Water Resources Research Institute
Annual Technical Report
FY 2003

Introduction

The Idaho Water Resoureces Research Institute (IWRRI) is housed at the University of Idaho. IWRRI is dedicated to supporting and promoting water and water-related research, education, and information transfer throughout Idaho. IWRRI collaborates with researchers and educators from all Idaho state universities; staff of local, state, and federal agencies; and private water interests.

The IWRRI is the only mechanism in the state that provides an autonomous statewide source of support for water research and training without regard to specific topic or discipline area. This is important because Idahos water problems cross multiple topics and disciplines and compartmental approaches to these problems are less effective. IWRRI is relied upon by state and federal agencies and private water interests to provide the objective expertise to address the needs of the state and region.

The Institute has been a strong proponent of education and outreach for both youth and adult audiences. It is through education that the public can make informed public policy decisions concerning water. It is also through education that individual citizens become engaged in the process through adjustments of their own attitudes and lifestyles.

Research Program

The Idaho Water Resources Research Institute’s research program is comprised of the following objectives: 1) To work with state and federal agencies and non-government organizations to identify water research needs of the state and region. 1) To promote water-related research relevant to state and regional needs. 2) To stimulate, coordinate, and provide leadership for water resources research within Idaho universities and collaborate with sister institutions in adjoining states. 3) To cooperate with and assist state and federal agencies and non-government organizations for the benefit of the citizens of Idaho and the region. 4) To encourage and facilitate public involvement in water resource programs within the state. 5) To promote water education within the state at the K-12, undergraduate, and graduate levels. 6) To develop funding for needed research and encourage cooperation with other research organizations.

Physically Based Models for Hydraulic Properties of Swelling Soils

Basic Information

Title:	Physically Based Models for Hydraulic Properties of Swelling Soils
Project Number:	2002ID4B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	1
Research Category:	Ground-water Flow and Transport
Focus Category:	Hydrology, Solute Transport, Agriculture
Descriptors:	Clays, Swelling and Shrinking, Physically Based Modeling
Principal Investigators:	Markus Tuller

Publication

1. Tuller, M., and D. Or, 2003. Hydraulic Functions for Swelling Soils: Pore Scale Considerations. Journal of Hydrology, 272:50-71.
2. Tuller, M., and K.B. Gebrehawariat, 2004. Experimental Studies on Swelling and Saturated Flow Behavior of Clay-Sand Mixtures (in preparation).

Basic Project Information

Title: Physically Based Models for Hydraulic Properties of Swelling Soils

Project Number: 2002ID4B

Start Date: 03/01/2003

End Date: 02/29/2004

Research Category: Basic Research

Focus Category #1: Hydrology

Focus Category #2: Solute Transport

Focus Category #3: Agriculture

Lead Institution: University of Idaho

Principal Investigators:

Markus Tuller
Assistant Professor of Soil and Environmental Physics
University of Idaho

Problem and Research Objectives:

Some of the most productive agricultural soils contain appreciable amounts of active clay minerals and exhibit shrink-swell behavior in response to changes in soil water content and chemical composition of the soil solution. Swelling and dispersion of clay minerals modify hydraulic soil properties and lead to increased surface runoff with negative impacts on water quality of rivers and lakes. Furthermore, cracks forming in dry clay soils provide fast preferential pathways for rapid transport of chemicals leading to potential risks for ground water contamination. In addition to myriad agricultural management and engineering problems associated with changes in mechanical properties and trafficability of such land surfaces, hydrologic predictions of flow and transport processes are seriously hampered. Changes in soil volume and pore space induced by shrink-swell behavior present a challenge to the development of predictive models for flow and transport, in particular to the development of constitutive hydraulic functions. Despite well-developed theory for crystalline and osmotic swelling of clay minerals, translation of lamellar-scale theory to formulation of constitutive hydraulic functions is lacking.

The objectives of the current project are based on the long term goals to develop a fundamental understanding and accurate description of water and solute behavior in environmental and agricultural systems with appreciable amounts of clay minerals, and to provide enhanced quantitative tools for environmental and agricultural management practices to control surface runoff, leaching, soil erosion, salinization, and sodicity. This requires the development of physically based pore- and sample-scale models for liquid retention and hydraulic conductivity considering the swelling and shrinking behavior of clay minerals. Within this context the specific objectives of the project were to:

(1) Develop a model for geometry and changes in clay fabric pore space with hydration state, clay mineralogy, and solution composition.

