

Comparing EXAFS with Sequential Extractions for Probing Metal Speciation in Contaminated Sediments

A. L. Dahl, E. Peltier, J.-F. Gaillard
Northwestern University, Evanston, IL, U.S.A.

Introduction

Although environmental regulations rely primarily on total metal concentrations as indicators of the contamination present in the environment, it has become apparent that total metal concentration is a poor predictor of toxicity and mobility and that assessing the various metal species present is more useful for predicting the fate of metals in aquatic systems. One of the most routinely used methods for estimating the speciation of trace metals in soils and sediments is the Tessier sequential extraction procedure [1]. While this method more precisely describes the metal species present in environmental samples, it relies on an operationally defined protocol that can easily give varying results depending on the experimental conditions [2].

A chemical method that uses x-ray absorption spectroscopy has been developed that more quickly and directly measures the metal species present in environmental samples [3]. This method, called x-ray absorption fine structure (XAFS), uses quadratic linear programming to fit a linear combination of standard reference spectra to the spectrum of an unknown sample.

The purpose of this research is to compare the results of these two methods to see if they give similar results, and we hope to validate both of them as useful analytical methods for measuring metal speciation in environmental samples. Initially, we analyzed sediment samples collected from a metal-contaminated site by using both methods. Because of conflicting results between the two methods, artificial samples were prepared by amending clean sediments with known amounts of several zinc phases and carried through the sequential extraction protocol. XAFS analysis was used to follow the speciation of the samples before and after each step of the sequential extraction procedure.

Methods and Materials

Sample Collection

Sediment samples were collected from two locations in Lake DePue, IL, by using a piston-core sampling device. Site Z was previously sampled in June 2001; it had Zn concentrations of approximately 1000 ppm. Site Low was selected to represent background sediments in Lake

DePue. Sediment from the cores was placed into plastic specimen cups with minimal headspace. The specimen cups were placed into an airtight ammunition box, which was flushed with nitrogen gas and transported on ice to minimize oxidation of the samples. Additional sediments for two of the amendment samples were collected from Dead Stick Pond in southern Chicago by using hand cores.

Sample Manipulation

Sediments from Site ZA and LowA were dried overnight in a 104°C oven. The dried sediments were crushed with mortar and pestle and sieved to <590 µm. Amended Samples A, B, D, and E were prepared by adding approximately 10,000 ppm zinc in various phases (see Table 1) to 10 g of dried sediments from Site LowA, followed by physical mixing of the samples. Sample A was redried after the addition of aqueous ZnSO₄. For Samples C and F, the amendments were added to approximately 15 g of wet sediment and 5 g of column water from Dead Stick Pond. The water was added to facilitate homogenizing the sample. After manual mixing and vortexing, the samples were centrifuged for 20 min at 3000 rpm, and the supernatant was discarded.

Table 1. Sample amendments.

Sample	Amended with	Corresponding extraction step
A	Aqueous ZnSO ₄	1
B	Zn-carbonate	2
C	Zn-goethite	3
D	Zn-sulfide	4
E	Zn-phosphate	Unknown
F	All phases (except phosphate) ^a	All steps

^aUsed Zn-bentonite and Zn-HFO instead of aqueous ZnSO₄ and Zn-goethite.

Sequential Extractions

The six amended and Site ZA samples were carried through the sequential extraction procedure developed by

Tessier [1] and summarized in Table 2. Five replicates of each sample were initially set up, with one replicate stopped after each step in the sequential extraction process so that the residual sediments could be analyzed by XAFS.

Table 2. Tessier method.

Step	Extractant	Target
1	1 M MgCl ₂ , pH 7, 1 h	Exchangeable
2	1 M Na-acetate, pH 5, 5 h	Carbonate bound
3	0.04 M NH ₂ OH-HCl-acetic acid, 6 h	Easily reducible oxides
4	H ₂ O ₂ -HNO ₃ , 85°C, 5 h followed by 3.2 M NH ₄ -acetate-HNO ₃ for 30 min	Organic matter and sulfides
5	Aqua regia	Residual fraction

X-ray Absorption Measurements

XAFS measurements were performed on the bending magnet beamline of the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT). A Si(111) monochromator was used to vary the x-ray energy from 200 eV below the absorption K edge of Zn (9659 eV) to 1000 eV above it. The incident and transmitted intensities were measured with ionization chambers, while the fluorescence signal was measured with a Stern-Heald “Lytle” detector. XAFS measurements were acquired in quick scanning mode (QXAS). Details of this method can be found in Ref. 3.

