Water Resources Institute
Annual Technical Report
FY 2005

Introduction

The University of Wisconsin Water Resources Institute (WRI) is based at UW-Madison as an academic unit of the universitys Graduate School and works with its Office of Research & Sponsored Programs to ensure compliance with university, state and federal guidelines. WRI is housed in the UW-Madison Aquatic Sciences Center (ACS), the administrative home of both WRI and the UW Sea Grant Institute. The staff at ACS provides support for WRI administration, research and outreach activities. The WRI also supports a library containing more than 26,000 volumes covering all major water topics. With nearly 75% of its current base budget targeted for research, the WRI is supporting 24 individual research projects that address a wide range of water-related issues and problems. Research projects fall into the following four thematic areas: groundwater, surface water, groundwater/surface water interactions and drinking water initiatives. Participants in WRI-supported projects include faculty, staff and students at UW System campuses at Madison, Milwaukee, Stevens Point, Whitewater, LaCrosse and Parkside; UW-Extension; the Wisconsin State Laboratory of Hygiene; U.S. Geological Survey, and individuals in private industry. In May 1984, Comprehensive Groundwater Protection legislation for Wisconsin (1983 Act 410, Wisconsin Statutes) was signed into law. One of the provisions of the bill was to establish a state Groundwater Coordinating Council (GCC) appointed by the legislature and the governor. Advisory to the GCC is the Groundwater Advisory Council (GRAC), which is appointed by the UW-Madison Chancellor. Because groundwater protection is deemed a priority issue by the WRI, the GRAC serves as an important advisory committee for the WRI. Composed of a diversity of representatives with a great deal of scientific, political and administrative experience, the GRAC has helped the WRI identify current and anticipated water problems and issues and establish priorities for initiating research projects. Since July 1989, the state has provided line item funding for groundwater research to the UW System. This Groundwater Research Program, administered by the WRI, currently funds 14 projects that provide a balanced program of laboratory, field and computer modeling studies and applications designed to preserve or improve groundwater quality. Charged with the primary mission to plan, develop and coordinate research programs that address present and emerging water- and land-related issues, the WRI has developed a broadly based statewide program of basic and applied research that has effectively confronted a spectrum of societal concerns. Institute staff; UW System faculty, staff and students; state administrators and other public officials; industry, and the public have come to rely on the WRI for objective, timely scientific information about water resources issues. The WRI ensures that this information reaches these individuals through its strong information dissemination/technology transfer program. An integral part of the WRIs total program is the training of students. Research projects have provided support and training for graduate and undergraduate students pursuing degrees in a wide range of disciplines.

Research Program

As established by Wisconsin's Groundwater Law of 1984, the state provides $300,000 annually to the UW System to support groundwater research and monitoring. In 1989, the WRI became the UW System's lead institution for coordinating the calls for proposals and peer reviews for distribution of the funds. To avoid duplication and better target groundwater research funding, several other state agencies (the departments of Commerce, Natural Resources, and Agriculture, Trade and Consumer Protection) agreed to partner with the WRI to establish an annual Joint Solicitation for Groundwater Research and Monitoring. This annual solicitation has funded more than 300 groundwater research and monitoring projects since its inception and has helped establish Wisconsin as a leader in groundwater research. The results of the Wisconsin Groundwater Research and Monitoring Program (WGRMP) are recognized internationally, and WRI plays an important role in coordinating project reporting and making all technical reports available though our institute's library and website.

Given the limited funding available through the annual 104(B) allocation, the Wisconsin WRI has decided to use its funds to participate in the WGRMP by supplementing this funding source and providing additional opportunities for groundwater research in the UW System. Our priorities for research are established annually by the Wisconsin Groundwater Research Advisory Council (GRAC) and included as part of the Joint Solicitation. The GRAC is our institute's advisory council and also convenes to make project funding decisions. All proposals submitted to the Joint Solicitation receive rigorous external peer review (coordinated by the WRI) and relevancy review by the Research Subcommittee of the state's Groundwater Coordinating Council. We believe that partnership with other state agencies provides us with the ability to fund highly relevant research and allows our limited funds for 104(B) to be leveraged to the fullest extent.

Foundry Slag for Treating Arsenic in Ground Water and Drinking Water

Basic Information

Title:	Foundry Slag for Treating Arsenic in Ground Water and Drinking Water
Project Number:	2005WI90B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	2
Research Category:	Engineering
Focus Category:	Groundwater, Treatment, Water Quality
Descriptors:	None
Principal Investigators:	Craig H Benson

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: Jim Hurley
Submitted: 7/12/2006

Project Title

WR04R008: Foundry Slag for Treating Arsenic in Groundwater and Drinking Water

Project Investigators

Craig Benson, University of Wisconsin-Madison

Progress Statement

Nine gray-iron slag samples from foundries throughout Wisconsin were obtained for study. A granular iron was also obtained for use as a control material.

The slags were crushed so that >95% of the material passed through a No. 4 sieve. The crushed material was then characterized for physical properties (classification, hydraulic conductivity, specific gravity). The crushed slags classify as either well graded or poorly graded sands. They have hydraulic conductivities on the order of 0.03 to 0.3 cm/s and specific gravities ranging from 2.2 to 3.23.

Each slag was characterized chemically in accordance with the criteria in the Wisconsin regulations for beneficial reuse of industrial byproducts (NR 538). Eight of the slags exceeded NR 538 Category 1 standards for iron and/or manganese. However, since Fe and Mn at these levels produce taste and odor concerns rather than health concerns, these results are not problematic. Total elemental analyses of the slags and iron showed nearly universal failure to meet the Category 1 criteria for arsenic, beryllium, and chromium. The granular iron, which is already used as a reactive medium for in situ arsenic treatment, had some the highest concentrations of these elements. Consequently these results do not negate the use of iron slags for in situ treatment of arsenic. X-ray fluorescence was used to determine the bulk composition of the slags. Silicon, calcium, magnesium, aluminum and iron were found to be the main constituents. The percentage iron by weight varied from 57% to <1%.

Two slag samples of intermediate iron content (19 and 7.5%) were selected for initial testing. Preliminary batch tests have shown that both of these slags and a 1:9 iron-sand mixture will remove both arsenic (III) and arsenic (V) from solution. For example, the total arsenic concentration in aqueous solutions was reduced from 500 ug/L to less than 10 ug/L within 24 hours. Kinetic batch studies indicate that the majority of this removal occurs within 3 hr. Further study is needed to confirm these results and to understand the removal kinetics.

Applications, Impacts & Benefits

This technology is a cost-effective way to deal with arsenic in ground water. Also, the technology has benefits in terms of sustainability, because an industrial byproduct is used as the reactive medium. The PI is currently exploring use of the technology at a Superfund site in California.

Patents & Copyrights

Patent or Copyright?	Patent
Status	Pending
Title	Patent submittal
Description	We have submitted a patent request to the Wisconsin Alumni Research Foundation.
Year Awarded	

Presentations & Public Appearances

Title	Byproducts as Reactive Materials for PRBs
Presenter(s)	I will be speaking on this topic as an invited panelist in the upcoming 5th International Conference on Environmental Geotechnics
Presentation Type	
Event Name	5th International Conference on Environmental Geotechnics
Event Location	Cardiff, Wales, UK
Event Date	6/6/2006
Target Audience	Scientific audience
Audience Size	500
Description	

Students & Post-Docs Supported

Student Name	Mitchell Eberhardt
Campus	University of Wisconsin-Madison
Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison
Degree	Expected Masters
Graduation Month	December
Graduation Year	2006
Department	Civil and Environmental Engineering
Program	Environmental Science and Engineering
Thesis Title	Metals Leaching from Gray Iron Slags Used in PRBs
Thesis Abstract	

Student Name	Sarah Gatzke
Campus	University of Wisconsin-Madison
Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison

Degree	Expected Other
Graduation Month	June
Graduation Year	2007
Department	Geological Engineering
Program	Geological Engineering
Thesis Title	
Thesis Abstract	

Student Name	Stacy Metz
Campus	University of Wisconsin-Madison

Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison

Degree	Expected Masters
Graduation Month	December
Graduation Year	2006
Department	Geological Engineering
Program	Geological Engineering
Thesis Title	Using Gray Iron Slags for Treating As in Groundwater
Thesis Abstract	

Occurrence of Estrogenic Endocrine Disruptors in Groundwater

Basic Information

Title:	Occurrence of Estrogenic Endocrine Disruptors in Groundwater
Project Number:	2005WI91B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	2
Research Category:	Water Quality
Focus Category:	Water Quality, Toxic Substances, Methods
Descriptors:	None
Principal Investigators:	William C. Sonzogni

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: miel barman
Submitted: 7/7/2006

Project Title

WR04R004: Occurrence of Estrogenic Endocrine Disruptors in Groundwater

Project Investigators

William Sonzogni, University of Wisconsin-Madison

Progress Statement

Overview of your progress on this project during the past year.

High capacity well sampling has been completed at 5 different Wisconsin municipalities, with 4 sampling events at each municipality. Samples have been collected at each site from 2 high capacity wells and the nearby surface water. Well water from two of the municipalities is further treated before distribution to the public. These post-treatment plant waters were also collected and tested. Quality assurance samples include 4 matrix spikes, 4 travel blanks, 4 lab water blanks, 2 lab water spikes and 3 replicates. All of the QC blanks have resulted in no detects. The spiked samples and replicates have resulted in recovery rates ranging from 71-124%. In all, 128 water samples were collected for this study. All of the samples were extracted through a C18 disk, the disk was then eluted with solvents to capture the estrogenic chemicals. The extracts were then tested for estrogenic activity using a breast cancer cell proliferation assay known as the E-Screen. All samples collected from the high capacity well sampling sites and all of the septic system samples have been assayed. The first round of sampling, occuring in November and December, for the high capacity wells had five of the six surface waters showing estrogenic activity which ranged from 0.05-0.09 ng/L with the sixth site having no estrogenic activity, while all of the well samples showed no estrogenic activity. The second round of sampling, occuring in February and March, for the high capacity wells had all six of the surface waters exhibiting estrogenic activity at an elevated rate from the first sampling. This activity ranged from 0.04-0.91 ng/L, while 4 of the systems showed no estrogenic acitivity in the wells and one site showing activity
A traditional septic system consists of a single septic tank and soil leach field. New treatment technologies have been developed in recent years to more effectively treat domestic wastewater; these advanced systems have been approved in Wisconsin and elsewhere in areas where conventional systems are prohibited. Over the past two years, 21 septic effluent samples were collected and analyzed, including 8 with no advanced pretreatment, 7 which had passed through a sand-filtration system, and 6 from aerobic treatment systems. Estrogenic activity ranged from 0.06 to 192.5 ng/L in the samples, with the highest level being found in a malfunctioning aerobic treatment system. Excluding this anomalous sample, the mean activities for samples with no pretreatment, aerobic treatment, and sand filtration were 23.7, 1.6, and 0.8 ng/L, respectively. This suggests that advanced pretreatment reduces the concentration of estrogenically active compounds being released to the subsurface.

Applications, Impacts & Benefits

Benefit: Groundwater from high capacity wells in Wisconsin showed no estrogenic endocrine disruptor activity, except a very small amount at one of the sites during one of the sampling events. We can, therefore, conclude that there is rarely infiltration of these contaminants from the surface waters into the nearby groundwaters.
Septic systems utilizing sand filtration provided cleaner effluent than systems using wisconsin mound systems.This suggests that advanced pretreatment reduces the concentration of estrogenically active compounds being released to the subsurface.

Partners

Name/Organization Affiliation Wisconsin Drinking Water Utility #1
Affiliation Type Government
Email
Description as per participation agreement, the facilities that provided samples for this project wish to remain anonymous.

Name/Organization Affiliation Wisconsin Drinking Water Utility #2
Affiliation Type Government
Email
Description as per the participation agreement, the facilities providing samples for this project wish to remain anonymous.

Name/Organization Affiliation Wisconsin Drinking Water Utility #3
Affiliation Type Government
Email
Description as per the participation agreement, the facilities providing samples for this project wish to remain anonymous.

Name/Organization Affiliation Wisconsin Drinking Water Utility #4
Affiliation Type Government
Email
Description as per the participation agreement, the facilities providing samples for this project wish to remain anonymous.

Name/Organization Affiliation Wisconsin Drinking Water Utility #5

Affiliation Type	Government
Email	
Description	as per the participation agreement, the facilities providing samples for this project wish to remain anonymous.

Groundwater sustainability in a humid climate: Groundwater pumping, groundwater consumption, and land use change.

Basic Information

Title:	Groundwater sustainability in a humid climate: Groundwater pumping, groundwater consumption, and land use change.
Project Number:	2004WI82G
Start Date:	9/1/2004
End Date:	8/31/2006
Funding Source:	104G
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	Water Use, Groundwater, Management and Planning
Descriptors:	None
Principal Investigators:	Madeline Beth Gotkowitz, David John Hart, Charles P Dunning

Publication

Annual Progress Report

Reporting Period: 7/1/2004 - 6/30/2005

Submitted By: Jim Hurley
Submitted: 7/12/2006

Project Title

WR04R009: Groundwater Sustainability in a Humid Climate: Groundwater Pumping, Groundwater Consumption and Land Use Change

Project Investigators

Madeline Gotkowitz, Wisconsin Geological and Natural History Survey

Progress Statement

We have compiled water-use, land-use, climate, and economic data for the two study areas, Sauk and Waukesha (Wisconsin) counties. The water-use data include records of pumping from private high capacity wells and municipal water utilities. The municipal water utility data came from annual utility reports filed with the Wisconsin Public Service Commission. Our database currently includes the following records for all municipal water utilities in Sauk and Waukesha counties:

1) Annual water sales in millions of gallons per year by category (residential, commercial, industrial) for the years 1988-2003.
2) Total water sold in millions of gallons per year for the years 1988-2003.
3) Total water pumped in millions of gallons per year for the years 1988-2003.

Private high-capacity well records in Sauk and Waukesha counties were obtained from the Wisconsin Department of Natural Resources. Each private high-capacity well record has been reviewed and assigned a water-use category that is consistent with the categories used in the annual utility reports. The available private high capacity well records do not contain sufficient information to estimate the water-use from these wells. Therefore, we have designed a stratified random sampling program to estimate the total annual pumpage from private high-capacity wells. We are in the early stages of this sampling program and have begun to request cooperation from well owners.
A GIS land-use dataset has been obtained for Waukesha County from the Southeastern Wisconsin Regional Planning Commission. Because no equivalent dataset is available for Sauk County, we are planning to estimate historical land-use trends in Sauk County using tax parcel records.
Historical records of temperature, precipitation, and growing degree days from weather stations in Sauk and Waukesha counties were obtained from the Midwestern Regional Climate Center. Population and economic data were obtained from the U.S. Bureau of Economic Analysis. We are in the preliminary stages of data analysis and have begun looking for correlations between municipal water-use and land-use, climate, and/or economic factors.

Applications, Impacts & Benefits

This progress report describes activites during the first year of a two-year project. The first year has involved an intensive records search and data compilation effort. As such, impacts and benefits of the project are limited to progress for team members in aquiring this information.

Interactions

Description	meeting with Chcuk Dunning USGS to discuss progress
Event Date	7/21/2005

Students & Post-Docs Supported

Student Name	Tara Root
Campus	University of Wisconsin-Madison
Advisor Name	Jean Bahr
Advisor Campus	University of Wisconsin-Madison
Degree	PhD
Graduation Month	August
Graduation Year	2005
Department	Geology and Geophysics
Program	Hydrogeology
Thesis Title	unrelated to current project
Thesis Abstract	unrelated to current project

Grant No. 04HQGR0034 The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling The Transport, Fate and Cycling of Mercury in Watersheds and Air Sheds

Basic Information

Title:	Grant No. 04HQGR0034 The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling The Transport, Fate and Cycling of Mercury in Watersheds and Air Sheds
Project Number:	2005WI150S
Start Date:	11/15/2003
End Date:	11/30/2006
Funding Source:	Supplemental
Congressional District:	
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	

Publication

1. Gorski, P.R., DE. Armstrong, J.P. Hurley and M.M. Shafer. 2006. Speciation of aqueous methylmercury influences uptake by a freshwater alga (Selenastrum capricornutum). Environmental Toxicology and Contamination. 25 (2): 534-540.
2. Branfireun, B.A., D. P. Krabbenhoft, H. Hintelmann, R. J. Hunt, J. P. Hurley, and J.W.M. Rudd. 2005. The Transport And Speciation Of Atmospheric Mercury In A Boreal Forest Wetland: A Stable Mercury Isotope Approach. Water Resources Research, v. 41, W06016, oi:10.1029/2004WR003219, 2005.
3. Hall, B.D., H. Manolopoulos, J.P. Hurley, J. J. Schauer, V.L. St. Louis, D. Kenski, J. Graydon, C.L. Babiarz, L.B. Cleckner, and G.J. Keeler. 2005. Methyl and total mercury in precipitation in the Great Lakes region. Atmospheric Environment. 39(39):7557-7569.
4. Stoor, R.W., J.P. Hurley, C.L. Babiarz and D.E. Armstrong. 2006. Subsurface Sources of Methylmercury to Lake Superior from a Wetland-Forested Watershed. In Press. Science of the Total Environment.
5. Chadwick, S.P., C.L. Babiarz, J.P. Hurley and D.E. Armstrong. 2006. Influences of iron, manganese,

and dissolved organic carbon on the hypolimnetic cycling of amended mercury. In Press. Science of the Total Environment.