(2) Incorporate other textural fractions (e.g., sand, silt) toward developing a complete pore scale model for clayey soils.

(3) Derive hydraulic functions for clay fabric and simple sand-clay mixtures

(4) Develop an upscaling scheme to represent sample and profile-scale behavior of clay soils constrained by measurable soil properties.

(5) Evaluate and refine pore and sample-scale models using feedback from measurements

Methodology:

The framework for modeling pore space changes is based on consideration of the soil clay fabric as an assembly of colloidal-size tactoids with lamellar structure. The arrangement of clay tactoids and the spacing between individual lamellae are functions of clay hydration state quantifiable via the disjoining pressure, dominated by a large electrostatic repulsive component. The DLVO theory developed by Derjaguin and Landau [1941], and Verwey and Overbeek [1948] was applied to derive relationships between lamellae spacing and bulk matric potential.

Silt and sand textural constituents are represented as rigid spheres interspaced by clay fabric in two basic configurations of "expansive" and "reductive" unit cells. Bulk soil properties such as clay content, porosity and surface area serve as constraints for the pore-space geometry. Liquid saturation within the idealized pore space is calculated as a function of chemical potential considering volume changes due to clay shrink-swell behavior. Closed-form expressions for prediction of saturated hydraulic conductivity are derived from calculations of average flow velocities in ducts and between parallel plates, and invoking proportionality between water flux density and unit hydraulic gradient.

A flexible wall permeameter is used to measure saturated hydraulic conductivity of clay-sand mixtures. A novel fully automated experimental setup that includes a volume change device with linear displacement transducers is used to measure maximum swelling ratios of clay soils.

Feedback from measurements is used for evaluation and refinement of the theoretical modeling efforts.

Principal Findings and Significance:

After developing a pore space evolution model and deriving physically based analytical solutions for liquid retention and saturated hydraulic conductivity as a function of soil chemical potential in the first project year we focused our efforts on measuring of saturated hydraulic conductivity and maximum swelling ratios. To investigate effects of pore fluid composition and clay content on permeability and swelling we conducted a series of experiments using NaCl solutions of different molarity for samples with varying clay content. The results clearly indicate that higher concentrated solutions result in larger volume expansion and higher conductivity. It is interesting to note that the hydraulic conductivity in general decreases rapidly with increasing clay content until a critical value of 35-40% clay is reached. For higher clay contents we observe a slight increase of permeability. These results provide exciting new insights for the design of clay caps and barriers that are of great economic importance. In contrast to common knowledge clay-sand mixtures with about 35-40% clay content show lower permeability than pure clay, therefore are better suited as liner and barrier material. We are currently utilizing these new findings to refine the previously derived pore scale model and to develop a realistic upscaling scheme for predictions at the sample scale. Current findings of this project were published in the Journal of Hydrology and disseminated through numerous invited presentations. We are currently in the final stage of preparation of a manuscript containing our recent experimental results to be submitted to Water Resources Research or Advances in Water Resources.

Future work will include the incorporation of confining stresses and preferential flow through surface crack networks to predict hydraulic properties of swelling porous media at the profile scale.

Descriptors: Clays, Swelling and Shrinking, Physically Based Modeling

Articles in Refereed Scientific Journals:

Tuller, M., and D. Or, 2003. Hydraulic Functions for Swelling Soils: Pore Scale Considerations. *Journal of Hydrology*, 272:50-71.

Book Chapters: NA

Dissertations: NA

Water Resources Research Institute Reports: NA

Conference Proceedings: NA

Other Publications:

Meeting Abstracts

Tuller, M., K. Gebrehawariat, D. Or, and B. Muhunthan, 2003. Experimental Studies on Swelling and Saturated Flow Behavior of Clay Soils. SSSA Annual Meeting Abstracts, November 2-6, Denver, Colorado.