The contribution of various Zn species to the $\chi(k)$ function of our samples was determined by using quadratic linear programming (QLP) to fit our sample spectra to a linear combination of the standard reference spectra shown in Table 3 [4] (see Fig. 1).

Table 3. XAFS standards.

Standard	Description
Zn-bentonite	Zn sorbed to bentonite
Zn carbonate	ZnCO ₃ -2Zn(OH) ₂ -xH ₂ O
Zn-goethite	Zn incorporated into goethite
Zn-HFO	Zn incorporated into hydrous ferric oxides
Zn-sulfide	ZnS
Zn-phosphate	Zn ₃ (PO ₄) ₂ -xH ₂ O
Aqueous zinc	20 Mm ZnSO ₄

Results

Sample ZA (unamended): The XAFS spectrum for Site ZA contains mostly zinc sulfide, with some zinc carbonate and perhaps a small amount of zinc phosphate.

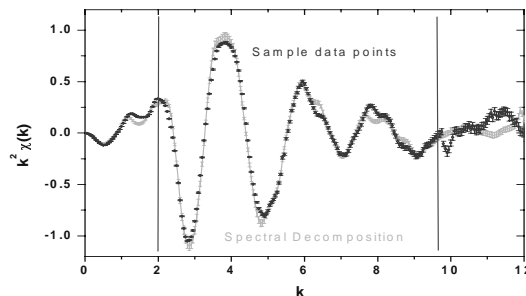


FIG. 1. Example of sample chi fit to standards.

As expected, a significant amount of the carbonate phase disappears after step 2. Because of the strong ZnS signal, we expected most of the zinc to come off during step 4. Unexpectedly, however, the zinc signal is undetectable with XAFS after step 3, suggesting that most of the zinc is removed from the sample by step 3. This is confirmed by analysis of the sequential extracts, which show most of the zinc extracted during step 3.

Sample A, aqueous zinc (as dissolved ZnSO₄): The XAFS spectrum of the wetted sample prior to any sequential extractions shows a significant carbonate contribution (63 ± 3%) and a small sulfide (7 ± 2%) contribution in addition to the expected aqueous signal (30 ± 2%). This redistribution from the aqueous phase probably occurs because the sample was dried after adding aqueous ZnSO₄ and then rewetted for the XAFS analysis. Despite the fact that the first step in the sequential extraction procedure is supposed to remove the aqueous or loosely bound metal, we continue to see a significant aqueous signal through step 2. The carbonate contribution is mostly gone, as expected, after step 2, while the sulfide signal is not large enough from the beginning to be measurable after step 3.

Sample B, zinc carbonate: As indicated by the Tessier extraction protocol, the majority of the zinc is removed during step 2 (75 ± 1%), although a significant amount comes off during step 3 (20 ± 1%). According to the XAFS analysis, the majority of the zinc present up until step 2 is in the carbonate form (78 ± 6%), indicating that little redistribution occurs during rewetting and step 1.

Sample C, zinc phosphate: The Tessier method does not consider metals associated with phosphates. Because past XAFS analysis indicated that zinc phosphates are present in areas of Lake DePue, we wanted to see how an amendment of zinc phosphate responded to the sequential extraction process.

Analysis of the filtrates shows that most of the zinc is removed during steps 2 (37 ± 1%) and 3 (54 ± 1%), which agrees fairly closely with the decreases in fluorescence peak height after each step.

Sample D, zinc goethite: Both the XAFS and sequential extraction data agree that most of the zinc is removed during step 3, which specifically targets metals associated with iron and manganese oxides.