6. Babiarz, C.L., J.P. Hurley, D.P. Krabbenhoft, T.R. Trinko, M. Tate, S.P. Chadwick and D.E. Armstrong. 2003. A hypolimnetic mass balance of mercury from a dimictic lake: results from the METAALICUS project. Journal de Physique IV. 107:83-86.

Introduction

There is considerable evidence that atmospheric transport, deposition, and reemission of Mercury (Hg) are key processes in the movement of this neurotoxin throughout the globe [1]. Historically, many of the mechanisms that control the cycling of Hg have been obscured by our inability to differentiate between that which is new to the system, and that originating from the historic pool. In the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS), stable isotopes of Hg were applied to both the lake and watershed as a tool for discovering key processes that control the environmental fate of Hg. These isotopic techniques have provided the first direct evidence of a whole lake and whole watershed response to "new" atmospheric inputs of Hg. In this section we describe the major goals of the METAALICUS project and the role of the University of Wisconsin research team.

METAALICUS Project

The overall goal of METAALICUS is to better define the timing and magnitude of the ecosystem response to changes in Hg loading [2]. It is our hypothesis that the sediments will be the ultimate sink for Hg, but the timing of that endpoint will be determined by a complex set of transport and transformation processes within both the lake and the surrounding watershed.

Rationale: Although the presence of methylmercury (MeHg) in fish is a natural occurrence, concentrations are often above the 0.5 ppm health advisory limit. Elevated concentrations are a concern due to the toxicity of MeHg and the exposure to humans and wildlife via fish consumption. Elevated MeHg concentrations have been observed in fish from remote water bodies that lack direct local sources of mercury (either natural or anthropogenic). The likely source of mercury to these remote systems is non-point atmospheric deposition of inorganic mercury. Once deposited, inorganic mercury is converted to MeHg by bacteria and enters the food chain.

The atmospheric pool contains mercury from both natural and anthropogenic sources. Natural sources include volcanoes and mineral deposits. Anthropogenic sources include emissions from coal combustion, waste incineration, mining, and other industrial processes. There has been much research on the impact of mercury emissions on fish mercury concentrations, and the efficacy of emissions controls on anthropogenic sources. In North America alone, emission controls for electric utilities have been estimated to cost billions of dollars per year. Despite this research activity, questions remain about the magnitude and timing the ecosystem response to changing mercury loads. Much of this uncertainty stems from an inability to differentiate between recently deposited mercury and the historic pool.

Recent advances in analytical capability allow the use of stable isotopes as an ambient-level tracer for new mercury in the environment [3, 4]. In addition, the Canadian Department of Fisheries and Oceans (DFO) operates a field station that specializes in watershed-scale experiments, and the principle investigators have obtained the necessary permits to apply the isotopes of mercury. This combination of resources and expertise makes the METAALICUS project a unique opportunity that may not be repeated due to the logistics and expense.

Project-Level Goals: The major goals of the METAALICUS project are to determine the fate and transport of the new Hg through an ecosystem, and to assess the watershed response due to changes in atmospheric Hg deposition. The questions that guided the development of the project were:

a) What is the relationship between the amount of Hg in atmospheric deposition and the amount of methylmercury in fish?
b) How quickly will the fish Hg levels respond to a change/reduction in mercury deposition?
c) How will environmental factors affect the magnitude and timing of the response?

Experimental Design: The METAALICUS project takes advantage of two major assets: (1) highly sensitive isotopic techniques for differentiating between new and old Hg, and (2) a research site that is unparalleled for a project of this scope and relevancy to the effects of power generation and transmission. The METAALICUS project is located within the Lake 658 watershed in the Experimental Lakes Area (ELA; Figure 1) – a research station operated by the Canadian Department of Fisheries and Oceans in northwestern Ontario. Lake 658 is an 8.3 Ha dimictic lake surrounded by a 42-Hectare forested upland, and a 2 Ha wetland on the western reach. There are three major environmental compartments in the study that each received a different isotope of Hg: The upland (^{200}Hg), the wetland (^{198}Hg), and the lake (^{202}Hg). By the end of autumn 2005, the lake and watershed had received 5 years of isotopic Hg additions at a level 5 times background atmospheric deposition. For a detailed description of isotope application methods, please see the Methods and Fieldwork section below.

Note: At the time this work was funded by Wisconsin Focus on Energy, the original phase of isotope addition had come to a close and the recovery phase was expected to begin. Based on the available data, however, the project team for the larger METAALICUS project agreed there was scientific merit in continuing to load the watershed with isotopic amendments of mercury. The main arguments for continuing the loading phase included the lack of steady-state in each compartment; the time-lag in the transport of the terrestrial spike into the lake, and the future ability to observe and interpret the spike. Consequently, isotopes were added to the watershed during each field season encompassed by the work presented here.

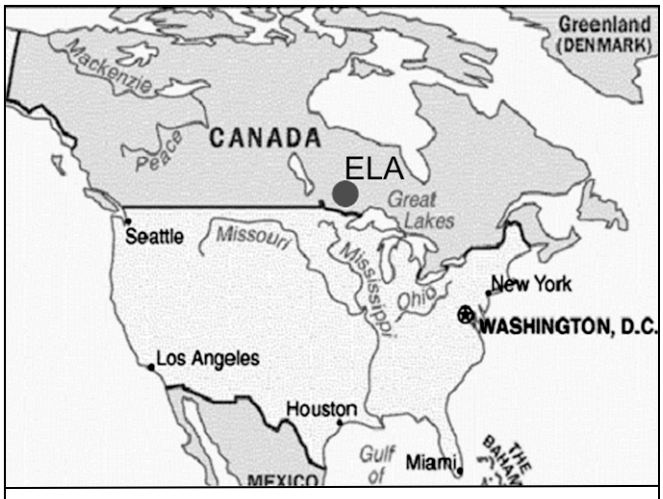


Figure 1. Location of study site

Participating institutions and research areas: Whole-watershed experiments require a diverse array of expertise. The METAALICUS project brought together a multidisciplinary team of 20 principle investigators from 12 US and Canadian institutions (Table 1). Each participating institution has been charged with evaluating a different aspect of the ecosystem response.

Table 1. Areas of specialty for each Institution and Principal Investigator

Institution	Investigators	Specialty
Freshwater Institute; Canadian DFO	Ken Beaty	Hydrology & Meteorology
Freshwater Institute; Canadian DFO	Paul Blanchfield	Fish Ecology
Freshwater Institute; Canadian DFO	Drew Bodaly	Biogeochemistry, Fish Studies
Freshwater Institute; Canadian DFO	Mike Paterson	Water column Invertebrates
Freshwater Institute; Canadian DFO	Cheryl Podemski	Benthic Invertebrates
Freshwater Institute; Canadian DFO	Michael Turner	Littoral Ecology
R & K Consultants	John Rudd; Carol Kelly	Biogeochemistry
Smithsonian Institution	Cindy Gilmour	Meth/Demeth,- Littoral Sediments
Tetra Tech Incorporated	Reed Harris	Whole-Ecosystem Modeling
Trent University	Holger Hintelmann	Water Chemistry, Hg Isotopes
United States Geological Survey	David Krabbenhoft	Hydrology, Upland Geochemistry
US Department of Energy	Steve Lindberg	Atmospheric Chemistry
University of Alberta	Vince St. Louis	Biogeochemistry; Litter-fall, Precip
University of Maryland	Andrew Heyes; Robert Mason	Meth/Demeth -Wetland/Upland Soils
University of Montreal	Marc Amyot	Photoreduction, Oxidation of Hg
University of Toronto	Brian Branfireun	Biogeochemistry, Terrestrial Studies
University of Wisconsin	James Hurley; Chris Babiarz	Hypolimnion Biogeochemistry

University of Wisconsin Scope of Work

In our experience, the strongest approach to research couples seasonal field observations with controlled laboratory experiments to fill gaps in knowledge that will improve our understanding of underlying processes and may also ground-truth environmental modeling efforts. This is an iterative process that builds strong hypothesis for future observation, experimentation, and improved ecosystem management.

Overview of Research Focus: The University of Wisconsin has participated in the METAALICUS project since its inception, and is primarily charged with examining the *hypolimnetic recycling and burial of Hg across the sediment-water interface.* Sediments are a major sink for Hg in the system because settling particles scavenge Hg from the water column. However, redox conditions at the sediment water interface, and in the overlying hypolimnetic waters during anoxia, are sites of intense recycling of Hg before eventual burial [5]. In addition to remineralization of Hg into the dissolved phase as particles fall, sulfur-reducing bacteria that thrive in anoxic conditions convert inorganic Hg(II) into MeHg [6 - 8] – the form of mercury that is bioaccumulative.

In broader terms, our research group addresses several questions that relate to our primary task:

A) How quickly will the lake respond to decreased atmospheric deposition?

B) What fraction of the recent Hg will ultimately be buried in the lake sediment and be "permanently" removed from the ecosystem?

C) What is the long-term importance of watershed type on MeHg formation, transport and bioaccumulation?

Detailed information on the transport and transformation of Hg is needed to understand both the short-term and long-term persistence of the amended isotopes in the watershed and lake. Modeling the fate of Hg in the environment is ultimately tied to the quantification of reaction

rates and the process pathways. Our interest is in the particular processes and pathways that dictate particle-water partitioning. These key focus areas are:

A. Processes at the sediment-water interface. Understanding the mechanisms that control permanent sedimentation and recycling of Hg and MeHg in the bottom waters, and in the neighboring sediment zone, is key to determining the residence time of Hg and MeHg in the lake. Particles reach this zone as either the remains of algae, or other biotic material, or inorganic particles. We need better information on the precise depth of the "active zone" in the sediments, and the key factors that either strip Hg from the lake, or bury it, or enhance its return for possible bioaccumulation.

B. Partitioning to Dissolved Organic Carbon (DOC) in soil water, wetland pore water, and lake water. We have developed state-of-the-art techniques to sample, process, and analyze Hg in the solid, colloidal, and aqueous phase. Our published data strongly identifies DOC as the key phase for transport of Hg from both soil water and wetland water into either groundwater or surface water.

C. Processes controlling initial uptake into algae. While our lake water studies have shown there is a rapid conversion of added isotopes of inorganic Hg to MeHg, a key step for bioaccumulation into higher trophic levels is the sorption of MeHg to algae. We have keen interest in this process and have developed a bioassay technique in conjunction with the Wisconsin State Laboratory of Hygiene. We seek to couple that work with the innovative use of stable isotopes, specific isolates of lake DOC, and inorganic ligands to examine the controls on MeHg uptake.

Specific actions funded by Wisconsin Focus on Energy:

The project entitled "Reduction in Mercury Loading: Timing and Magnitude of an Ecosystem Response" was funded by the Wisconsin Focus on Energy to cover four specific actions tied to in-lake processes:

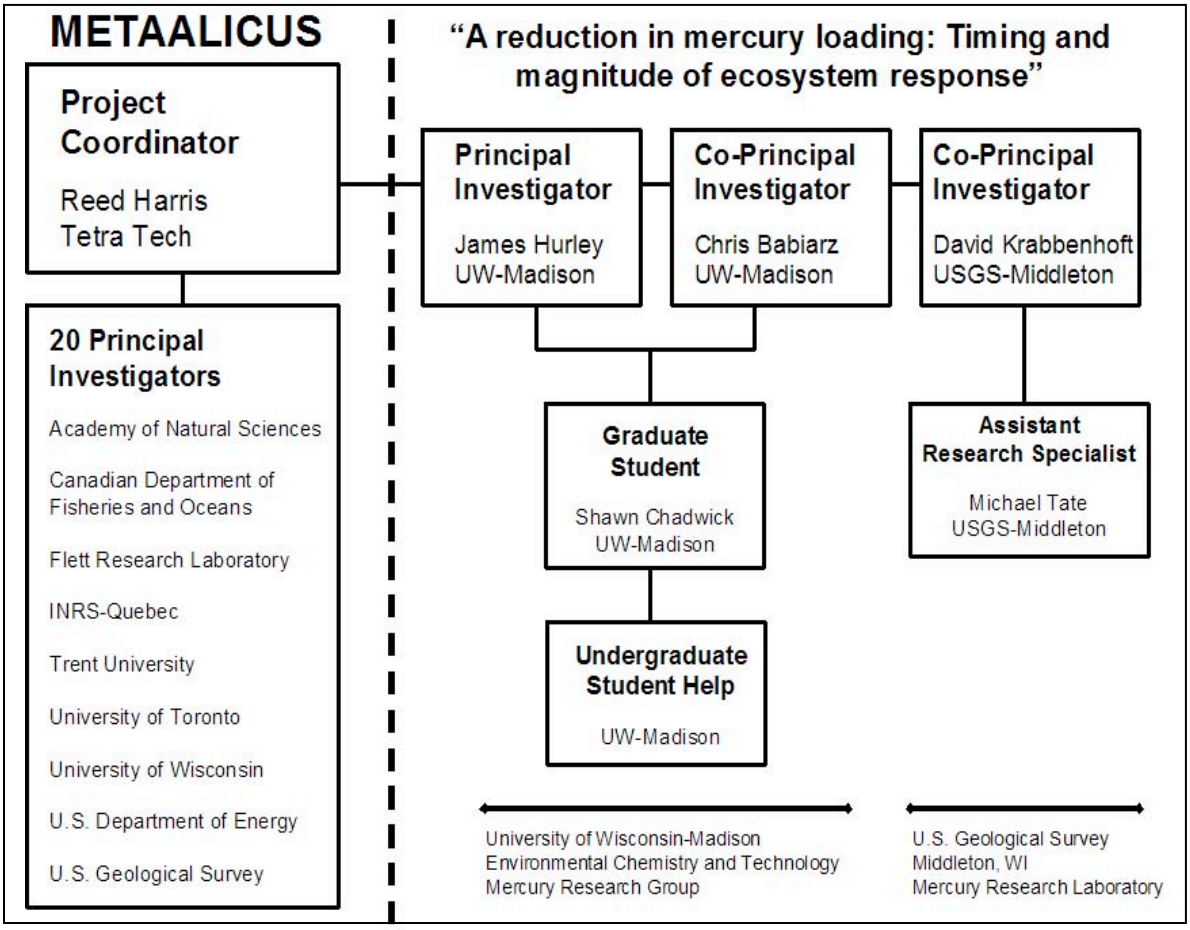
a) ***Mixed-Core Experiments*** *to assess post-depositional migration, long-term methylation/demethylation, and estimate net burial rates for Hg in pelagic and littoral sediments.*
b) ***Lake Profiles & Sediment Trap Deployment*** *to establish the hypolimnetic mass balance for Hg in the lake. Establish the importance of turnover in redistributing recently deposited Hg throughout the lake.*
c) ***Resin, Pigment, Optical, and Size-fractionation of Dissolved Organic Carbon (DOC)*** *to establish the importance of DOC character on Hg transport and transformation.*
d) ***Bioavailability Work*** *to determine the changing availability of the spiked Hg over time.*

In addition to these actions, the United States Geological Survey provided in-kind expertise to carry out an action item tied to terrestrial processes: **Soil zone translocation, humus leaching, and methylation experiments.** The purpose of these experiments are three-fold: to determine the factors responsible for the lag in response observed from the terrestrial compartment; to evaluate the relative importance of erosion versus soil-zone mobilization via humic acids on the

long-term transport of Hg from the upland to the lake; and to determine the controlling factors leading to MeHg occurrence in terrestrial soils. This work was not directly supported by Wisconsin Focus on Energy, and is therefore not reported here.