Students Supported:

The project provided support for Kidane Gebrehawariat a masters student majoring in Soil and Environmental Physics

Improved Short Term Operational Streamflow Forecasting for Snow Melt Dominated Basins

Basic Information

Title:	Improved Short Term Operational Streamflow Forecasting for Snow Melt Dominated Basins
Project Number:	2003ID10B
Start Date:	1/1/1997
End Date:	1/1/1997
Funding Source:	104B
Congressional District:	1
Research Category:	Climate and Hydrologic Processes
Focus Category:	Surface Water, Water Quantity, Methods
Descriptors:	
Principal Investigators:	Von P. Walden, Karen S Humes

Publication

1. Brian Harshburger, Troy Blandford, Brandon Moore, Karen Humes, Von Walden, Russell Qualls, and Wenguang Zhao, 2004, Improved short-term operational streamflow forecasting for snow-melt dominated basins in Idaho, in American Association of Geography Annual Conference, Philadelphia, PA.

Basic Project Information

Title: Improved Short-term Operational Streamflow Forecasting for Snow-melt Dominated Basins

Project Number: KEK303
Start Date: March 1, 2003
End Date: February 28, 2004
Research Category:
Focus Category #1: SW
Focus Category #2: MOD
Focus Category #3: WQN
Lead Institution: University of Idaho

Principal Investigators:

Name: Von P. Walden
Title During Project Period: Assistant Professor
Affiliated Organization: Department of Geography, University of Idaho

Name: Karen S. Humes
Title During Project Period: Associate Professor
Affiliated Organization: Department of Geography, University of Idaho

Problem and Research Objectives:

Most of Idaho's winter precipitation is stored as snow at high elevations and contributes to streamflow during the spring season. The timing of the accumulation and melt of the snow pack is crucial for decision-makers in federal and state agencies, as well as Idaho citizens whose livelihoods are directly affected by water availability (for example, farmers and tourism operators).

The objective of this project is to develop a short-to-medium range forecast system for streamflow prediction within small basins in the state of Idaho. This research is highly applied and is intended to bridge the gap between models in the hydrological and meteorological research communities, utilize newly available satellite data products, and fulfill the needs of operational agencies. This project is organized into three main activities: (1) Evaluation and validation of meteorological forecasts for use by the Snowmelt Runoff Model (SRM), (2) Validation of SRM on representative basins using actual surface and streamflow observations (retrospective analysis), (3) Development of an interface between SRM and meteorological forecast model output, real-time data from surface observations, and operational snowcover data (MODIS) from remote sensing.

Methodology:

The Snowmelt Runoff Model (SRM) is used to simulate and forecast daily streamflow in high-resolution (catchment scale) sub-basins of the Snake River (Big Lost and Big Wood River Basins). Model inputs include both forecasted and actual surface observations of precipitation, temperature and snow-covered area (SCA). SRM is a quasi-distributed model, thus input values are distributed among several hydrologic response units (HRUs) within the watershed. Several disaggregation schemes are being evaluated to determine the best way to divide up the basin into HRUs (slope, aspect, elevation, land cover, etc.). Spatial interpolation schemes, which incorporate topographic information, are being used to convert point-based ground measurements of precipitation and temperature into aerial values. This includes both the use of synthetic stations (a spatial weighted average of all stations located in each basin) and other more contemporary methods (i.e. detrended kriiging, PRISM). These values are used in both retrospective analyses (to fine tune the model) and to update the model in forecast mode. Retrospective analysis is used to identify the optimal parameter values (degree-day factor, runoff coefficients, etc.) for input into SRM. This provides a set of pre-tested values, which are needed to run the model in forecast mode. Real-time forecasts of meteorological variables, such as temperature and precipitation, will eventually be incorporated into SRM, to predict streamflow for one to two weeks into the future.

Principal Findings and Significance:

We have evaluated several different approaches for incorporating meteorological forecasts into SRM. We have chosen to use model results produced by NOAA's Climate Diagnostics Center (Hamill et al., 2004) rather than our original plan to use either MM5 results from the University of Washington or NOAA's Eta Meso-west model. The reasons for this decision are that the CDC model produces 2-week forecasts rather than the shorter-term forecasts produced by the MM5 and Eta Meso-west models. Also, the CDC model has a long historical forecast record (1978-current), which can be used to "downscale" the forecast model output to individual meteorological stations within snowmelt basins. We plan to use the downscaling procedure outlined by Clark et al. (2004) to provide meteorologic forecasts because they've demonstrated good results in snowmelt-dominated basins in the West.

