of metal sulfide solubilization in this step.

From the results presented here, it is clear that direct methods of determining metal speciation in solid phases are vastly preferable to chemical extraction techniques. The collection of X-ray absorption spectroscopy data, however, requires access to a source of high energy X-rays, which are currently available at relatively few locations.

2. Chemical Mapping of Metal Concentration and Species in Wetland Sediments.

Introduction: An additional strength of using X-Rays to probe metals in environmental samples is the ability to focus the beam to a relatively some spot. This provides the potential for performing spatially resolved studies of the distribution of metals by measuring the relative intensity of the fluorescence signal in conjunction with the chemical mapping of metal speciation. The mapping of metal species requires however numerous hours of beamtime since it requires acquiring at each individual spots high quality XAS spectra. In this project, we primarily focused on demonstrating the feasibility of the approach using an instrumental set up that could be easily implemented on a bending magnet beamline. This approach makes use of a poly-capillary optic known as a Kumakhow lens.

Instrumental Setup: The instrumental setup is presented in Figure 3. The sample is mounted on a X-Y stage (Newport) that was controlled through a dedicated computer running SPEC. A poly-capillary lens (X-ray Optical Systems, Inc.) was positioned after an Oxford ion chamber used to monitor the incident beam energy. The sample was positioned on the stage at 5 cm from the end of the poly-capillary optic. A multi element solid-state detector (Canberra) was used to monitor the fluorescence coming from the sample. In the mapping mode the specimen was scanned on a regular grid mesh. In order to determine relative concentration maps, the fluorescence signals of various elements are recorded. After mapping the sample, spectra can be collected at specific locations within the specimen.

Figure 3: Schematic Diagram of the Instrumental Setup.

Results: Within the time frame of this project we were able to perform only a few chemical maps. We first performed feasibility trials on samples where we could expect large variations of concentrations. In these cases, the results obtained demonstrate well the potential of the approach. An example of the distribution of elements within a sample of a separated soil particles is shown in Figure 4.

Figure 4: Chemical maps of Zn and Cu in soil particles.

In addition, we have applied this approach to map the distribution and speciation of Zn within wetlands sediments. In this case the results were disappointing because the Zn distribution showed very little change within the surface area covered. In addition, the chemical speciation of Zn changed very little even as a function of depth within the sediments. The speciation remained primarily controlled by the presence of sulfide species. These studies need to repeated across redox gradients where significant changes should be expected for the species controlling the fate of metals.

Potential Applications/Benefits

The principal application of this research should be in the area of wetland management and remediation of contaminated sediments. The determination of the chemical speciation of metals in sediments is key for assessing the potential of wetland systems for immobilizing metals and therefore acting as "natural kidneys". We showed that conventional approaches used for determining chemical speciation by indirect wet chemical methods lead, when the sediments are anoxic, to an underestimation of the sulfide fraction that can be construed as metal bound to oxides. For management purposes, this has important implications since sulfides will not be stable if the sediments are re-oxygenated by exposure to the air. It is therefore cardinal, in order to avoid the release of metals to maintain the wetlands continuously flooded. This practice may not be compatible with other use of wetland systems, for example increasing their denitrification potential by alternating oxic and anoxic cycles. We are currently investigating alternate methods for determining metal speciation based on wet chemical methods that are less subject to bias and work best in the case of anoxic sediments.

Keywords

metal speciation, wetlands, XAS, sequential extractions, chemical mapping.

Lay Summary

Many wetlands from the southern part of Lake Michigan contain elevated concentrations of a number of metals such as zinc and lead. This is related to the operation of metal smelters and steel mills and the disposal of slag that was often used to fill in low-lying, marshy land. Atmospheric deposition and industrial activity have also contributed to increases in the ambient concentrations of metals within this region. Since many of these elements can be toxic to plants and animals, even in very small amounts, they pose a potentially significant threat to the healthy functioning of the wetland ecosystem.

The objective of this project was to test the validity of an operationally defined method by means of a direct approach based on x-ray absorption spectroscopy. The comparison of speciation results indicates that one step in the operationally defined method leads to a bias. The conventional method, that is widely used by many regulatory agencies, lead to a misrepresentation of the metal sulfide pool. The conventional analysis tends to decrease artificially the concentration of metal-sulfides that constitute a stable, and thought as relatively inert, phase. The direct implication of this research is that it may be more beneficial to leave contaminated sediments in place if a large fraction of metals is present as sulfides. However, conventional speciation schemes will tend to under-report this fraction, potentially leading to ill-advised remediation plans.

International Implications

The determination of metal speciation in sediments is performed routinely in Europe using method that employs the reagents that causes the reported artifacts. Given that other reports have questioned these sequential extractions procedures, it is likely that these operationally defined methods will be revisited.

Publication

Peltier, E.F., Dahl. A.L., Gaillard, J-F. (2005) **Metal Speciation in Anoxic Sediments: When Sulfides can be Construed as Oxides (http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/es049212c)**. Environmental. Science & Technology, 39, 311-316. (availability to the publication is limited to the institutions with a subscription to **Environmental Science & Technology**.)

Undergraduate/Graduate Students Supported

This project provided partial support for the following students:

Rocio Granados-Lopez: B.S. (2003)
Undergraduate Visiting Scholar from the University of Sevilla, Spain.
Escuela Politecnica de Ingenieros
Universidad de Sevilla.

Mohit Barghava: M.S. (2004)
Title: *Chemical Speciation in Sediments Using Direct and Indirect Methods of Speciation.*
Department of Civil and Environmental Engineering
Northwestern University
Defended June 24, 2004

Amy L. Dahl: Ph.D. (2005)
Title: *Comparison of direct and operational methods for probing metal bioavailability and speciation in aquatic systems.*
Department of Civil and Environmental Engineering
Northwestern University
Defended March 10, 2005

Back to Research Project List (../../research_waterquality.php)

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