Organizational Chart: Our research group at the University of Wisconsin is one of 12 institutions involved with the larger METAALICUS project (see left hand side of Figure 2). Our work was performed in close cooperation with Dr. David Krabbenhoft and his laboratory at the Middleton office of the United States Geological Survey. Dr Krabbenhoft provided in-kind support for the project through use of the analytical instrumentation to analyze the samples for mercury isotopes. His research group also provided data and expertise regarding the terrestrial component of the project. This information and support was critical for completing and interpreting the results. This report covers the work coordinated by Dr. James Hurley and Dr. Christopher Babiarz at the University of Wisconsin.

Figure 2. Organizational chart for the University of Wisconsin research group.



Methods and Field Work

Spike Applications

Isotopes of mercury were applied to the lake and watershed using three methods that were tailored to the local terrain and required weather conditions. Each method was used for a different compartment of the L658 basin: terrestrial, shoreline, and lake. In all cases, the target application rate was 25 µg/m^2/yr (approximately four times the ambient wet deposition rate for mercury at ELA).

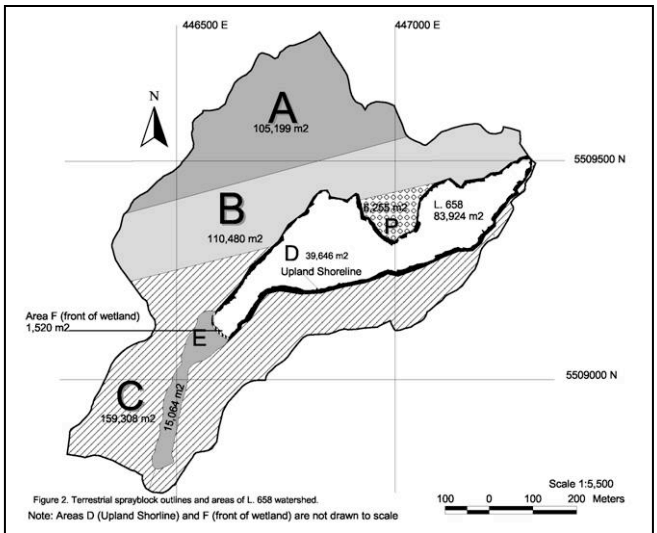


Figure 3. Lake 658 watershed spray zones.

Terrestrial: For the terrestrial isotope application, the watershed was split into four areas that were sprayed by airplane (Figure 3): One block for the wetland (E) and three blocks for the upland (A, B, and C). To minimize drift of the spray mist outside of the spray blocks, the spray nozzles were opened and closed by GPS technology. The nozzles were programmed to open 20 meters after entering a spray block and close 20 meters before exiting a spray block. This resulted in 20-meter buffer zone around the outer edge of each block. The buffer zone was sprayed using a different method (see below)

In order to mimic wet deposition and minimize evaporative loss of the isotope, the terrestrial isotope would ideally be applied during a light rain. This is difficult in practice and two criteria were established for the terrestrial application: 1) heavy rainfall should occur within 1 hour of spraying onto dry foliage, and 2) winds should be less than 15 km/hr.

Shoreline: In order to minimize overspray of the terrestrial isotope onto the lake, the 20 meter buffer zone surrounding the shoreline (D and F in Figure 3) was sprayed by fire hose. A 2000 liter plastic tank was secured to a floating barge. The tank was filled with low-DOC water from nearby Lake Winnange because it did not contain the lake isotope. The shoreline was divided into several 20m x 20m plots that were systematically treated as follows: The isotope was mixed into the water stream at the nozzle using a device that diluted 1 liter of spike solution into ~350 liters of lake water. The water was evenly sprayed over the plot, saturating the canopy and ground vegetation. The process was deigned to approximate a 1 cm rain event in order to match the precipitation requirement of the terrestrial application (see above). Additional criteria for the shoreline isotope application included low prevailing winds that were in the direction of the shore.

Lake: Application of the lake isotope occurred by boat. The spike solution was mixed into several 20-L carboys of lake water, and the solution was pumped into the wash of a trolling motor. Two small boats were driven around the lake in a random pattern, making sure to cover

the entire surface of the lake. The entire process took several hours to ensure good mixing and minimize the pumping rate. Additional criteria for the lake isotope application included low wind and low light conditions (dusk/night) to avoid photo-reduction and evasion of the isotope.

Field Apparatus

Specialized apparatus required for field sampling was manufactured for this project. All construction material was compatible with trace-metal clean techniques (Teflon, acrylic, polyethylene or polypropylene). All sampling devices and bottles were pre-cleaned using rigorous trace-metal clean protocols.

Water Column: Samples were obtained at depth using an all Teflon sampling line and weight connected to a peristaltic pump. The sampling depth was determined by lowering the weight and tubing with a metered Kevlar rope that was pre-cleaned. Samples near the sediment-water interface were collected using a Close Interval Sampler (CIS; see below) that was placed on the sediment surface by a SCUBA diver in June 2001 [5]. Particulate Hg samples were collected in-line on pre-ashed quartz fiber filters rated at a 0.7 µm pore size (Whatman QMA). Filtered Hg samples were collected through in-line polyethersulfone filtration capsules rated at 0.45µm pore size (Meissner filtration products).

Close Interval Sampler: For accurate sampling of water just above the sediment-water interface, we employed a close-interval sampler. The device holds several Teflon ports at precise depths above the sediment-interface. Long sampling lines connect the ports to outlets at the surface of the lake (see Figure 4). A separate device was placed in each basin of the lake by SCUBA and was allowed to winter-over each season by submerging the outlet ports below the ice line.

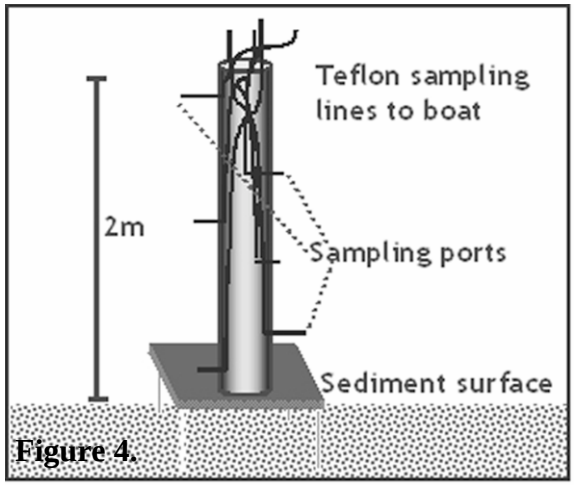


Figure 4.

Sediment Traps: Acrylic barrels (approximately 81 cm long and 14.5 cm internal diameter) were suspended by Kevlar ropes from a floating array. Based on the design of Dean et al. [9], the barrels include a funnel to focus material into a bottle. The Trap dimensions are designed to minimize losses and over trapping due to internal lake currents. Traps were deployed in two week intervals to avoid complications from decaying matter and transformation of mercury into methylmercury. Trap material was sieved at 243 microns to remove large particles and biota that would lead to over estimates of the sedimentation flux.

Sediment Coring: To collect sediment cores, we employed short acrylic tubes (approximately 30 cm long by 4.5 cm internal diameter). Cores were collected carefully by SCUBA to ensure that the interface was not disturbed. Cores were extruded on site and sliced at 1 cm intervals into pre-cleaned and pre-weighed vials. Sediments were frozen at the field station at the end of the field day.

Laboratory Methods

We employed state-of-the-art trace level analytical and sampling tools throughout the project.

Isotopic Hg analysis was determined using a Perkin-Elmer Élan 6100 (ICP-MS) that is dedicated for Hg-only analysis. This ultra-sensitive instrument is housed in a state-of-the-art Hg analytical facility operated by Dr. David Krabbenhoft at the USGS in Middleton, Wisconsin. The instrument is fitted with a continuous flow-injector analyzer system, and an inline gold amalgamation system, that allows for rapid sample throughput and low-level detection. The method, modeled after the pioneering work of Hintelmann, et al. [10, 11], has an absolute detection limit of about 1 pg Hg, or about 0.05 ng L^{-1}. The minimum detectable amount of MeHg is also 1 pg.

Bioassay techniques that were developed in conjunction with the Wisconsin State Laboratory of Hygiene (WSLH) were used to assess the bioavailability of old versus new Hg. The WSLH is part of the University of Wisconsin and operates a state of the art biomonitoring facility. In short, cultures of algae (*Selenastrum Capricornutum*) are exposed to test waters that contain a spike of MeHg. Uptake and partitioning of the added mercury is determined after a set incubation time. In essence the exposure is a competitive ligand experiment and gives a relative assessment of the binding strength of the ligands in the test water.

Modeling efforts were supported by providing data from this project to Reed Harris at Tetra Tech Incorporated. Mr. Harris has been instrumental in designing a world-class interactive model of mercury cycling in lakes (the MCM model). The data will improve the calibration of the model for better predictive capacity, and will allow researchers to pose strategic "what if" questions while designing future research studies. At the present time, Tetra Tech is in legal proceedings over ownership of the model. As a result, the MCM model is not presently available for use.

Ultrafiltration techniques were employed to isolate the colloidal-phase. In short, several liters of water are circulated tangentially across a membrane. Some of the water passes through the membrane and is collected as the "permeate." The remaining water is recirculated until the concentration factor reaches approximately 5. More information on ultrafiltration techniques can be found elsewhere [12].

Resin Techniques

We used Chelex and DEAE resins to determine the portion of weakly-bound Hg(II) in solution. Both techniques offer a standardized method of comparing natural waters against the chelation strength of the resins. Dissolved Hg(II) is retained on Chelex resin, and negatively charged DOC is retained on DEAE.

Iron speciation

We used several techniques to characterize the speciation of iron in natural waters. These include ammonium oxalate extraction (to determine the concentration of amorphous iron) and an optical technique based on phenanthroline chelation (to determine the dissolved phase concentration of Fe(II) and Fe(III)).

Field Campaigns

We completed 12 field campaigns during the course of the project and collected over 1400 individual samples for total and methylmercury analysis. Each campaign usually consisted of four people and three days on site. Table 2 indicates the focus of each field trip. In October 2004 several people joined our field campaign including: geochronology experts Dr. Daniel Engstrom of the Minnesota Science Museum and Drs Edward Swain and Bruce Monson of the Minnesota Pollution Control Agency. These scientists collected and sliced sediment cores from Lake 658 for lead-210 analysis. The results were used to determine the historical sedimentation record of the lake including focusing factors. This information will help us estimate the time-dependant burial of mercury in the sediments of the lake – a critical component of the hypolimnetic mass balance (a major objective of the project).

Table 2: Summary of Field campaigns for the project.

	2003					2004						2005				
	June	July	Aug	Sept	Oct	May	June	July	Aug	Sept	Oct	May	June	July	Aug	Sept
Lake Profiles	1	1	1	1	1	1	1	1	1	1	1				1	
Sediment Traps		2	2	2	1		3	2	2	2	1					1
DOC SUVA/Pigments	1	1	1	1	1	1	1	1	1	1	1				1	
DEAE/Chelex Resin work		1	1		1				1		1					
Sediment Collection	1				1		1				1					
Mixed-Core Experiments	← Incubation →										1					
Bioavailability Work								1							1	

This table indicates the total number of sampling trips in a given month to collect samples from each row/category.

Results and Discussion

Results by our research team indicate that newly deposited Hg is very reactive in each compartment, but the time scale of transport and transformation varies widely. For example, on the short time scale (minutes/hours/days), new Hg is largely bound to particles in each compartment. On the moderate time scale (weeks/months), new Hg is transformed into MeHg (the bioaccumulative form) in the lake and wetland. On the long time scale (years/decades) the effects are difficult to assess given the relatively recent application of the isotopes to the watershed. In the Terrestrial compartment, however, there is some indication of delayed erosion transport of new Hg and/or delayed release of Hg by humic acids (after aging in upland soils). Below we describe the results from each of the key actions funded under this project in more detail.

Action: Mixed-Core Experiments.

Objective: Assess post-depositional processes migration, long-term methylation/demethylation, and estimate net burial rates for Hg in pelagic and littoral sediments.

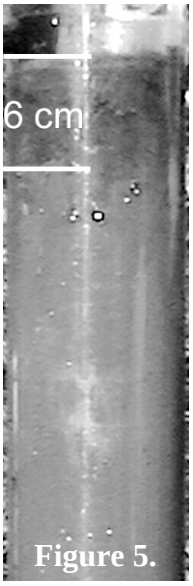


Figure 5.

Methods: Before the first spike was applied to the lake (June 2001), we placed several acrylic barrels at the bottom of the lake that were filled with homogenized sediment and evenly spiked with different isotopes of Hg (^{201}Hg, and Me^{199}Hg). These mixed-cores were incubated in both the pelagic and littoral regions of the lake. The cores were removed from the lake by SCUBA in October 2004 after ~40 months of incubation. Funding from Wisconsin Focus on Energy allowed us to double the incubation time and reduce uncertainty in the results. The sediments were sliced on site and stored frozen for analysis of isotopic Hg, isotopic MeHg, carbon content, water content, and bulk density.

Outcome: Because the original cores were well mixed, any change to the native Hg profile will indicate the mobility of old Hg. Changes to the ^{201}Hg and Me^{199}Hg profiles will either indicate methylation/demethylation or post-depositional migration of recently deposited Hg with depth. Changes in the ^{202}Hg or Me^{202}Hg will indicate near surface recycling of new Hg. Samples are currently under analysis but visual inspection indicates a substantial layer of recently deposited flock (see Figure 5). Measurements of bulk density show a slight increase in density with depth, but are effectively uniform throughout (Figure 6). Like the rest of the lake, most of the sediments are composed of soft organic material. The lack of a strong shift in density between the recent accumulation and the mixed sediment indicates good agreement with typical sediment accumulation in the lake.

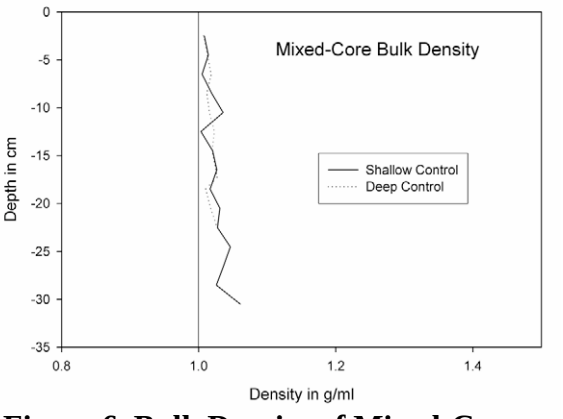


Figure 6. Bulk Density of Mixed-Cores

Action: Lake Profiles & Sediment Trap Deployment.

Objective: Establish the hypolimnetic mass balance for Hg in the lake. Establish the importance of turnover in redistributing recently deposited Hg throughout the lake.

Methods: Water column profiles were collected in both the East and West basins of Lake 658. Typical sampling depths were 2, 5, 7, 9, and 13 m below the water surface. Additional samples were obtained at 5, 10, 20, 40, and 80 cm above the interface to better define important hypolimnetic processes in that region. In addition to Hg samples, we collected ancillary data on temperature, pH, dissolved oxygen, redox potential, conductivity, DOC, suspended particulate matter (SPM), and major ions (primarily Fe and Mn).

Sediment traps were deployed in each basin to collect falling particulate matter. Positioning of the traps was just below the average thermocline (7 m), and just above the sediment water interface (9 m in the east basin, 13 m in the west basin). Differences between upper and lower traps help assess Hg transport, transformation, and dissolution from particles. Traps were deployed during ice-free periods and processed on a bi-weekly basis. Analytes for all samples collected under this action item included total mercury, MeHg and a subset of the following ancillary measurements as appropriate: Major ions, pH, conductivity, temperature, DO, DOC, Redox potential, SPM, LOI, pigments.

Outcome: Native total mercury (HgT) concentrations in the water column were fairly uniform during the 2003 and 2004 field seasons. Concentrations in 2003 ranged from 3 to 9 ng L^{-1} in the filtered phase. Larger concentrations were observed during the summer months in the hypolimnion. The Lake isotope amendment ranged from 0.2 to 1.7 ng L^{-1} in the filtered phase. The Wetland and Upland isotope amendment was rarely detectable, but ranged from 0 to 0.1 ng L^{-1}. At times, the Lake isotope amendment was up to 30% of the native pool in the filtered phase. Filtered phase isotopic Hg remained largely in the epilimnion until the thermocline broke down. During most of the year, transport of isotopic Hg from the epilimnion to the hypolimnion was primarily through particulate matter. The concentration of isotopic Hg on falling particles ranges from 0 to 0.88 ng L^{-1} reaching 141% of the native HgT on particulates (58% of the sum total). Methylated lake isotope reached 180% of the native MeHg concentration on particles (42% of the sum total). These results show that the new Hg is reactive and preferentially binds to particles.