The results from the retrospective model runs indicate that SRM accurately simulates both the timing and magnitude of stream discharge peaks within the snowmelt season. This includes both the peak flow and other (much smaller) discharge events. The average R^2 value for the retrospective model runs was approximately 0.93 with an average volume difference of 7%. The shape of the simulated hydrographs were similar to the actual, however the modeled recession limbs tended to be less steep than the actual. We have also evaluated several basin disaggregation and spatial interpolation methods, with varying degrees of success; however further analysis is needed.

We have preliminarily tested the model to assess its medium range forecasting ability. A forecast was issued for a one week period in April. In doing this, we have successfully integrated various data into SRM, including MODIS snow-cover images and temperature and precipitation forecasts issued for a single location within the Big Wood River Basin.

References:

Hamill, M., J.S. Whitaker, and X. Wei, 2004: Ensemble Forecasting: Improving medium range forecast skill using retrospective forecasts. *Monthly Weather Review,* 132, 1434-1447.

Clark, Y.M., S. Gangopadhyay, L. Hay, B. Rajagopalan and R. Wilby, 2004: The Schaake Shuffle: A Method for Reconstructing Space-Time Variability in Forecasted Precipitation and Temperature Fields. *Journal of Hydrometeorology,* 5, 243-262.

Descriptors:

Articles in Refereed Scientific Journals: N/A

Book Chapters: N/A

Dissertations and Theses:

"Improved Short-term Operational Streamflow Forecasting for Snow-melt Dominated Basins in Idaho", by Brian Harshburger, PhD in progress

"The evaluation of the lapse rate and advanced spatial interpolation methods for input into SRM ", by Troy Blandford, M.S. in progress

"The evaluation of meteorologic forecasts for input into SRM", by Brandon Moore, M.S. in progress

Water Resources Research Institute Reports: N/A

Conference Proceedings:

AAG 2004 abstract: "Improved short-term operational streamflow forecasting for snow-melt dominated basins in Idaho", by Brian Harshburger, Troy Blandford, Brandon Moore, Karen Humes, Von Walden, Russell Qualls, and Wenguang Zhao.

Other Publications: N/A

Validating Meta(loid) Flux Predicitons from Lake Coeur d'Alene Sediments Using Contaminated Ponds as Mesocosms

Basic Information

Title:	Validating Meta(loid) Flux Predicitons from Lake Coeur d'Alene Sediments Using Contaminated Ponds as Mesocosms
Project Number:	2003ID11B
Start Date:	1/1/1997
End Date:	1/1/1997
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Sediments, Toxic Substances, Geochemical Processes
Descriptors:	
Principal Investigators:	Matthew Morra, Daniel Strawn

Publication

1. 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.

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 SO_4^{2-} were present in the pore water at detectable concentrations in spring, but only minimal SO_4^{2-} was detected in summer-collected pore water samples. Fe^{2+} 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}	**mg kg^{-1}**	**mg kg^{-1}**	**mg kg^{-1}**	**mg kg^{-1}**	**mg kg^{-1}**	**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}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	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.

Metal(loid) Cycling in Lake Coeur d'Alene, ID

Basic Information

Title:	Metal(loid) Cycling in Lake Coeur d'Alene, ID
Project Number:	1999ID0011G
Start Date:	9/1/1999
End Date:	6/30/2003
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Hydrogeochemistry, Water Quality,
Descriptors:	Water Quality Monitoring, Metals
Principal Investigators:	Matthew Morra

Publication

1. Toevs, G.R., M.J. Morra, S.E. Fendorf, M. Polizzotto, L. Winowiecki, and B. Bostick. XAS characterization of Fe and S in mining-impacted sediments of Lake Coeur dAlene, Idaho. Environ. Sci. Technol. (in preparation, not yet submitted).
2. Toevs, G.R., M.J. Morra, S.E. Fendorf, B.C. Bostick, M. Polizzotto, L. Winowiecki, and S.A. Wood, Diagenesis of Heavy Metal-Contaminated Sediments in Lake Coeur dAlene as Related to Water Quality, in Abstracts of the Annual Meetings of the Soil Science Society of America, Nov. 2-6, Denver, CO.

