

Report for 2003ID11B: Validating Meta(loid) Flux Predictions from Lake Coeur d'Alene Sediments Using Contaminated Ponds as Mesocosms

- Conference Proceedings:
 - DOUGLAS C. FINKELNBURG, GORDON R. TOEVS, and MATTHEW J. MORRA, 2003, Metal(loid) Solubility as Affected by Redox Changes in Mining-Impacted Sediments (Abstract), in Abstracts of the Western Society of Soil Science, Logan, UT, June 13-16.

Report Follows

Basic Project Information

Title: Validating Metal(loid) Flux Predictions from Lake Coeur d'Alene Sediments Using Contaminated Ponds as Mesocosms

Project Number: 2003ID11B

Start Date:

End Date:

Project Type: Research

Focus Category #1: Sediments

Focus Category #2: Toxic substances

Focus Category #3: Geochemical processes

Lead Institution: University of Idaho

Principal Investigators:

Matthew J. Morra
Daniel G. Strawn
University of Idaho

Problem and Research Objectives:

Lake Coeur d'Alene (CDA) in Idaho is the second largest natural lake in the Inland Northwest. Lake CDA provides drinking water for at least five communities and serves as a primary recreational area for inhabitants of the Pacific Northwest. Over the last century Lake CDA became, and continues to be, the major collecting bed for contaminated sediments produced during mining and ore processing activities. As a result of these mining activities tailings enriched in Pb, Zn, As, Cd, and other trace elements were deposited in stream banks and bars along the South Fork and main stem of the Coeur d'Alene River. These materials have been regularly resuspended during periods of high stream flow and secondarily transported into Lake CDA. The USGS has estimated that as much as 85% of the lake bottom is contaminated with metal(loids) (Horowitz et al., 1992).

The overriding concern of management agencies responsible for lake water quality is the potential release of the accumulated metal(loids) into the overlying water column. However inadequate information exists at this time to make accurate predictions of metal(loid) release. The Coeur d'Alene Tribe, EPA, Idaho Department of Environmental Quality, and local citizens groups need such information in order to develop a plan for managing ever increasing use of the lake resource. It is feared that continued development within the region will alter lake nutrient status leading to eutrophication and the promotion of trace element release (Woods, 1989). Unfortunately, projections of metal(loid) release are based on models which may not accurately describe geochemical principles controlling the important processes. There is a need for validating benthic flux model predictions to facilitate management decisions.

Our objectives are to 1) determine whether there is currently a significant flux of metal contaminants from the sediment to the water column and 2) predict how anthropogenic alteration of Lake CDA trophic status will influence this flux. It has been

assumed that eutrophication will promote trace element release (Woods, 1989). This prediction is based on the assumption that metals in the lake occur predominantly in their oxide and hydroxide forms, and that there is no anoxic metal binding mechanism. Thus one of the principal means of keeping toxic trace elements immobilized in lakebed sediments may be to carefully manage the lake nutrient status to avoid the development of anoxic conditions. Others have suggested that a large fraction of metal(loid) contaminants partition with a chemically refractory sulfidic phase (Harrington et al., 1998; 1999) and that these metal sulfides are inherently stable under reducing conditions. The mechanisms responsible for metal retention and cycling remain uncertain, making accurate assessments of current flux and predictions of future environmental contamination difficult. Our proposed research is focused on resolving the controversy by using small ponds to directly determine metal flux prior to the development of anoxic conditions and comparing this flux to that which occurs after the onset of anoxic conditions. We will use a benthic flux model to make predictions and then validate the model using the data collected under anoxic conditions.

Harrington et al., 1999. Environ. Sci. Technol. 33:203-204.

Harrington et al., 1998. Environ. Sci. Technol. 32:650-666.

Horowitz, A.J. et al., 1992. U.S.G.S. Open file Report 1992, 92-109.

Woods, P.F. 1989. U.S.G.S. Water-Resources Investigations Report 89-4032.

Methodology:

Suitable ponds with a history of aerobic/anaerobic transitions were identified in the Lake CDA area. Core samples from the ponds were obtained with hollow plexiglas tubes, as performed in our previous studies, and measured for total metals to characterize the sediments and determine the magnitude of metal contamination. Five peepers (equilibrium samplers) were installed in accessible, metal-contaminated ponds. Peepers 20 cm wide and 50 cm in length have been constructed by machining two rows of 25 cells each into a 1.9-cm thick plexiglass sheet. Cells are spaced 1.5 cm apart and hold 10 mL in volume. A 0.2- μm Nylon filter (Osmonics) separates the sediment from the peeper reservoirs. Peepers were placed vertically in the sediment leaving approximately four cells above the sediment/water interface. After 4 wks of equilibration, the peepers were extracted and the water within the cells removed with a syringe. Extracted samples were stored anaerobically and transported to the laboratory where metal concentrations, pH, alkalinity, and major cations and anions were measured. We have completed four peeper deployments and will continue sampling for the next year. Porosity of the sediment will be determined on cores taken at the time of peeper retrieval. The chemical data obtained on the pore water samples and the physical data determined for the sediment samples will be used in an equilibrium model. Equilibrium modeling will be done to determine the speciation of metals in the porewater and to assess the importance of various processes in mobilizing metals from solid phases into the porewater using the computer program PHREEQC. The flux of dissolved elements across the sediment-water interface by molecular diffusion is calculated using Fick's First Law. Modeling and flux calculations will be performed prior to the onset of anaerobic conditions. Model predictions of metal flux from the sediment will be compared to actual measured metal concentrations under anaerobic conditions.

Principal Findings and Significance:

Our research in ponds along the Coeur d'Alene River indicates that a very different situation exists in these ponds as compared to Lake Coeur d'Alene. Our research with the lake sediments has shown that an oxic sediment cap of 1-2 cm exists at the sediment water interface. Redox potentials decrease rapidly below those depths such that sulfate reduction is occurring and pyrite is being formed through diagenesis. However, the dominate solid phase mineral governing soluble metal(loid) concentrations is the Fe-containing mineral siderite. The very large Fe:S ratio precludes extensive sulfide complexation with toxic metal(loid)s. Reductive dissolution of Fe-containing minerals below 2 cm results in high concentrations of metal(loid)s, especially As, in the sediment porewater. Arsenic concentrations near 1.5 mg L⁻¹ have been measured in sediment porewaters from Lake Coeur d'Alene. The extent of flux of these metal(loid)s from the sediment to the overlying water remains a question. The oxic sediment at the interface acts as a barrier to scavenge As and decrease or eliminate its flux into the water column.

However, we have collected sediment porewater samples from the ponds for a 1-year period and have yet to measure significant concentrations of metal(loid)s, despite the fact the total metal(loid) concentrations in these pond sediments (Table 1) exceed those of the lake sediments (Table 2). Nitrate and SO₄²⁻ were present in the pore water at detectable concentrations in spring, but only minimal SO₄²⁻ was detected in summer-collected pore water samples. Fe²⁺ was found to increase with depth both in spring and summer pore water samples averaging 135 mg/L in summer and 85 mg/L in spring porewater samples. Our investigations indicate that redox changes in saturated sediments may not be extreme enough to cause seasonal metal(loid) release. Our hypothesis is that the sediments within the ponds are maintained at much lower redox potentials than those in the Lake. Metal(loid)s are therefore never associated with oxidized iron minerals, but are sequestered with reduced minerals, possibly the original mined materials. Thus, reductive dissolution is insignificant and soluble metal concentrations remain below our limits of detection. From a practical management perspective, perhaps contaminated materials along the Coeur d'Alene River are least damaging if low redox conditions can be maintained. Flooding these areas for wildlife habitat or wild rice production may be options.

Table 1. Schlepp Pond total metal analysis.

	As	Cd	Fe	Mn	Pb	S	Zn
	mg kg⁻¹						
Min	53.48	26.31	66914	6217.14	4295.01	5594.29	3754.29
Max	297.82	104.28	101468	10258.86	14597.64	11072.39	10811.91
Avg	171.29	60.10	84398	7857.48	6706.96	8711.17	6881.02

Table 2. Lake Coeur d'Alene total metal analysis of contaminated sites.

	As	Cd	Fe	Mn	Pb	S	Zn
	mg kg⁻¹						
Min	94.89	17.52	36421	3944.06	1618.57	1426.43	2292.26
Max	278.54	44.22	115147	10566.30	5699.80	5334.69	4064.96
Avg	153.08	27.78	80020	6930.66	3851.35	3426.27	3277.04

Descriptors: heavy metals, mining, sediments, contaminant flux

Articles in Refereed Scientific Journals:

Book Chapters:

Dissertations:

Water Resources Research Institute Reports:

Conference Proceedings:

Other Publications:

Meeting Abstracts

Metal(loid) Solubility as Affected by Redox Changes in Mining-Impacted Sediments.
DOUGLAS C. FINKELNBURG, GORDON R. TOEVS, and MATTHEW J. MORRA.
Abstracts of the Western Society of Soil Science, Meetings held in Logan, UT, June 13-16.

Students Supported:

Douglas C. Finkelnburg, MS student in Environmental Science.*
Gordon R. Toevs, Ph.D. student in Soil & Land Resources.*

*Student stipends were paid on non-USGS funds, but operating expenses and travel were paid by 104B grant funds.