Partitioning of Hg to particles can be expressed as:

$$K_D = 1000 \times \frac{[Hg]_p}{[Hg]_f} \quad \text{(units: L/Kg)}$$

Where K_D is the partition coefficient; $[Hg]_p$ is the concentration of mercury on particles (in ng/g); and $[Hg]_f$ is the concentration of mercury in the filtered phase (in ng/L). As the amount of mercury associated with the particulate phase increases (with respect to the filtered phase) the value for K_D also increases.

The correlation between native and lake-spike partitioning to particles is shown in Figure 7. Any deviation from a 1:1 correlation indicates that the native and lake-spike pools of HgT are

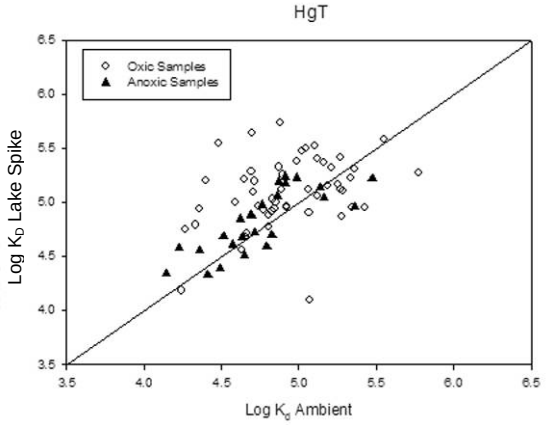


Figure 7. *Correlation between native and lake-spike partitioning coefficients for HgT in Lake 658.*

behaving differently in L658. The observed shift toward larger partition coefficients for the lake-spike may result from several processes. First, most of the shift occurs in the oxic waters of the epilimnion (open symbols in Figure 7) and may reflect the introduction method. Recall that the isotope is introduced by boat into the top meter of the lake at a rate 5x the annual wet deposition. The partition coefficient is an equilibrium-based concept and the shift may reflect a short-term kinetics-based phenomenon. If so, the shift will likely diminish as the isotope is incorporated into the system after the isotope additions end. This hypothesis is backed by the near 1:1 correlation for hypolimnetic samples which presumably reflects Hg that has been recycled through the ecosystem.

Another hypothesis for the shift is that epilimnetic particles have a different chemical character than hypolimnetic particles. Epilimnetic particles presumably have a larger percentage of living biotic material than those in the hypolimnion. We hypothesize that strong metal-binding ligands are associated with this biotic material. As the biotic particles die and decompose, mercury associated with material is released to the dissolved phase. The near 1:1 correlation in the hypolimnion suggests that the metal-binding ligands associated with the remaining recalcitrant material are relatively weak. As oxygen is depleted in the hypolimnion, lake-spike and native mercury behave similarly with respect to particle partitioning.

The monthly sedimentation flux for mercury in 2003 is presented in Figure 8. Also plotted is the filtered-phase concentration of mercury at the depth of deployment for each set of sediment traps. In general, filtered-phase concentrations are relatively constant at a given depth, varying by only 1-2 ng/L across the field season. This is especially true for the oxic waters in the epilimnion (closed symbols in figure 8). In the suboxic waters of the hypolimnion, there is a general trend toward higher concentrations with time – especially for the lake-spike (open symbols in figure 8). This trend likely reflects the schedule of lake-spike additions that run on 2-week intervals from June through October. As explained further below, however, fall overturn plays an important role in the cycling of mercury in L658 (note the late-October increase in lake-spike HgT concentration on panel C of figure 8).

The flux of particulate mercury to the deep sediment traps is generally larger than that to the shallow traps; this observation is especially true for MeHg (panels B & D in Figure 8). In addition, lake-spike MeHg flux approaches the magnitude of the native MeHg flux throughout most of the year. This observation indicates that the lake-spike is readily available for methylation in the system and may provide anecdotal evidence that all MeHg in the ecosystem is new (or at least behaves as though it is constantly refreshed or recycled).

Calculations of the residence time of Hg in the lake and its long-term fate (i.e. relative proportion buried, bioaccumulated, or evaded) are forthcoming in manuscripts for peer-reviewed journals.

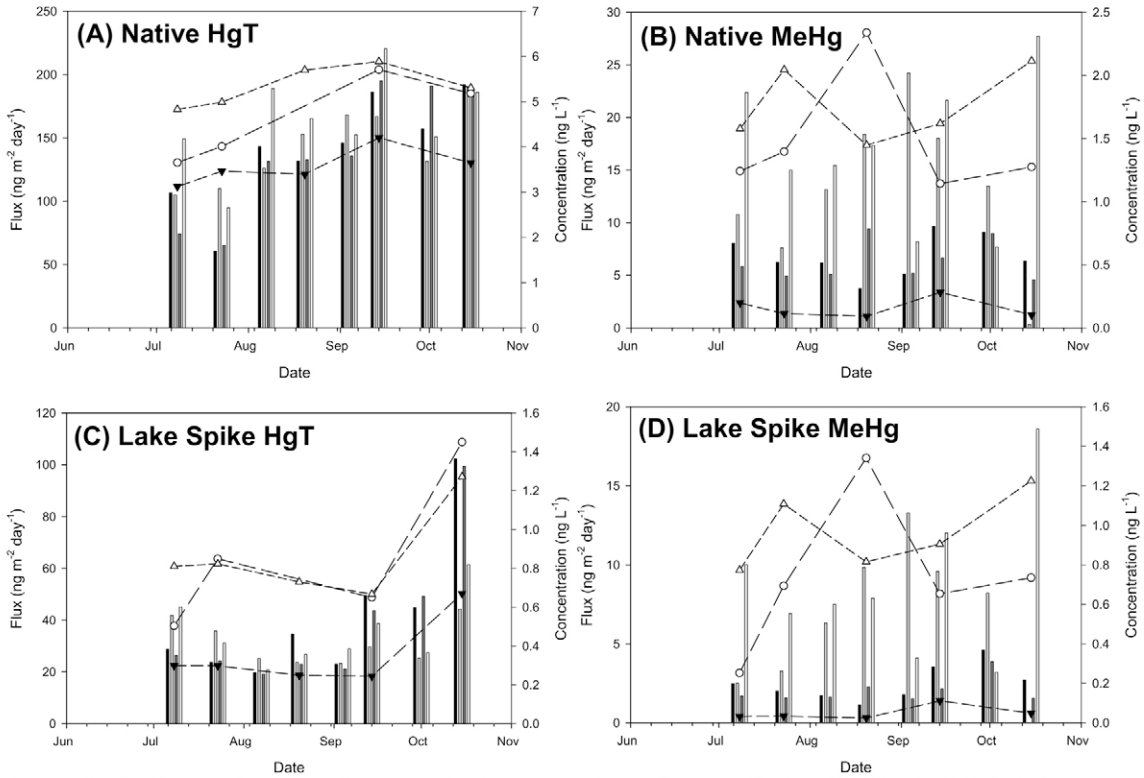


Figure 8. Sedimentation flux of mercury in the east and west basins of Lake 658 for the 2003 field season. Bar groupings are as follows (from left to right): East 7m, East 9m, West 7m, West 13 m. Lines represent the concentration of mercury in the filtered phase (0.45 µm) at the depth of trap deployment. Open circles represent the East Basin 9m traps. Open triangles are the West basin 13 m traps. Closed triangles represent the West basin 7 m traps (in 2003, the East basin 7 m traps were not deployed). **(A)** Ambient HgT; **(B)** Ambient MeHg; **(C)** Lake spike HgT; and **(D)** Lake spike MeHg.

Action: Resin, Pigment, Optical, and Size-fractionation of DOC

Objective: Establish the importance of DOC character on Hg transport and transformation.

Methods: Our lab has been developing methods to better characterize the role of DOC and Fe/Mn redox cycle on cycling of Hg in Lake 658. DOC has long been indicated as a transport vector for Hg in freshwaters [13-15]. The better we can describe the chemical character of DOC, the better we can establish the underlying ligands and mechanisms that control the fate of Hg in freshwater systems. We used Chelex and DEAE resins to assess the binding of mercury to DOC. We also made Specific Ultraviolet Absorption (SUVA) measurements to characterize the relative aromaticity of DOC (an indication of terrestrial vs. in-lake production). Pigment samples also help establish terrestrial versus in-lake carbon sources by identifying and quantifying degradation products. Ultrafiltration was used to isolate the importance of colloidal material in the partitioning and transport of mercury.

Outcome: The results from these experiments suggest a dynamic cycle of mercury transport and transformation in the hypolimnion. Key factors in this cycle include the mineralization of aliphatic particulate matter that settles from the epilimnion, the coupling with the oxidation/reduction cycle of iron, and the association of mercury with colloidal phase organic carbon.

A typical summer profile of DOC is presented in Figure 9. The concentration of DOC increases with depth and the highest concentrations were observed just above the sediment-water interface. This enrichment has been hypothesized to result from mineralization of recently-fallen planktonic particles and the release of DOM associated with iron oxides particles as they dissolve under reducing conditions in the hypolimnion [16] (See reprint in the appendix).

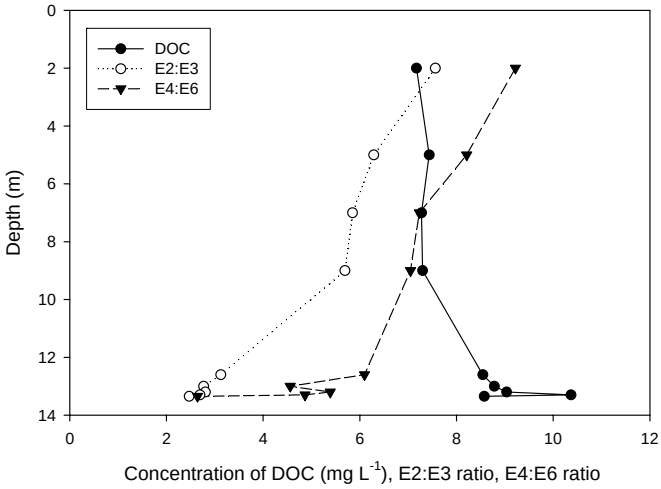


Figure 9. The concentration of DOC, the E2:E3 ratio, and the E4:E6 ratio in the west basin of Lake 658 (18 August 2003). As the concentration of DOC increases with depth, the character of the DOC appears more terrestrial in nature.

This hypothesis is supported by supplemental information from optical characterization of DOC and analysis of pigments. Our primary optical method was specific UV absorbance (SUVA). Defined as the UV absorbance of a water sample (at a given wavelength) normalized for DOC concentration, it is a useful parameter for estimating the dissolved aromatic carbon content in aquatic systems [17-19]. This is particularly true at 254 nm where SUVA is strongly correlated with percent aromaticity. SUVA can be a semi-quantitative measure of chemical character by expressing the term as a ratio of absorbance at two paired wavelengths.

For example, the E2:E3 ratio is defined as the UV absorbance at 254 nm divided by the UV absorbance at 365 nm. A low value for the E2:E3 ratio is indicative of highly-condensed terrestrial (i.e. allochthonous) carbon while a high ratio is indicative of more aliphatic planktonic (i.e. autochthonous) carbon. The E4:E6 ratio is defined as the UV absorbance at 465 nm divided by the UV absorbance at 665 nm. The E4:E6 ratios for humic acids are usually less than 5.0 while ratios for fulvic acids range from 6.0 to 8.5 [20].

On August 18, 2003, both the E2:E3 and the E4:E6 ratios decreased with depth in Lake 658 (Figure 10). This observation suggests that the molecular weight and aromaticity of DOC increases with depth (a phenomenon described as condensation by Chin *et al.* [17] and Peuravuori *et.al.* [18]). Both the E2:E3 and E4:E6 ratios support the hypothesis that deep hypolimnetic carbon is more terrestrial in nature. However, these results must be viewed in context of additional information. For example, the concentration of iron also increased with depth in the hypolimnion. Both Fe(II) and Fe(III) absorb UV light, and research has shown that

Fe can lead to artificially high values for SUVA at 254 nm [19]. In addition, our pigment data suggests that autochthonous carbon is important in the hypolimnion. The highest concentrations of chlorophyll-a, pheophytin-a, and pheophorbide-a (indicators of carbon produced in-lake) were collected from depths just above the sediment-water interface.

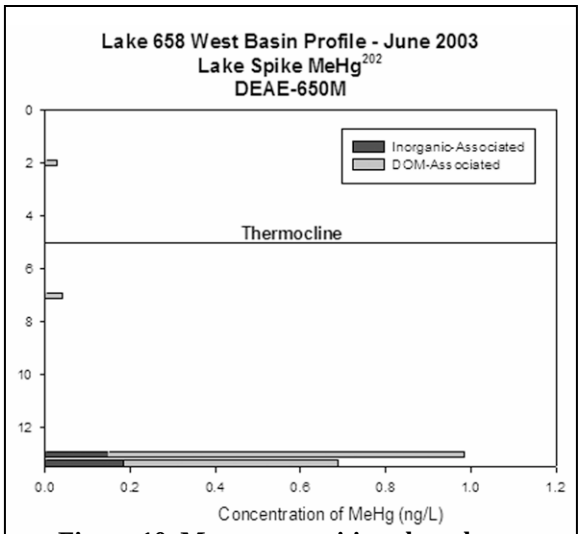


Figure 10. Mercury partitions largely to the organic fraction

In this milieu of organic and inorganic particles, mercury is primarily associated with the organic phase (Figure 10). The association is pronounced in the oxic epilimnion where aliphatic particles are generated and inorganic iron hydroxides are in very low concentration. The importance of these inorganic particles grows in the anoxic hypolimnion where they deliver mercury to the lake bottom. Together these observations suggest that the sediment-water interface is an important site for particle transformation and that mercury will be recycled in the hypolimnion before eventual burial.

Action: Bioavailability Work.

Objective: Determine the availability of the spiked Hg to algae over time.

Methods: Bioassays were conducted in cooperation with the WI State Laboratory of Hygiene Biomonitoring Group using the technique developed by Gorski and Shafer. Dr. Patrick Gorski, Dr Helen Manolopoulos, and Rebecca Moore performed the bioassays on waters from several compartments in Lake 658. These included ELA rain water and water-column samples from the epilimnion and hypolimnion. The bioassay on rain water was conducted under three conditions: full strength rain, 50:50 mixture of rain water and Lake Michigan water, and full strength Lake Michigan water. The idea was to test the change in bioavailability as rain is mixed with receiving waters. Additional water from an ELA stream was collected and ultrafiltered to determine bioavailability from terrestrial waters (a large portion of the overall mercury mass-balance budget)

Outcome: Initial results on the water column samples from 2002 were discarded because the spike levels were too low for the technique to work. Samples were collected again in 2005 and the bioavailability tests are currently in progress. The results will help determine the strength of competitive ligands in ELA lake waters and stream waters. The bioassay on ELA rainwater from 2004 suggests that the receiving water and the 50:50 mixture of rain and receiving water have similar uptake by the algae.

Value and Transferability of the Results

Results from METAALICUS are valuable because the project is unique and the information obtained is readily transferable to other ecosystems. The project will not likely be repeated due to the cost ($670,000 USD per year for stable isotopes alone) and the necessary permitting (achieved at ELA). This internationally renowned project brings together top experts in the environmental field and builds upon Wisconsin's proactive approach to better understand complex environmental issues. The use of mercury stable isotopes is a powerful tool that enhances the quality of information obtained by the project. Isotopic techniques allowed us to probe process-level questions and apply the results to other ecosystems. Understanding the factors controlling transport and transformations of mercury is key to predicting the long-term effects of management decisions regarding Hg emissions.

Among the key findings of this study is the unique behavior of "new" versus "old" mercury. For example, partitioning data suggests that "new" Hg in the epilimnion is more particle reactive than old mercury. Particle transport may then preferentially deliver new mercury to sites of methylation – as supported by the rapid conversion of the inorganic spike to the methylated form within 2-weeks of the initial introduction. As the mercury "ages" the partitioning behavior becomes indistinguishable from the historic pool. These results suggest a rapid response to decreases in atmospheric loading of mercury directly to the lake surface.

Outreach Efforts

Information obtained from this project has been disseminated through several outreach efforts. These include collaboration with outside scientists, participation and presentations at scientific conferences and workshops, publication of peer-reviewed manuscripts, and reports to funding agencies and stakeholders.