Basic Project Information

Title: Metal(loid) cycling in Lake Coeur d'Alene, Idaho as controlled by reduced sulfur species

Project Number: 1999ID0011G

Start Date: 9/1/99

End Date: 6/30/03

Project Type: Research

Focus Category #1: Toxic substances

Focus Category #2: Sediments

Focus Category #3: Water quality

Lead Institution: University of Idaho

Principal Investigators:

Matthew J. Morra
R. Frank Rosenzweig*
University of Idaho
* Currently at the University of Montana

Problem and Research Objectives:

Lake Coeur d'Alene (CDA) is the second largest natural lake in the Inland Northwest. It lies between the Selkirk and the Coeur d'Alene Mountains and extends northward from the St. Joe River to the headwaters of the Spokane River. Lake CDA provides drinking water for several communities and serves as a primary recreational area for inhabitants of the Pacific Northwest. Over the last century Lake CDA became the major collecting bed for sediments impacted by human activities in its two major drainages. These activities include recreation, logging, and agriculture. In the Coeur d'Alene River Basin these activities also included mining and ore processing. Mining went largely unregulated in Idaho's Silver Valley from the 1880s until 1968, and as a result, tailings enriched in Pb, Zn, As, 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. Over the years numerous environmental studies have been carried out in this region, all confirming that sediments enriched in As, Cu, Cd, Fe, Mn, Pb, Sb, Zn, and other trace metals have been deposited throughout the lake. The USGS has estimated that as much as 85% of the lake bottom is contaminated with metal(loids) (Horowitz et al., 1992).

Because of its scenic beauty the region around Lake CDA is currently undergoing rapid development. As a result, we may expect additional human impact on this system in the form of increased nutrient loading and mechanical disturbance. It has been demonstrated that such phenomena can result in transient contaminant solubilization. Therefore empirical models that predict the fate and stability of metal(loid) contaminants under various perturbing influences are urgently needed by state, regional, and federal water quality regulators. Such models will facilitate management decisions ensuring continued protection of human health and environmental quality.

Our previous work thus indicates that reduced sulfur species may play an important role in controlling the cycling of metal(loid) contaminants in Lake CDA. We therefore propose to characterize this key variable controlling metal(loid) transport and bioavailability. More specifically, we will 1) identify and quantify sulfur species present in sediment pore waters, 2) develop an equilibrium model describing metal-sulfur speciation, 3) correlate model predictions with total soluble Pb, Cd, and Zn concentrations, and 4) predict metal flux from the sediment to the overlying water column. Our overall objective is thus to develop a clear understanding of sulfur biogeochemistry within the lake sediments, providing appropriate data that will contribute to the development of models focused on the fate of metal(loid)s within the sediments. Ultimately such models will be used to predict how anthropogenic alteration of the lake will modify metal(loid) cycling and potentially increase environmental deterioration. This research will ensure protection of regional water resources impacting northern Idaho and eastern Washington.

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

Methodology:

We sampled along a contamination gradient in the Lake, obtaining porewater and core samples on which to perform chemical analyses essential to modeling efforts. The study was conducted over two annual cycles and samples were collected in the spring, summer, and fall of each year in order to define temporal changes.

Peepers to obtain sediment porewater were installed by diverd at three different locations where metal contamination varies. Sediment cores were also collected at these different locations using polycarbonate pipe. Sediment and pore water analyses were performed with the specific objective of providing necessary data for equilibrium modeling of metal speciation and benthic flux calculations for Pb, Zn, and Cd. Elemental analyses for Pb, Zn, and Cd was performed using a Thermo Jarrell Ash IRIS ICP. Samples obtained from the peepers were also analyzed using polarographic techniques to speciate soluble sulfur compounds. Equilibrium modeling was 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 MINTEQA2. The flux of dissolved elements across the sediment-water interface by molecular diffusion was calculated using Fick's First Law and the established concentration gradient across the sediment-water interface.

During the course of our investigations we realized that additional characterization of sediment geochemistry was necessary. As a result, we initiated spectroscopic studies to characterize sulfur and iron species within the sediments. X-ray absorption spectroscopy (XAS) data collection was performed at the National Synchrotron Light Source (NSLS) in Brookhaven, NY and the Stanford Linear Accelerator Center in Palo Alto, CA.