Sample E, zinc sulfide: Unlike Site ZA, both analyses of the sample amended with ZnS show that most of the zinc is removed during step 4 as expected (70% and 78%, respectively), although a significant amount is found in the filtrate after step 3 (20%). XAFS analysis of the sediments reveals that most of the zinc is present as zinc sulfide throughout each step of the extraction process until step 4, after which there is insufficient zinc to be detected by XAFS.

The concentration of ZnS in the amended sediments is significantly higher than the concentration in the unamended sample, and a large amount of the ZnS did come off the amended sample during step 3. Perhaps ZnS is actually targeted by the third step in limited amounts, and whatever ZnS remains after step 3 is removed during step 4.

Sample F, all phases (except phosphate): The XAFS and sequential extraction results agree surprisingly well with the expected phases dropping out during the expected steps, and only a small amount of redistribution or incomplete extraction is observed (Fig. 2). The exchangeable phase was not adequately represented by the zinc-bentonite phase, however, so we cannot confirm the effectiveness of the first step in the extraction procedure.

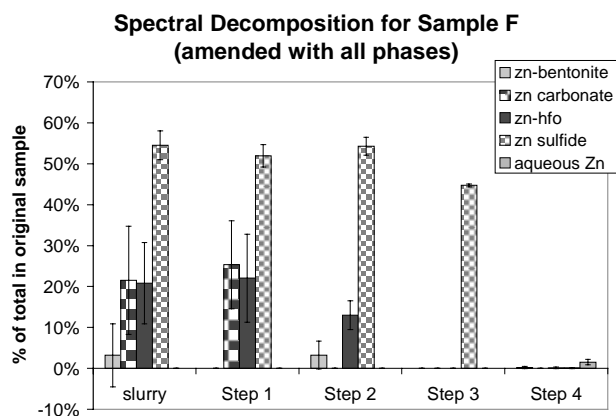


FIG. 2. Results for Sample F.

Discussion

Two methods for measuring zinc speciation in sediments were compared: XAFS and sequential extractions. Results indicate that the methods agree with each other when applied to samples artificially amended

with the various zinc phases targeted by the Tessier method of sequential extraction, particularly for the carbonate phase (step 2), iron and manganese oxide phase (step 3), and sulfide phase (step 4). However, when applied to samples from the natural environment, XAFS and the sequential extraction method give conflicting results. Our results show that zinc phosphates are extracted during multiple phases and can therefore be confused with the other phases specifically addressed by the method. Furthermore, while the sequential extraction of our natural samples removes most of the zinc during the third step, which targets metals associated with iron and manganese oxides, XAFS analysis does not detect any zinc associated with iron and manganese oxides but rather detects a distinct ZnS phase not confirmed by step 4 in the extraction method. It is not clear why sulfides would be attacked under the reducing conditions of step 3, but it is obvious that zinc sulfides present in our natural sediments are different from the powder zinc sulfide we used to artificially amend our samples.

Acknowledgments

Fellowship support was provided through the National Defense Science and Engineering Graduate Fellowship Program sponsored by the U.S. Department of Defense. Portions of this work were performed at the DND-CAT Synchrotron Research Center located at sector 5 of the APS. DND-CAT is supported by E. I. DuPont de Nemours & Co., The Dow Chemical Company, the U.S. National Science Foundation through Grant No. DMR-9304725, and the State of Illinois through the U.S. Department of Commerce and the Illinois Board of Higher Education, Higher Education Cooperation Act IBHE-HECA Grant No. NWU 96. Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

- [1] Tessier, Campbell, and Bisson, "Sequential extraction procedure for the speciation of particulate trace-metals," *Anal. Chem.* **51**, 844-851 (1979).
- [2] Rapin et al., "Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure," *Environ. Sci. Technol.* **20**, 836-840 (1986).
- [3] Gaillard, Webb, and Quintana, "Quick x-ray absorption spectroscopy for determining metal speciation in environmental samples," *J. Synchrotron. Radiat.* **8**, 928-930 (2001).
- [4] Vandenberghe and Boyd, "Semidefinite programming," *Siam Rev.* **38**, 49-95 (1996).