Collaboration: In addition to collaboration with scientists associated with the METAALICUS project, we invited several specialists to join us during our field campaigns or perform cooperative work. This expanded the impact of the project and strengthened the interpretation of the results.

Notable collaboration within the METAALICUS project included close cooperation with the USGS isotope laboratory operated by Dr. David Krabbenhoft (Middleton, WI) and coordinated field campaigns with Cindy Gilmour of the Academy of Natural Sciences in Maryland (presently with the Smithsonian Institution). Dr. David Krabbenhoft graciously offered in-kind support for this project by providing access to specialized analytical equipment for isotope analysis. We have also worked with his research team to accomplish many field tasks that benefited both research groups. Dr. Gilmour was responsible for collecting littoral zone sediment cores that complement those we collected from the hypolimnetic zone. Together we have mapped the deposition of mercury to the sediments across the entire lake.

In February 2004 our research group organized a meeting to discuss the in-lake results. The meeting brought together the principle investigators on the project from at least five institutions to synthesize the data to date. The primary goal was to prepare a mass balance budget for the lake and discuss manuscripts in advance of the annual METAALICUS project meeting.

Notable collaboration outside of the METAALICUS project included Nives Ogrinc of the J. Stefan Institute in Ljubljana, Slovenia, and Dr. Daniel Engstrom of the Minnesota Science Museum. Dr. Ogrinc is an expert in carbon cycling and identifying the origin (i.e. terrestrial vs. in-lake production). In June 2004, we prepared and delivered subsamples from our archived sediment trap material to Dr. Ogrinc. Her analysis will help us interpret the recycling and remineralization of carbon at the sediment-water interface.

Dr. Daniel Engstrom was brought on board to determine the historical sedimentation record of Lake 658 and estimate the time-dependant burial of mercury – a critical component of the hypolimnetic mass balance (and a major objective of this project). On December 15th 2005, we held an all-day meeting with Dr. Engstrom at the St Croix Watershed Research Station in Marine on St. Croix, MN. During that meeting we combined and reviewed our data sets on Hg and Pb-210 in sediments of L658. The outcome of the meeting was a framework for describing sedimentation processes and a plan of action for synthesizing the data into manuscript on net accumulation of Hg in L658 sediments.

Workshops:
Dr. James Hurley served on the Steering Committee for the Seventh International Conference on Mercury as a Global Pollutant (June 30 to July3, 2004). He made trips to Ljubljana, Slovenia in 2003 and 2004 to plan the conference. He was instrumental in developing the program and to a lead on providing opportunities for students.

In November 2004, Dr. James Hurley served on the Science Advisory Council of the Collaborative Mercury Research Network (COMERN) in Gimli, Manitoba. The goal of COMERN is to integrate research toward a better understanding of processes ruling mercury exchange and accumulation in wide-scale ecosystems in the northern part of the American continent. The meeting provided an opportunity for multidisciplinary discussion and integration of METAALICUS results.

On March 3, 2005, Dr. Christopher Babiarz participated in a one-day workshop comparing results from the METAALICUS project with those of the ACME project (Aquatic Cycling of Mercury in the Everglades).

Since October 2001, Dr James Hurley, Dr. David Krabbenhoft, and Dr. Christopher Babiarz have served on the Conference Organizing Committee for the Eighth International Conference on Mercury as a Global Pollutant (August 6-11, 2006, Madison, Wisconsin, USA). Dr. Hurley Co-Chairs the conference with Dr. David Krabbenhoft, and Dr Babiarz serves as conference secretariat. The fourth member of the Conference Organizing Committee serves as the technical chair (Dr. James Wiener of the University of Wisconsin – La Crosse). The Conference Organizing Committee has set three principal goals for the conference: to enhance the synthesis of information; to enhance the integration of science and policy concerning environmental

mercury pollution; and to increase participation by under-represented groups, including graduate students, beginning professionals, and representatives of developing nations. The conference received nearly 1100 abstracts (a new record for the conference series), and significant progress has been achieved toward each goal. For more information, visit www.mercury2006.org

Presentations:
Graduate student Shawn Chadwick presented a paper entitled: "Speciation controls on the fate and transport of mercury and methylmercury across biogeochemical gradients" at the American Water Resources Association (AWRA) meeting in Wisconsin Rapids (March 4-5, 2004). This meeting brings together environmental scientists and managers in Wisconsin to discuss current research affecting state water resources.

Our research group presented two posters on the METAALICUS project at the 7th International Conference on Mercury as a Global Pollutant in Ljubljana, Slovenia, June 27- July 2, 2004. This conference is the preeminent international forum for dissemination of scientific advances on mercury. Four hundred and fifty scientists from 47 countries attended the 5-day conference. Our contributions focused on the transformation and fate of mercury in the hypolimnion of Lake 658. Christopher Babiarz presented early results from our overall scientific approach in a poster entitled: "Towards a Hypolimnetic mass balance: Early results from the METAALICUS project." Shawn Chadwick presented the partitioning behavior of mercury at the oxidation/reduction boundary in a poster entitled: "Speciation controls on the fate and transport of mercury and methylmercury across biogeochemical gradients"

Shawn Chadwick gave a presentation entitled "Kinetic studies of mercury (II) speciation with dissolved organic matter" at the 27th Midwest Environmental Chemistry Workshop (October 15-17, 2004 in Madison WI). The MWECW has become the preeminent venue for Midwestern graduate students in environmental science to discuss their research among colleagues.

Dr. Christopher Babiarz gave an invited presentation on METAALICUS results at the Fall Meeting of the American Geophysical Union (December 14-17, 2004 in San Francisco, CA). The presentation was entitled "Transport and transformation of mercury through soils from contrasting watersheds: Implications for resource management." The presentation was the only talk on mercury in a session about Soil Retention of Atmospheric Solutes. The session also included presentations on sulfate, nitrate, and aluminum that allowed cross-disciplinary discussion.

Publications and reports: In addition to quarterly progress reports to the Environmental Research Program of Wisconsin Focus on Energy, we have also prepared manuscripts for peer-reviewed publication. One manuscript written by Shawn Chadwick et al. was recently published in Science of the Total Environment. The paper is reproduced in the Appendix and is entitled "Influences of iron, manganese and dissolved organic carbon on the hypolimnetic cycling of amended mercury."

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Providing Communities with the Groundwater Information Needed for Comprehensive Planning

Basic Information

Title:	Providing Communities with the Groundwater Information Needed for Comprehensive Planning
Project Number:	2005WI151O
Start Date:	7/1/2003
End Date:	6/30/2005
Funding Source:	Other
Congressional District:	1st
Research Category:	Ground-water Flow and Transport
Focus Category:	Hydrology, Conservation, Water Use
Descriptors:	comprehensive planning, water supply
Principal Investigators:	Douglas S. Cherkauer

Publication

1. D. Alessi and d. Cherkauer. 2005. Providing Communities with the Ground Water Information Needed for Comprehensive Planning.Wisconsin Water Resources Association Meeting March, 2005 (Best student paper).
2. Cherkauer, D.S., and S.A. Ansari. 2005. Estimating groundwater recharge from topography, hydrogeology and land cover. Ground Water 43(1).

Project Summary

Title: Providing Communities with the Ground Water Information Needed for Comprehensive Planning

Project ID: WR03R0007

Investigators:

PI: Douglas S. Cherkauer, Professor, Department of Geosciences, University of Wisconsin-Milwaukee

PAs: Daniel Alessi, Alison Coulson, both formerly of University of Wisconsin-Milwaukee

Period of Contract: July 1, 2003 to June 30, 2005

Background/Need: Communities which rely on ground water as their sole source of water need to factor the magnitude and limits of their resource and ways to protect it into their development plans. Most of these communities do not, partly because they don't understand their ground water supply and don't know what information they need or where to obtain it.

Wisconsin now requires that communities adopt a comprehensive plan. The rules make passing reference to water resources and ground water supply, but typically the plans only include very cursory reference to them. Land use plans are primarily driven by economics and transportation; rarely does water supply influence the end result.

Objective: The primary purpose of this study was to assess the water resources of a ground water using community and then to work with that community so that it could design a comprehensive land use plan that protects its water supply. An outcome from the process is development of the procedure needed to get the right ground-water information to the community.

Methods: The study was structured as a complete analysis of the quantity of the ground water resource in the study area. During the project, information was shared with Town officials in order for them to incorporate it into their planning and administrative processes. Once the state-funded project was completed, an assessment was made to determine which information was most relevant and usable from the community's perspective.

Richfield was openly receptive to the idea of the study and willing to consider incorporation of the information into their comprehensive land use plan. That planning process began shortly after the ground water project started. The Town instituted a 12 month moratorium on new developments to coincide with its planning process and, coincidentally, the first half of this project's study period.

This study determined the underlying hydrogeology and the main sources and sinks of ground water within the Town. It developed a full ground-water budget using a calibrated, steady state flow model. The PI then worked with the community to provide them the information, to interpret it for them, to aid in its incorporation into their planning, and to establish a mechanism to protect their resource into the future.

Results: Richfield's ground water is primarily recharged by rainfall and snowmelt within the Town. It discharges mainly to the Town's surface waters and surrounding communities. As a consequence, Richfield is in control of its own water supply and the impacts that human actions will have on its lakes, streams and wetlands.

Town leaders decided that they wanted to protect its supply and surface waters. With input from this project, they decided to do so by:

1. developing a land use plan which protects sensitive ground-water area (both sources and baselevels),
2. limiting population density so that the combined human and environmental demand for water would never exceed the lowest expected recharge inputs, and
3. adopting an ordinance that requires determination of both the water demand and anticipated drawdowns resulting from new developments beforehand and then rejects projects which do not meet prescribed, acceptable drawdowns.

Population density is limited within the community's land use zoning by requiring a relatively large individual lot size for residences and that new developments cluster structures in such a way that a minimum of 30% of the total development remains as green space. Water intensive commercial or industrial development is discouraged. A development which fails to meet drawdown limits (< 1 foot at any property boundary and < 0.5 feet at any perennial surface waterway) must be redesigned to augment natural recharge or reduce water demand before it will be accepted.

Communication with townspeople and their leaders is key to getting them to understand their water system and how best to manage it. In this project, we used articles in the town newsletter, presentations before the general public and at official town meetings and annual reports to get our concepts out. Discussions with the volunteer well owners was also a major factor, because they spread information among their neighbors. The project's final report is attached in Appendix II and is designed to provide information in simple verbiage and US measures. It is also posted on the Town's website.

Implications and Recommendations: The most important information needed by a ground-water community is a good understanding of the geology, sources, sinks and water balance of their aquifer system. Presentation and interpretation of this basic information helped residents and their leaders understand where their water comes from. Interaction with the users at all levels was also crucial in developing the awareness that led this community to create a long term plan and supporting laws to sustain their water supply for most, is not all, future conditions.

Our experience was that the ground water model was probably not necessary in the process and tended to be misunderstood by the public – as having greater predictive resolution than is actually possible.
The next step in this process will be to convince other communities to repeat this study.

Related Publications: D. Alessi won best student poster presentation at Wisconsin Water Resources Assoc. March, 2005

Key Words: Ground Water Resources, Community Planning, Water Budget, Recharge

Funding: University of Wisconsin System

Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation

Basic Information

Title:	Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation
Project Number:	2005WI152B
Start Date:	7/1/2003
End Date:	6/30/2005
Funding Source:	104B
Congressional District:	1st
Research Category:	Engineering
Focus Category:	Geochemical Processes, Solute Transport, Toxic Substances
Descriptors:	groundwater, remediation
Principal Investigators:	Zhaohui Li

Publication

1. Li, Z. (2004). Surfactant-Enhanced Oxidation of Trichloroethylene by Permanganate Proof of Concept, Chemosphere 54, 419-423.

Project Summary

Title: Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation

Project ID: WR03R009

Investigators: Dr. Zhaohui Li, Associate Professor of Geology, Department of Geosciences, University of Wisconsin – Parkside

Period of Contract: 07/01/2003 – 06/30/2005

Background/Need: At some heavy industrial sites and DOE nuclear weapon manufacture and test sites, free phase chlorinated solvents in soils and aquifers impose potential threat to groundwater. Pump-and-treat, a common practice to remove subsurface contaminants proved inefficient to remove these solvents, due to their lower water solubility and higher density. Although the contaminant extraction efficiency increased dramatically in the presence of surfactant, the extracted water will need further onsite decontamination. Oxidation of chlorinated solvent by permanganate is an emerging technology. However, the reaction occurs only in dissolved phase. Thus, a test for combination of surfactant solubilization with permanganate oxidation was proposed.

Objectives: The central goal of this research is to test the feasibility of using surfactant to significantly increase the solubility of chlorinated solvents while using permanganate to degrade solubilized chlorinated solvents. The objectives are to investigate the effects of types of surfactants, concentration of surfactants and of permanganate on oxidation of different types of chlorinated solvents.

Methods: The tests were conducted in batch, column as well as 3-dimensional tank scales. Batch tests were focused on effects of types of surfactants, concentrations of surfactants and permanganate on reduction kinetics of chlorinated solvents. The best surfactant with an optimal concentration was tested in one-dimensional column studies to investigate the efficiency of present surfactant on TCE reduction by permanganate at different volumes of free phase TCE. Finally, a 3-dimensional tank test was performed to verify the column test results. Aqueous concentrations of chlorinated contaminants, permanganate, and product chloride were monitored with time to determine the reaction rate and rate constants as well as the TCE removal efficiency.

Results and Discussion: Batch results showed that chloride production, an indication of TCE degradation, followed a pseudo-first-order reaction kinetics with respect to $KMnO_4$ in the presence of free phase TCE. A higher chloride production rate was seen when anionic surfactant, particularly sodium dodecyl sulfate (SDS), was present. When the surfactant concentration was less then its critical micelle concentration (CMC), the TCE reduction rate constant k_{obs} increased by a factor of three while the TCE half-life $t_{1/2}$ decreased by three folds. With the surfactant concentration greater than the CMC, further increase in k_{obs} and decrease in $t_{1/2}$ was seen. The reaction rates also increased when ninate 411 and Calfax, both anionic surfactants, were present in the system at concentrations of 0.1, 0.3 and 1.0%. Contrast to the much greater enhancement for TCE oxidation, no significant increase in PCE oxidation by $KMnO_4$ in the presence of SDS was found.

Column experiments on fine beach sand lasted for only 6 hours. A higher effluent chloride (about 20%) and TCE (about 100%) concentration was found from the columns eluted with 1% SDS, indicating enhanced solubilization and oxidation of

TCE. However, hydraulic conductivity of the sand decreased significantly caused by precipitates of MnO_2, making it essentially impermeable after 6 hours. Column experiments on well sorted coarse Ottawa sand showed increase in effluent TCE concentration during earlier stage of flushing. TCE concentration decreased much faster in the presence of SDS. For example, after 1 mL of TCE was placed in the columns, the effluent TCE concentration for the columns fed with SDS and permanganate was below 5 mg/L after 1740 to 1870 minutes. While for columns fed with permanganate only, it took 2200 and 4400 minutes before the effluent concentration reached 5 mg/L or below. For the columns fed with SDS and permanganate, The highest effluent TCE concentration was about 1700 mg/L when SDS was present contrast to less than 300 mg/L when SDS was absent, indicating enhanced solubilization. In addition, MnO_4 breakthrough occurred after 21-25 hour injection when SDS was present. Without SDS, MnO_4 breakthrough occurred 45-70 hours later. The earlier MnO_4 breakthrough indicates exhaustion of dissolved TCE during the flushing stage. Chloride analysis revealed a slightly high chloride concentration in the earlier stage of the column experiment and chloride concentration decreased quickly once permanganate is seen in the effluent. Mass balance of TCE eluted plus chloride generated showed that only 25-50 % of the input TCE was either eluted or degraded, the rest may be entrapped within the sand, possibly due to the formation of MnO_2 zone, or being transformed into other intermediates which were not monitored.

The 3-dimensional tank test further confirmed the results from column study, i.e. with the presence of surfactant SDS a higher amount of TCE was removed within given time. Furthermore, visualization showed that a MnO_2 precipitation front was formed much quickly when 1% SDS was present.

Conclusions/ Implications/ Recommendations:

The research shows that anionic surfactants, such as SDS, are able to increase the chloride production in batch test. In column tests, the removal of TCE in the presence of SDS is faster, particularly when the volume of free phase TCE was large. Although no clogging was found when course Ottawa sand was used in the column study, the decrease in hydraulic conductivity when fine beach sand was used imposes a limitation to the method.

Related Publications:

Li, Z. (2004). Surfactant-Enhanced Oxidation of Trichloroethylene by Permanganate – Proof of Concept, *Chemosphere* **54**, 419-423.