Principal Findings and Significance:

Results indicate that at the time of sampling, the water column was oxic, suboxic conditions were established within 5 cm of the sediment-water interface, and anoxic conditions were established at 10 cm. Pore-water Fe concentrations increase with depth to concentrations between 30 and 60 mg L^{-1} Fe at 30 cm. The reductive dissolution of Fe oxides is releasing both Fe, As, and potentially Pb into the pore water. Maximum As pore-water concentrations of 1.5 mg L^{-1} were obtained from the site downstream from the Coeur d'Alene River delta. This site (Peaceful Point) also had the highest total As in the sediment and we believe that the small particle size of the sediment at this site greatly affects the sorption potential of heavy metals. Total sediment and pore-water data indicate that diagenetic reactions are taking place within the sediment and are responsible for the release of redox-sensitive metals into the pore water. No significant concentrations of sulfur species were found it the sediment porewater, indicating that sulfur may not be as important in metal sequestration as originally thought.

It also appears that the oxic 2 cm of sediment below the sediment-water interface acts as a boundary prohibiting the release of As into the overlying water. Preliminary zinc fluxes that were calculated indicate the potential for a positive Zn flux out of the sediment of Lake Coeur d'Alene.

Spectroscopic analysis of the sediment indicated that diagenetic reactions appear to be responsible for pyrite formation, since pyrite concentration in the sediments increases with depth. In contrast to original hypothesis, the dominate solid phase mineral governing soluble metal(loid) concentrations is the Fe-containing mineral siderite. Siderite concentrations increase with sediment depth, such that approximately 80% of the iron is in the form of this mineral. There is insufficient S within this system to participate in a significant portion of the sorption reactions.

Understanding metal cycling and the role of diagenesis in sediment has important implications for future water-quality monitoring efforts on the lake as well as health concerns associated with the use of the lake. It is apparent from our work, that the very large Fe:S ratio precludes extensive sulfide complexation with toxic metal(loid)s. The oxic to suboxic layer of sediment at the water interface acts as a barrier for As transport into the overlying water. Maintaining the current trophic status of the Lake such that the sediment-water interface remains oxic to suboxic should be an important objective of any management plan.

Descriptors: Heavy metals, Lakes, Mathematical models, Water chemistry

Articles in Refereed Scientific Journals:

Toevs, G.R., M.J. Morra, S.E. Fendorf, M. Polizzotto, L. Winowiecki, and B. Bostick. XAS characterization of Fe and S in mining-impacted sediments of Lake Coeur d'Alene, Idaho. Environ. Sci. Technol. (in preparation, not yet submitted).

Book Chapters:

Dissertations:

Water Resources Research Institute Reports:

Conference Proceedings:

Other Publications:

Meeting Abstracts

Diagenesis of Heavy Metal-Contaminated Sediments in Lake Coeur d'Alene as Related to Water Quality, Toevs, G.R., M.J. Morra, S.E. Fendorf, B.C. Bostick, M. Polizzotto, L. Winowiecki, and S.A. Wood. Abstracts of the Annual Meetings of the Soil Science Society of America, Nov. 2-6, Denver, CO.

Students Supported:

Gordon R. Toevs, M.S. student in Soil & Land Resources.*

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Information Transfer Program

Consistent with our mandate, the Idaho Water Resources Research Institute at University of Idaho, has endeavored to promote and coordinate education and information transfer. These efforts have been in coordination with Idaho's water resource agencies, and the Idaho Department of Education. The following is a list of water quality education/information transfer programs which emphasize cooperation and collaboration. These activities are not directly funded with USGS funding.

Project WET (Water Education for Teachers)Idaho, an interdisciplinary, supplementary water education program for Idaho educators, was active this past year. The goal of Project WET is to facilitate and promote an awareness, appreciation, and understanding of Idahos water resources through the development and dissemination of classroom-ready teaching aids. Like other successful natural resource education programs, Project WET emphasizes teaching students how to think, not what to think. In this past year there were 12 workshops with 220 teachers participating.

The Idaho Water Resources Research Institute also participated in Splash Water Festivals, Water Awareness Week, Idaho Salmon and Steelhead Days, geothermal education programs, the Ground Water Awareness Project, and watershed programs.

Idaho Water Resources Research Institute research activities also provide outreach and education. Many research projects have specific outreach components identified in proposals and work plans. Researchers participate in public meetings and hold workshops related to their specific projects. Several Institute researchers have been involved with the Idaho Legislature's Interim Committee on Natural Resources to identify aquifer management needs and approaches.

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Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	0	0	0	0	0
Masters	3	1	0	0	4
Ph.D.	1	0	0	0	1
Post-Doc.	0	0	0	0	0
Total	4	1	0	0	5

Notable Awards and Achievements

Publications from Prior Projects