Key Words: Permanganate, Perchloroethylene, Trichloroethylene, Surfactant.

Funding: Funding was provided by the State of Wisconsin Groundwater Research Program through the University of Wisconsin Water Resources Institute.

A Combined Hydrogeologic/Geochemical Investigation of Groundwater Conditions in Waukesha County, Wisconsin

Basic Information

Title:	A Combined Hydrogeologic/Geochemical Investigation of Groundwater Conditions in Waukesha County, Wisconsin
Project Number:	2005WI153O
Start Date:	6/29/2003
End Date:	7/1/2005
Funding Source:	Other
Congressional District:	1st
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Use, Water Supply, Water Quantity
Descriptors:	water use; water supply
Principal Investigators:	Tim Grundl

Publication

Validation of transport of VOCs from Composite Liners

Basic Information

Title:	Validation of transport of VOCs from Composite Liners
Project Number:	2005WI154O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Engineering
Focus Category:	Solute Transport, Geochemical Processes, None
Descriptors:	remediation; groundwater treatment
Principal Investigators:	Tuncer B. Edil, Craig H Benson

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: Jim Hurley
Submitted: 7/11/2006

Project Title

WR05R008: Validation of Transport of VOCs from Composite Liners

Project Investigators

Craig Benson, University of Wisconsin-Madison

Christopher Carlsen, Wisconsin Department of Natural Resources

Tuncer Edil, University of Wisconsin-Madison

Progress Statement

Tasks Completed

Target Compound Selection
Five volatile organic compounds (VOCs) were selected among frequently detected VOCs in Wisconsin Landfills, considering classes, melting points, boiling points, gas chromatographic retention times and contrasts of density, solubility, molecular diameter, and aqueous diffusion coefficient. Selected VOCs are Methylenechloride, Trichloroethylene, Chlorobenzene, Toluene, and Methyl Tertiary Butyl Ether.

VOC Analytical Method Development
Gas chromatograph (GC) will be used with sample direct extraction/injection method for VOC analysis. When conducting diffusion tests with columns and tanks, the amount of sample extraction is critical and should be minimized not to affect the diffusion. The detection method also should be simple minimizing loses of VOCs. After careful evaluation, sample direct extraction/injection method was selected over SPME (Solid Phase Micro-Extraction) method because of the simplicity and the leakage of SPME sampler during sampling. The effect of sample extraction was evaluated using HYDRUS-2D transport code, and the results have shown that the concentration differences were less than 1 % except at the bottom (2.9 %) for 5 µl of pore fluid extraction per sampling port a week for a year. Therefore, extracting less than 5 µl every 2 weeks is adopted and considered not to seriously affect the VOC diffusive transport.

Selection and Characterization of Liner Soil
Kamm clay, which is used in Dane county sanitary landfill, will be used for the compacted clay layer material in the experiments. It has been obtained and characterized.

Column and Tank Design
Test columns and tanks have been designed to detect the VOC concentrations using sampling ports in the clay layer to monitor the VOC breakthrough. Tanks are large-scale. Selection of parts that are non-reactive with the VOCs is in progress. The columns and tanks are being assembled.
Batch Test
Batch tests are in progress with five VOCs and the selected liner soil, and the method is being adjusted to minimize the error.

Batch test are conducted in different concentrations with multi-solutes and single-solutes adjusting the soil-solution ratio. Partition characteristics of the selected VOCs will be assessed through batch isotherms.

Applications, Impacts & Benefits

A two-stage study is proposed. The first stage consists of large-scale laboratory experiments to verify existing transport models for composite liners. Causes and mechanisms of VOC transport through composite liners will be assessed, and the models will be adapted if necessary. In the second stage, the verified transport model for composite liners will be coupled with a two-dimensional flow and contaminant transport model (HYDRUS-2D). The coupled models will be used to assess long-term impacts of VOCs on groundwater for typical site conditions and existing lining technologies. Changes to landfill design practices may also be suggested based on the findings of this assessment.

Committees, Memberships & Panels

Group Name	5th International Conference on Environmental Geotechnics June25-30, 2006 Cardiff, New Wales, UK
Description	Invited to serve on a panel. Discussion of the VOCs escape from landfills received wide-spread attention during conference discussion sessions.
Start Date	6/25/2006
End Date	6/30/2006

Arsenic Species (III,V) Distribution in Wisconsin Groundwaters: Field Measurements and Prediction Using Multivariate Analysis of Geochemical Data Prediction Using Multivariate Analysis of Geochemical Data

Basic Information

Title:	Arsenic Species (III,V) Distribution in Wisconsin Groundwaters: Field Measurements and Prediction Using Multivariate Analysis of Geochemical Data Prediction Using Multivariate Analysis of Geochemical Data
Project Number:	2005WI155O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Groundwater, Geochemical Processes, Water Quality
Descriptors:	arsenic speciation; analytical chemistry
Principal Investigators:	Martin Shafer, James Schauer

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: Martin Shafer
Submitted: 7/7/2006

Project Title

WR05R001: Arsenic Species (III,V) Distribution in Wisconsin Groundwaters: Field Measurements and Prediction Using Multivariate Analysis of Geochemical Data Prediction Using Multivariate Analysis of Geochemical Data

Project Investigators

Kristie Ellickson, University of Wisconsin-Madison
James Schauer, University of Wisconsin-Madison
Martin Shafer, University of Wisconsin-Madison

Progress Statement

The primary objectives of this two year study are to:

1. Perform a meta-analysis on existing groundwater data for co-variation of geochemical analytes and test their association with total arsenic concentrations using multivariate methods. (Years 1 and 2).
2. To identify the most likely inorganic arsenic species (oxidation states III or V) for each identified principal component of the existing data based on known geochemical mechanisms for arsenic release. (Year 2).
3. To directly measure arsenic speciation and important geochemical parameters in 50 of the previously analyzed sites to test the predictions developed in objectives 1 and 2. These new data will be analyzed by factor analysis and arsenite and arsenate concentrations compared to previous predictions. (Year 2).

In year one, we have nearly completed objective 1, and have assembled all the sampling and analytical tools to complete objective 3. Field work for objective 3 will begin in late July or early August of 2006. A brief summary of our accomplishments follows.

Basic geochemical and arsenic data from the following systems/studies has been assembled into a large Access database. This effort likely represents the largest of its type to date.

1. Oakland County Michigan. 37 samples. [Ground-Water Quality Atlas of Oakland County, MI. Water-Resources Investigation Report 00-4120]
2. Mahomet Aquifer Illinois; Champaign and Tazwell counties. 144 samples. [Illinois Department of Natural Resources, WMRC Report RR-107, May 2004].
3. Idaho – Washington County. 75 samples. [Ground water Quality Technical Report No. 6. Idaho Division of Environmental Quality, September 1995].
4. Minnesota Pollution Control Authority. 954 samples.
5. New Jersey. 170 samples. [Ambient Ground Water Quality in the Newark Basin, New Jersey. By M.S. Serfes, Digital compilation by G.C. Herman and M.S. Serfes, N.J. Geol. Survey Digital Geodata Series DGS96-3].

6. Ohio. 72 samples. [WDR-OH-AR-02.2. 2003 USGS Water Data Report OH-3-2].
7. Ohio. 21 samples. [Miami, OH].
8. New England Coastal Basin. 804 samples. [USGS Water Resources Investigations Report 99-4162]. 1999.
9. Wisconsin. 2648 samples. [Department of Natural Resources, Municipal and Private Wells].
10. Ontario, Canada. 430 samples.

We have over 5355 sample records in the database as of June 2006. The geology covers several aquifers across the Midwest, with a range of deposit types as well (Precambrian, Cambrian, Ordovician, Cretaceous, Devonian, and mixed Quaternary).

In addition to the arsenic data (speciated in a few studies), we have incorporated the following supporting geochemical data from each sample (Note: the degree of comprehensiveness of the geochemical data varies among the studies).

1. Well depth
2. Temperature
3. pH
4. Specific Conductance
5. Dissolved Oxygen
6. Dissolved Solids
7. Hardness/Alkalinity
8. Carbonate/Bicarbonate
9. Sulfate
10. Phosphate
11. Chloride
12. Bromide
13. Fluoride
14. Calcium
15. Magnesium
16. Potassium
17. Silica
18. Nitrogen Species (ammonia, nitrate, nitrite)
19. Dissolved Organic Carbon
20. Trace metals [Al, Sb, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Sr, U, V, Zn.

Factor analysis is in progress and is expected to be complete by mid-late July. The unbalanced and imperfect nature of the various datasets has complicated application of certain statistical approaches, so we have in specific cases segregated the database to improve data matrix completeness.

We have prepared 75 field sampling kits that will provide a very comprehensive analytical characterization of the chosen wells.

1. Arsenic speciation/separation will be carried out on site using an As(V) specific solid phase sorbent placed in miniature columns.
2. Fe(II) using on-site ferrozine complexation
3. Nitrogen species (nitrate, nitrite, ammonia) by discrete analyzers
4. Silica b discrete analyzer
5. Sulfide using both ISE (in SAOB buffer) and HPLC-Molybdenum blue approaches
6. Chloride, Sulfate by Ion Chromatography
7. Elemental Analysis by High Resolution ICP-MS (30 elements)
8. DOC by high temperature combustion
9. Oxygen isotopes (18O/16O) by isotope ratio mass spectrometry
10. Temperature, pH, Specific Conductance, Redox Potential, Dissolved Oxygen by multiparameter sonde

Applications, Impacts & Benefits

The release mechanism for arsenic in ground water is a critical factor for understanding and predicting levels of arsenic species in ground/drinking water. Therefore this effort should be of major interest to environmental chemists and environmental health scientists. These results will be useful to regulators for health-based decision making and prioritization of monitoring efforts. This work may also provide a tool to use extant basic geochemical data where arsenic concentrations are not available or are suspect. Since we can interpret the data with relation to total arsenic as well as arsenite concentrations, our approach should be a useful tool for predicting mechanisms driving total arsenic mobilization as well as mechanisms leading to the mobilization of the most toxic form of arsenic.

Partners

Name/Organization	David Johnson
Affiliation	Wisconsin Department of Natural Resources
Affiliation Type	Government
Email	
Description	

Students & Post-Docs Supported

Student Name	Kristie Ellickson
Campus	University of Wisconsin-Madison
Advisor Name	Martin Shafer
Advisor Campus	University of Wisconsin-Madison
Degree	Post Doc
Graduation Month	
Graduation Year	
Department	State Laboratory of Hygiene
Program	American Public Health Laboratory Fellowship
Thesis Title	
Thesis Abstract	

Student Name	Jackson Helmer
Campus	University of Wisconsin-Madison
Advisor Name	Martin Shafer
Advisor Campus	University of Wisconsin-Madison
Degree	Other
Graduation Month	

Graduation Year	
Department	
Program	Undergraduate Student
Thesis Title	
Thesis Abstract	

Mercury Speciation Along a Groundwater Flowpath

Basic Information

Title:	Mercury Speciation Along a Groundwater Flowpath
Project Number:	2005WI156O
Start Date:	7/1/2004
End Date:	6/30/2006
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Groundwater, Hydrogeochemistry, Toxic Substances
Descriptors:	mercury; speciation; methylation
Principal Investigators:	David Armstrong, Christopher L. Babiarz

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: David Armstrong
Submitted: 7/7/2006

Project Title

WR04R001: Mercury Speciation along a Groundwater Flowpath

Project Investigators

David Armstrong, University of Wisconsin-Madison

Christopher Babiarz, University of Wisconsin-Madison

Progress Statement

Our goal is to characterize the transport and transformations of mercury in groundwater along a well-characterized ground water flow path. Our research is being conducted at the USGS WEBB site at the Allequash Creek Watershed in northern Wisconsin. The approach involves sampling flow regimes along instrumented and characterized flow paths with emphasis on the hyporheic zone. We have conducted sampling campaigns on dates selected based on important seasonal and flow-regime events, obtaining separate samples for analysis of total mercury, methyl mercury and associated parameters. The data are used to investigate the role of geochemical conditions and Hg speciation in controlling levels of methyl mercury in subsurface waters, especially hyporheic zones. Collection of field samples has been completed. We are in the process of completing the analyses of total and methyl mercury on the samples collected and analyzing the results.

Applications, Impacts & Benefits

Accumulation of methylmercury in aquatic foodwebs poses a health threat to aquatic organisms and humans. Anoxic zones in shallow groundwater are an important site of methylmercury formation. To manage contaminated watersheds, and to predict recovery rates in response to reduced mercury loadings, information is needed on the factors controlling the transport of mercury to these zones of methylation, and on subsequent net methylation rates. Information from our research will advance our understanding of mercury transport and methylation in groundwater and watershed response to mitigation of mercury inputs.

Committees, Memberships & Panels

Group Name	Mercury as a Global Pollutant
Description	Christopher Babiarz is member of the planning committee for the 8th International Conference on MERCURY as a GLOBAL POLLUTANT to be held in Madison, WI on August 6-11, 2006. He also help to organize in a recent Workshop devoted to drafting a "declaration" on the state of mercury as a glogal pollutant, a scientific consensus that could be used in policy decisions around the world. More that 40

of the world's leading mercury researchers participated in the Workshop.

Start Date
End Date

Interactions

Description We interact with an international network of scientists involved in mercury-related research. These interactions occur in part through collaborative research projects, including the "Mercury Experiment to Assess Atmospheric Loading in Canada and the Unites States" (METAALICUS) project, a current project located at the Canadian Experimental Lakes Area. We work closely with scientist from the US Geological Survey at the Allequash Creek experimental site.

Event Date

Partners

Name/Organization US Geological Survey
Affiliation
Affiliation Type Government
Email
Description The USGS, through the North Temperate Lakes WEBB project, has instrumented the field site at Allequash Creek. We collaborate closely with scientists from the Wisconsin USGS Offices in sample collection, analyses, and modeling. Collaborators from the USGS include David Krabbenhoft, Randy Hunt, and John Walker.

Name/Organization Center for Limnology
Affiliation Trout Lake Field Station
Affiliation Type University
Email
Description We benefit from location of our field work at a site which is located near the Trout Lake Field Station and a research site for the Long Term Ecological Research Program managed through the Center for Limnology at the UW-Madison. Benefits include sharing of data and use of facilities at the research stations.

Students & Post-Docs Supported

Student Name Shawn Chadwick
Campus University of Wisconsin-Madison

Advisor Name David Armstrong
Advisor Campus University of Wisconsin-Madison

Degree PhD
Graduation Month August
Graduation Year 2006
Department

Program	Environmental Chemistry and Technology
Thesis Title	Fate and Transport of Ambient and Amended Mercury in a Stratified Temperate Lake
Thesis Abstract	

Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil

Basic Information

Title:	Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil
Project Number:	2005WI157O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Not Applicable
Focus Category:	Solute Transport, Agriculture, Hydrology
Descriptors:	soil science; unsaturated zone
Principal Investigators:	Birl Lowery, John Norman

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: Jim Hurley
Submitted: 6/30/2006

Project Title

WR05R002: Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil

Project Investigators

Brian Lepore, University of Wisconsin-Madison
Birl Lowery, University of Wisconsin-Madison
John Norman, University of Wisconsin-Madison

Progress Statement

We have conducted several field experiments to date. The results from all of these experiments indicate potential for rapid (bypass) flow of water through the rootzone resulting in potential groundwater contamination from agricultural materials, including manure and nitrogen fertilizer. One set of our experiments included repeated ponded infiltration measurements near Juneau, WI. Experiments were conducted at this site because surface applied manure had been transported (infiltrated), within 12 hours, to the groundwater following rain on snow covered ground; and the resulting contamination led to pollution of several domestic wells. Our experiments showed steady-state ponded infiltration rates greater than 25 cm hr-1.

A second set of experiments, which are being conducted at the University of Wisconsin-Madison Agricultural Research Station in Arlington, WI, also showed rapid rates of steady-state ponded infiltration. In these second experiments high time resolved soil tension, water content, and drainage lysimeter data are being collected to further characterize soil physical conditions during rapid water infiltration. We will continue to conduct these experiments throughout the summer of 2006. These data will be used to parameterize and validate process based computer models which include macropore flow.

Applications, Impacts & Benefits

The impact of these field experiments and the computer modeling simulation studies to follow, will provide a better understanding of the types of landscapes and weather events which lead to increased potential for rapid and dramatic groundwater contamination. The modeling studies will allow us to begin studying the impacts of different management decisions on risks of groundwater contamination.

Students & Post-Docs Supported

Student Name	Brian Lepore
Campus	University of Wisconsin-Madison

Advisor Name	Birl Lowery
Advisor Campus	University of Wisconsin-Madison

Degree	PhD
Graduation Month	
Graduation Year	2007
Department	Soil Science
Program	Soil Science
Thesis Title	
Thesis Abstract	

Student Name	Unknown Undergrad 1
Campus	University of Wisconsin-Madison

Advisor Name	
Advisor Campus	University of Wisconsin-Madison

Degree	Other
Graduation Month	
Graduation Year	
Department	
Program	
Thesis Title	
Thesis Abstract	

Student Name	Unknown Undergrad 2
Campus	University of Wisconsin-Madison

Advisor Name	
Advisor Campus	University of Wisconsin-Madison

Degree	Other
Graduation Month	
Graduation Year	
Department	
Program	
Thesis Title	
Thesis Abstract	

Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer

Basic Information

Title:	Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer
Project Number:	2005WI158O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Geochemical Processes, Toxic Substances, Non Point Pollution
Descriptors:	pesticides; nitrate; unsaturated zone
Principal Investigators:	George J. Kraft, Bryant Browne

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: george kraft
Submitted: 7/3/2006

Project Title

WR05R003: Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer

Project Investigators

Bryant Brown, University of Wisconsin-Stevens Point

George Kraft, University of Wisconsin-Stevens Point

Progress Statement

- A project team of consisting of UW-Stevens Point water resources scientists, U-Platteville agricultural system scientists, Wisconsin Geological and Natural History, geologists and geophysicists, and Discovery Farm outreach staff has been assembled.

- A preliminary set of 9 boreholes, mostly financed by a grant that leverages this project, was installed to gain insight to the hydrogeology of the area.

- Two boreholes were installed to fulfill the objectives of this study.

- All boreholes have been geophysically logged.

- Piezometer material was evaluated for potential sources of analytical interferences. Piezometer design has been altered as a result.

Applications, Impacts & Benefits

- A better understanding of the hydrogeology of the study site has resulted at this point. We are too early in the research process to have more concrete application, impact, and benefits.

Other Project Support

Source	University of Wisconsin System - Consortium
Dollar Value	$40,000
Description	The research dollars of the Joint Solicitation project have leveraged UW-System Consortium funds
Start Date	7/1/2006

End Date	6/30/2008

Partners

Name/Organization Affiliation	University of Wisconsin - Platteville
Affiliation Type	University
Email	
Description	This research takes place on the UWP farm, and we are using their facilities to make inferences about groundwater quality in the larger landscape.

Name/Organization Affiliation	Wisconsin Geological and Natural History Survey
Affiliation Type	University
Email	
Description	We are jointly exploring the hydrogeology of the study area.

Name/Organization Affiliation	UW-Discovery Farms
Affiliation Type	University
Email	
Description	Together we are using the outcomes of the research to inform an agricultural audience about groundwater impacts of farming practices.

Transient Functioning of a Groundwater Wetland Complex, Allequash basin, Wisconsin

Basic Information

Title:	Transient Functioning of a Groundwater Wetland Complex, Allequash basin, Wisconsin
Project Number:	2005WI159O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Wetlands, Groundwater, Climatological Processes
Descriptors:	goundwater modeling; wetlands; riparian zone
Principal Investigators:	Mary Anderson

Publication

1. Lowry, C.S., M.P. Anderson, R.J. Hunt. 2006. Modeling groundwater flow and heat transport within a fen/stream complex. In: Proceedings of MODFLOW and More 2006: Managing ground water systems, IGWMC, Golden, Colo. 5 pp.

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: Mary Anderson
Submitted: 6/27/2006

Project Title

WR05R007: Transient Functioning of a Groundwater Wetland Complex, Allequash basin, Wisconsin

Project Investigators

Mary Anderson, University of Wisconsin-Madison

Progress Statement

We are investigating transient hydrologic processes in a wetland in northern Wisconsin (Vilas County). Twelve nests of multilevel piezometers were installed along two transects in the fen/steam complex along Allequash Creek to monitor hydraulic head and temperature in the subsurface. Stream stage and discharge in the creek are also being monitored. Some measurements are recorded remotely and available online as they are recorded. Ground penetrating radar, GPR, was used to delineate the thickness of peat within the wetland. The GPR survey was also helpful during the installation of piezometers so that we could locate piezometers in both the peat and underlying sand. There are a number of groundwater seeps (or rivulets) discharging into the wetland. These rivulets have a diverse collecttion of biota. Temperature measurements in one of the groundwater seeps (rivulets) were used to calculate the magnitude of upward velocity of groundwater discharging to the seep. A two- dimensional groundwater flow and heat transport model of one of the transects was developed as a scoping model. Our eventual objective is to use temperature measurements to constrain a three-dimensional model of transient groundwater flow as the temperature signal is more pronounced than are fluctuations in head. Parameter sensitivity calculated during model calibration show that characteristics of the peat are important model parameters. Sensitivity results also showed that all thermal targets have global significance within the model while only select hydraulic head targets have global significance. Future work will expand the observation network within the peat to support the three dimensional model. With the US Geological Survey, we will install a fiber optic cable in the creek to monitor temperature in the stream at high spatial and temporal resolution during September 2006.

Applications, Impacts & Benefits

--Our use of Ground Penetrating Radar to delineate the vertical extent of peat in the wetland has attracted interest by consulting firms who have inquired about the application for their own problems.

--We were selected as one of several sites to test a fiber optic cable being rented by the U.S. Geological Survey. The student working on this project, Chris Lowry, participated in training to use the cable in May 2006 at the USGS research site in Cape Cod, MA. Expenses for the training were paid by the USGS. The cable will be deployed at our site during Sept. 2006.

Interactions

Description	We have interated with a research group in Germany who have developed a heat transport code called SHEMAT.
Event Date	

Journal Articles & Other Publications

Publication Type	Other Publication
Title	Modeling groundwater flow and heat transport within a fen/stream complex
Author(s)	Lowry, C.S., M.P. Anderson, R.J. Hunt
Publication/Publisher	MODFLOW and More 2006: Managing ground water systems, IGWMC, Golden, CO
Year Published	2006
Volume & Number	
Number of Pages	5
Description	Proceedings volume. Paper presented at an international conference in May 2006
Any Additional Citation Information	

Other Project Support

Source	USGS
Dollar Value	$100,000
Description	The USGS provides logistical support and transportation to and from the site.
Start Date	
End Date	

Partners

Name/Organization	Randy Hunt & John Walker
Affiliation	U.S. Geological Survey
Affiliation Type	Government
Email	
Description	We work closely with the USGS- Middleton, WI office on all aspects of this project. They provide logistical support for field, lab and modeling work and some additional funding as well as field eqipment and free consultation.

Name/Organization	Long Term Ecological Research Project (LTER)
Affiliation	UW-Madison
Affiliation Type	University
Email	
Description	We are working at the LTER site in Northern Wisconsin which is administered by the UW-Madision through its NSF sporspored research project at Trout Lake. Housing is provided free of charge at the Trout Lake Station. Some field eqipment is also provided.

Students & Post-Docs Supported

Student Name	Christopher Lowry
Campus	University of Wisconsin-Madison
Advisor Name	Mary Anderson
Advisor Campus	University of Wisconsin-Madison
Degree	PhD
Graduation Month	June
Graduation Year	2008
Department	Geology & Geophysics
Program	Geology
Thesis Title	Transient groundwater hydrology in a wetland (working title)
Thesis Abstract	not yet available

Assessing the Ecological Status and Vulnerability of Springs in Wisconsin

Basic Information

Title:	Assessing the Ecological Status and Vulnerability of Springs in Wisconsin
Project Number:	2005WI160O
Start Date:	7/1/2005
End Date:	6/30/2005
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Ecology, Water Supply, Surface Water
Descriptors:	springs; ecology; vulnerability
Principal Investigators:	Susan Swanson, Kenneth R Bradbury, David Hart, David John Zaber

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: Jim Hurley
Submitted: 7/13/2006

Project Title

WR05R004: Assessing the Ecological Status and Vulnerability of Springs in Wisconsin

Project Investigators

Kenneth Bradbury, Wisconsin Geological and Natural History Survey
David J. Hart, Wisconsin Geological and Natural History Survey
Susan Swanson, Beloit College
David Zaber, University of Wisconsin-Madison

Progress Statement

Introduction
The need for a clear understanding of the ecological status of springs provides the overall motivation for this project. The current understanding of springs ecology in Wisconsin and elsewhere is limited while the ecology of lakes, streams and wetlands has been extensively studied. The topic is relevant in Wisconsin because the State has taken steps to protect springs that result "in a current of flowing water with flows of a minimum of one cubic foot per second at least 80 percent of the time" (2003 Wisconsin Act 310, p.2), and the Wisconsin Department of Natural Resources (WDNR) is charged with evaluating impacts to these springs that may result from groundwater pumping by high-capacity wells. We hope to provide a mechanism to evaluate impacts and provide feedback to the question of whether springs covered under Act 310 are sufficient to protect the range of Wisconsin's spring resources.

The project includes cataloging historical and existing spring resources in Iowa and Waukesha Counties using a geographic information system (GIS) and characterizing a subset of springs in the two counties using a comprehensive springs classification system in development by Springer et al. (in prep.). This information will be used to develop typical hydrogeological conceptual models and associated descriptions of typical ecological characteristics of springs in each region.

Springs GIS Development
The springs GIS development began in July and August 2005. We converted all historical information from the Wisconsin Conservation Department's 1958-59 spring surveys of Iowa and Waukesha Counties to an electronic format and digitized the historical spring locations. We also explored the following resources on springs in each county and converted them to an appropriate electronic format.
1. USGS Geographic Names Information System (GNIS). (ArcGIS shapefiles)
2. WDNR Surface Water Resources for each county. (ArcGIS shapefiles)
3. WDNR Guide to Hook and Line Fishing Regulations (2005-06). (found not to contain relevant information)
4. The Great Waukesha Springs Era (Schoenknecht, 2003) and personal communication with John Schoenknecht. Mr. Schoenknecht is a local expert on historical springs in the City of Waukesha and helped to identify the locations of springs within the city limits. (ArcGIS shapefile)

5. Iowa County Groundwater Advisory Panel. In coordination with Paul Ohlrogge, the Community Resource Development Agent for Iowa County, we sent maps of the springs in Iowa County to their Groundwater Advisory Panel. The panel, composed primarily of town mangers, provided feedback on locations of springs in Iowa County. (ArcGIS shapefile)
6. Iowa County and Waukesha County Parcel Maps and Tax Ownership Data. These GIS resources were acquired from the land information offices in each county. They were used to determine ownership for properties on which springs are thought to be located. Phone numbers for property owners were then determined using on-line resources. (Excel spreadsheet)

We identified and collected contact information for current owners of properties with historical springs in Iowa and Waukesha Counties. Property owners for approximately 67% of the springs in Iowa County were identified (271 of 406) and property owners for approximately 72% of the springs in Waukesha County were identified (186 of 265). The property owners were contacted by phone to ask whether a spring exists on the land today. Where one or more springs exist, the property owner was asked to describe the emergent setting, the volume of spring flow, and the persistence of spring flow. Through this process, we have confirmed the presence or absence of approximately two-thirds of the Iowa County historical springs for which property owner contact information is available. Phone calls to Waukesha County property owners continued through June 2006.

Spring Surveys
We used the springs GIS database to characterize the distribution of springs in each county with respect to geologic formation, proximity to stratigraphic contact, elevation, slope, and aspect. This information was used in association with the property owners' descriptions to select up to 30 springs in Iowa County for monitoring purposes. We spent most of June in the field surveying these springs for the suite of hydrological, physicochemical, and ecological characteristics included in the Springer et al. (in prep.) classification system. We completed all of the Iowa County spring surveys by the end of June 2006. The same process was conducted for the Waukesha County springs, and fieldwork is scheduled for July 2006.

We also selected three springs in Iowa County to monitor on a bi-monthly basis during 2006. The full suite of hydrological, physicochemical, and ecological characteristics included in the Springer et al (in prep.) classification system are collected and recorded during each bimonthly event. Flow is measured on a monthly basis. Two of the springs (both named Big Spring) are located in northern Iowa County, one near Highland and the other near Otter Creek. An additional spring, which is being monitored as part of a complementary geological study being conducted by the WGNHS, is located in Governor Dodge State Park. The three springs occur at different stratigraphic positions, topographic elevations, and aspects. They also vary in terms of their level of disturbance. Monitoring events took place on Jan. 31st/Feb. 1st (full suite), Feb. 22nd (flow), March 9th (full suite), April 22nd (flow), May 24th (full suite), and June 13th (flow).

References
Springer, A.E., Stevens, L.E., Anerson, D.E., Parnell, R.A., Kreamer, D.K., and Flora, S.P., in prep., A comprehensive springs classification system: integrating geomoprhic, hydrogeochemical, and ecological criteria, in Stevens, L.E., and Meretsky, V.J., eds., Every last drop: ecology and conservation of springs ecosystems in North America: Tucson, AZ, University of Arizona Press.

Applications, Impacts & Benefits

• Application(s) – The springs GIS for Iowa and Waukesha Counties, which was developed in the first year of this project, was used to characterize the distribution of springs in each county with respect to geologic formation, proximity to stratigraphic contact, elevation, slope, and aspect. This information was used in association with private property owners' descriptions of springs to select up to 30 springs in Iowa County for monitoring purposes. The same procedure is being followed for Waukesha County. In the future, we hope that the springs GIS will serve as a working model for the types of spatial and attribute data necessary to make initial assessments of the ecological status of spring resources elsewhere in the State.

• Impacts – The spring surveys that are being conducted in Iowa and Waukesha Counties in June and July, 2006 are the first comprehensive spring surveys in these regions since 1959.

• Benefits – The physical, biological, and sociocultural data that we are collecting will allow us to make assessments of the ecological status of typical spring systems in each county. This is a critical first step in assessing vulnerability to groundwater pumping because it provides baseline conditions to which changes can be compared. To further address the issue of

vulnerability, the data we collect will allow us to formulate viable hydrogeological conceptual models of the typical spring systems in each county, which may be useful for modeling studies if high-capacity wells are proposed in the future. In addition, we will identify ecological functions of these typical spring systems that may be vulnerable to changes induced by altered flow regimes, thereby stressing dependent biota.

Interactions

Description

On July 1st, 2005 we participated in a meeting of four groups involved in springs-related research across the State of Wisconsin (UW-Green Bay, UW-Eau Claire, Wisconsin Wildlife Federation, Beloit College/UW-Arboretum/Wisconsin Geological and Natural History Survey (WGNHS)). Representatives from the U.S.Geological Survey (USGS) also attended. Three of the projects are funded by Wisconsin Department of Natural Resources (WDNR) and/or UW-Water Resources Institute (WRI) and one Wisconsin Wildlife Federation project is supported by a Joyce Foundation grant. The meeting was held at the UW-Arboretum and was coordinated by Jeff Helmuth (WDNR). It focused on explaining research goals for the respective projects and setting up lines of communication among the research groups and interested parties. This Spring Projects Coordination Group decided to continue to meet periodically throughout the year.

Event Date

7/1/2005

Description

As proposed, we invited Abe Springer (Northern Arizona University) and Larry Stevens (Stevens Ecological Consulting) to Madison in early October 2005. They discussed their comprehensive springs classification system, which we are implementing and modifying for springs in Wisconsin, at a one-day meeting held on October 4th at the UW-Arboretum. We initially proposed to invite WDNR personal to the meeting, but the number of participants increased to include all of the members of the Spring Projects Coordination Group.

Event Date

10/4/2005

Description

On October 5th, a smaller group including our project members, Mark Leach (UW-Arboretum), and UW-Geology Department graduate students, traveled to Iowa County to visit several spring complexes that are representative of typical spring systems in the county. In addition, Madeline Gotkowitz (WGNHS) provided background on the complementary geological investigation that the WGNHS began in Iowa County in 2005. The field trip provided opportunities for Dr.s Springer and Stevens to better understand typical spring systems in Wisconsin and opportunities for us to test the Springer et al. (in prep.) classification system and discuss appropriate modifications for Wisconsin spring systems prior to initiating our own field program.

Event Date

10/5/2005

Description

The Spring Projects Coordination Group also met on April 12, 2006 at the Southern District office of the WDNR. Several representatives from the WDNR also attended this meeting, which focused on providing updates on the four projects to the Groundwater Advisory Committee, which was created by 2003 WI Act 310 to make recommendations to the State Legislature regarding future groundwater

management needs in Wisconsin. As a result of the presentations made by Ken Bradbury (WGNHS) and Jake Macholl (WWF) to the Groundwater Advisory Committee, we plan to help coordinate a springs fieldtrip in conjunction with a future meeting of the committee.

Event Date 4/12/2006

Students & Post-Docs Supported

Student Name Brandon Bartkowiak
Campus Beloit College

Advisor Name
Advisor Campus Beloit College

Degree Other
Graduation Month
Graduation Year
Department Geology
Program
Thesis Title
Thesis Abstract

Student Name Becky Carvin
Campus University of Wisconsin-Madison

Advisor Name
Advisor Campus University of Wisconsin-Madison

Degree Masters
Graduation Month
Graduation Year
Department Water Resources Management
Program Institute for Environmental Studies
Thesis Title
Thesis Abstract

Student Name Natalie Hunt
Campus University of Wisconsin-Madison

Advisor Name
Advisor Campus University of Wisconsin-Madison

Degree Masters
Graduation Month
Graduation Year

Department	Water Resources Management
Program	Institute for Environmental Studies
Thesis Title	
Thesis Abstract	

Evaluation of On-Site Wastewater Treatment as a Source of Antibiotic Resistance Genes in Groundwater

Basic Information

Title:	Evaluation of On-Site Wastewater Treatment as a Source of Antibiotic Resistance Genes in Groundwater
Project Number:	2005WI161O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Biological Sciences
Focus Category:	Toxic Substances, Solute Transport, None
Descriptors:	microbiology; antibiotics; on-site treatment
Principal Investigators:	Trina McMahon

Publication

Annual Progress Report

Reporting Period: 7/1/2005 - 6/30/2006

Submitted By: Jim Hurley
Submitted: 7/14/2006

Project Title

WR05R006: Evaluation of On-Site Wastewater Treatment as a Source of Antibiotic Resistance Genes in Groundwater

Project Investigators

Katherine McMahon, University of Wisconsin-Madison

Progress Statement

We have collected samples from groundwater wells and septic tanks at our study site (a subdivision near Sun Prairie, WI) and have extracted DNA from them. We are currently analyzing these samples for the presence of tetracycline resistance genes. We will continue to collect samples quarterly.

Applications, Impacts & Benefits

Not yet applicable.

Students & Post-Docs Supported

Student Name	Erin Seyfried
Campus	University of Wisconsin-Madison
Advisor Name	Katherine McMahon
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month **Graduation Year**	
Department	Civil and Environmental Engineering
Program	Environmental Engineering
Thesis Title	TBD
Thesis Abstract	

Information Transfer Program

University of Wisconsin-Water Resources Institute - Information Transfer

Basic Information

Title:	University of Wisconsin-Water Resources Institute - Information Transfer
Project Number:	2005WI89B
Start Date:	3/1/2005
End Date:	2/28/2006
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Anders W. Andren, Jim Hurley, JoAnn M. Savoy

Publication

1. Atchison, Dustin; Ken Potter, Linda Severson. 2006. Design Guidelines for Stormwater Bioretention Facilities. Madison: University of Wisconsin Water Resources Institute. 33 pages.
2. Anderson, Mary P.; Melissa D. Masbruch. 2005. Delineation of Flow Paths, Capture Zones, and Source Areas in Allequash Basin, Vilas County, Wisconsin. Groundwater Research Report for project WR04R002. University of Wisconsin Water Resources Institute, Madison, Wis. 16 pp.
3. Cherkauer, D.S. 2005. Providing Communities with the Ground Water Information Needed for Comprehensive Planning. Project completion report to the University of Wisconsin Water Resources Institute, Madison, Wis. 11 pages.
4. Klett, N.; T.B. Edil, C.H. Bensen, J. Connelly. 2005. Evaluation of Volatile Organic Compounds in Wisconsin Landfill Leachate and Lysimeter Samples. Project completion report to the University of Wisconsin System Groundwater Research Program for project WR03R006, Evaluation of Contamination of Groundwater around Landfills. 585 pages.
5. LePain, David; Kenneth R. Bradbury, Michael K. Cobb. 2005. Hydrostratigraphy of West-Central Wisconsin: A new approach to groundwater management. Project completion report to the University of Wisconsin Water Resources Institute, Madison, Wis. 10 pages.
6. Li, Zhaohui. 2005. Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation. Project completion report to the University of Wisconsin Water Resources Institute, Madison, Wis. 16 pp.
7. Markham, L.; ChinChun Tang, Bobbie Webster, Chuck Dunning. 2005. Development of Tools to Address Groundwater in Comprehensive Planning. Project completion report to the University of

Wisconsin Water Resources Institute, Madison, Wis. 26 pages.
8. Schauer, James Jay; Jeremy Olstadt, Jon Standridge1, Sharon Kluender. 2005. A Comparison of Ten USEPA-Approved Enzyme-Based Total Coliform/E. coli Tests for Microbiological Groundwater Monitoring and Laboratory Consultation. Project completion report to the University of Wisconsin Water Resources Institute, Madison, Wis. 16 pages.
9. Cobb, M.; D. LePain, K. Bradbury. 2005. Hydrostratigraphic Data Resources for West-Central Wisconsin. Wisconsin Geological and Natural History Survey Open-File Report 2005-04.
10. Olstadt, J.; J. J. Schauer, J. Standridge, and S. Kluender. A Comparison of Ten U.S. EPA-Approved Total Coliform/E. coli Tests. Submitted to Journal of Water and Health.
11. Cherkauer, D.S., and S.A. Ansari. 2005. Estimating groundwater recharge from topography, hydrogeology and land cover. Ground Water 43(1).
12. Masbruch, M.D., 2005, Delineation of Source Areas and Characterization of Chemical Variability using Isotopes and Major Ion Chemistry, Allequash Basin, Wisconsin. M.S. Thesis, Department of Geology and Geophysics, University of Wisconsin-Madison, 131 pp.
13. Masbruch, M.D.; R.J. Hunt, and M.P. Anderson. 2005. Investigation of Three Flowpaths of Different Lengths, Allequash Basin, Vilas County, Wisconsin (abstract). In: Wisconsin's Waters--A Confluence of Perspectives, annual conference of the Wisconsin Section of the American Water Resources Association, Delavan, Wis., p. 44.
14. Masbruch, M.D.; R.J. Hunt, and M.P. Anderson. 2005. Delineation of Flow Paths and Processes Affecting Chemical Variability, Allequash Basin, Wisconsin (abstract). In: Geological Society of America Abstracts with Programs, annual meeting, Salt Lake City, Utah, October 2005.
15. Lowry, C.S., M.P. Anderson, R.J. Hunt. 2006. Modeling groundwater flow and heat transport within a fen/stream complex. In: Proceedings of MODFLOW and More 2006--Managing groundwater systems, IGWMC, Golden, Colo. 5 pp.

Information Transfer

Highlights of the reporting period, March 1, 2005 through February 28, 2006, include planning for the Eight International Conference on Mercury as a Global Pollutant, a new Water Resources Library Web site, Wisconsin's Water Library for Kids (*aqua.wisc.edu/waterlibrary/kids*), and the publication of "Design Guidelines for Stormwater Bioretention Facilities". In addition, WRI continued to publish a quarterly newsletter, maintain several Web sites, cosponsor the AWRA Wisconsin Section conference, support a library and issue additional publications.

Conferences

Work continued on the Eight International Conference on Mercury as a Global Pollutant to be held in Madison on August 6-11, 2006. This conference has become the preeminent international forum for formal presentation and discussion of scientific advances concerning environmental mercury pollution. The depth, breadth, and pace of scientific discovery on the sources, environmental transport and fate, biogeochemical cycling, and adverse effects of mercury have increased enormously since the inaugural conference was convened in Sweden in 1990. In view of proposed U.S. and international actions on mercury emissions, the 2006 conference will present a timely opportunity to assimilate, synthesize, and disseminate scientific knowledge and technical information in a form useful to policy discussions involving mercury in the environment. To learn more, visit the conference Web site at *mercury2006.org/Default.aspx?tabid=1435.*

The Water Resources Institute once again cosponsored the American Water Resources Association, Wisconsin Section annual meeting. "Wisconsin's Water Resources: Conflicts & Collaborations" was held March 2-3, 2006 in Elkhart Lake, Wisconsin. Plenary, oral and poster sessions addressed both surface water and groundwater issues in Wisconsin. Other sponsors of the conference were the UW-Stevens Point Center for Watershed Science and Education, the Wisconsin Department of Natural Resources and the Wisconsin District of U.S. Geological Survey.

Water Resources Publication

In February 2006, WRI and the UW-Madison Department of Civil & Environmental Engineering published "Design Guidelines for Stormwater Bioretention Facilities" by Dustin Atchison, Ken Potter and Linda Severson. This manual provides design guidelines and a numerical model (RECARGA) that can be used for creating bioretention facilities for small-scale stormwater management that promotes infiltration of storm water in order to reduce its

volume, improve its quality and increase groundwater recharge. A basic bioretention facility is commonly referred to as a rain garden. It is a landscaped garden in a shallow depression that receives storm water from nearby impervious surfaces.

UW Water Resources Library Outreach Activities
During the past year, the UW Water Resources Library maintained its involvement in outreach while continuing to serve university system faculty, staff and students. A highlight of the past year was the launch of a new library outreach Web site, **Wisconsin's Water Library for Kids** (*aqua.wisc.edu/waterlibrary/kids*).

From Dr. Seuss to a simple explanation of the water cycle, "Wisconsin's Water Library for Kids" features children's books with aquatic themes that have won awards or appeared on best books lists. Most books are for preschool through second grade children, although there are also materials for older kids. Besides fiction and nonfiction books, the Web site also has ideas and resources for story hours.

Users can browse recommended reading lists by topic (frogs, fish and fishing, Great Lakes, water pollution, etc.) and age group. Any adult Wisconsin resident can check out books online and pick them up at their local public library.

Library staff involved three students from the UW School of Library and Information Studies in the development of the site. Tina Yao, the ASC Art Director, used pictures from the Water Library's Allied Drive Story Hour series to design the site.

Library staff also continued to be involved in the "Allied Drive Story Hours" doing a story hour in July 2005 based on picture books about frogs. Allied Drive is a neighborhood of Madison, Wisconsin which is pocket of poverty and crime. The "Allied Drive Story Hours" began during the summer 2004 when the Water Resources Library launched the first of a series of story hour programs. The project has since become a partnership between six other specialized campus libraries, the UW-Madison School of Library and Information Studies, and the Madison School and Community Recreation Safe Haven Childcare Program. The library's July story hour received television coverage.

Web Sites
WRI maintains several other Web sites in addition to the site for the Eight International Conference on Mercury as a Global Pollutant described above. The **UW Water Resources Institute Web Site** (*wri.wisc.edu*) introduces users to the Wisconsin program and includes a variety of information for those interested in water-related issues and research. During the past year, the following sections were updated: project listing, groundwater research database, funding opportunities and conference information.

The **ASC Publications Store** (*www.aqua.wisc.edu/publications*) features publications from both the Water Resources and Sea Grant Institutes. During the reporting period, the publication described above, “Design Guidelines for Stormwater Bioretention Facilities” was added to the online store.

The **Wisconsin Water Policy Inventory** (*www.aqua.wisc.edu/waterpolicy*) is a web-based tool for researching the state’s major policies pertaining to water. This project enables Wisconsinites to browse state policies by category or to search using keywords.

Library Web Sites

In addition to the new **Wisconsin’s Water Library for Kids** described above, the Water Resources Library maintains several Web sites, all of which were updated during the past year. The **Water Resources Library Web Site** (*wri.wisc.edu/library*) introduces UW-Madison faculty, staff and students to the library services tailored to them. Two of the most popular pages on that site are “Guide to Finding a Water-Related Job” (*wri.wisc.edu/library/finding_jobsall.html*) and “Guide to Finding Water-Related Information” (*library.wisc.edu/guides/WaterResources/index.htm*).

Wisconsin’s Water Library (*aqua.wisc.edu/waterlibrary*) continues to make the books and other materials of the Water Resources Library available to any Wisconsin resident. During the past year, staff updated the entire site and added several special features or annotated reading lists on popular topics, including “Great Lakes Ships and Shipping”, “Did you know? Learn more about Wisconsin Waters and the Great Lakes”, and “Aquaculture, A Resource Guide”. The most popular pages on the Water Library are “Wisconsin Water Facts” (*aqua.wisc.edu/waterlibrary/facts.asp*), “Native Americans and the Environment” (*aqua.wisc.edu/waterlibrary/nativeamericans.asp*) and “Environmentally-friendly Lawn and Garden Care” (*aqua.wisc.edu/waterlibrary/lawn.asp*).

The popularity of the library Web sites continues to grow. From August 2003 to April 2006, the number of visits per day to the Water Library Web site has grown from 45 to about 300. The average user likes what he sees and spends about 10 minutes on the site. Our library sites (Wisconsin’s Water Library + Water Resources Library + our material on the UW-Madison Libraries site) currently receive over 500 unique visits per day.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	3	0	0	10	13
Masters	2	0	0	5	7
Ph.D.	0	1	0	3	4
Post-Doc.	0	0	0	2	2
Total	5	1	0	20	26

Notable Awards and Achievements

MICROBIOLOGICAL GROUNDWATER MONITORING. Protecting groundwater from microbial contamination is a top public health priority. The United States and Canada experience significant levels of gastrointestinal disease from drinking water, more than 70 percent of which is associated with contaminated well water. A University of Wisconsin WRI project examined the strengths and weakenesses of 10 enzyme-based tests approved by the U.S. Environmental Protection Agency for detecting total coliform and E. coli in drinking water. The results suggest these tests differ significantly in their ability to detect/enumerate total coliforms and E. coli and to suppress false positive results from Aeromonas, a non-coliform organism. The most significant of these findings was the inability of some test method/sample matrix combinations to even detect E. coli in high concentrations.

METHYLMERCURY FORMED IN GROUNDWATER. A WRI study conducted at the Allequash Creek watershed in northern Wisconsin determined that anoxic zones in shallow groundwater are an important site of methylmercury formation. This information will advance our understanding of mercury transport and methylation in groundwater and watershed response to mitigation of mercury inputs.

ESTROGENIC ENDOCRINE DISRUPTORS NOT FOUND IN GROUNDWATER. A Wisconsin WRI-funded analysis of multiple groundwater samples from high capacity wells at five Wisconsin municipalities showed no estrogenic endocrine disruptor activity, leading the investigators to conclude that no infiltration of these contaminants from surface water into nearby groundwater is occurring. Also, analysis of multiple samples of septic influent, effluents, monitoring wells and soil water indicate septic systems using the biomicrobic aerobic and sand filtration system provided cleaner effluent than mound systems.

SMART GROWTH' PLANNING. The State of Wisconsin has mandated comprehensive Smart Growth land use planning by the year 2010 for every township, city and county in the state. Communities that rely on ground water as their sole source of water need to assess the magnitude and limits of their source(s) of water as part of their comprehensive development plan, yet most have little expertise in quantifying and protecting their water supply. A two-year project funded by the University of Wisconsin Water Resources Institute (WRI) partnered with such a community (Richfield, Wis.) to determine what kinds of

groundwater supply information was most relevant and usable for land use planning from a community's perspective. This study determined that the most important information needed by such a community is a good basic understanding of the geology, sources, sinks and water balance of its aquifer system so that residents and community leaders know where their water comes from. Interaction with users at all levels is also crucial to developing the awareness needed to create a long-term land use plan and supporting laws to ensure a sustainable water supply under foreseeable future conditions. The next step is to share this model with other communities to help them plan how best to actively manage and protect the recharge areas that supply their water.

RAIN GARDENS COMPUTER MODEL AND DESIGN MANUAL. One product resulting from a recently completed Wisconsin WRI research project is a user-friendly computer model for designing and evaluating stormwater bioretention facilities, commonly called rain gardens. This model has been adopted and is recommended by the Wisconsin Department of Resources (WDNR) for use in meeting its new stormwater infiltration regulations. The model software and user manual are available free of charge via the WDNR website. Another product from a related WRI project is a rain garden design manual that incorporates use of the computer model. Published in February 2006 by the University of Wisconsin Water Resources Institute, "Design Guidelines for Stormwater Bioretention Facilities" also may be downloaded free of charge from the UW-Madison Aquatic Sciences Center's online Publications Store, which during May-June 2006 recorded more than 1,800 downloads of this publication.

Publications from Prior Projects

1. 2004WI113O ("An Assessment of Aquifer Storage Recovery for Selected Representative Hydrogeologic") - Articles in Refereed Scientific Journals - Hunt, Randall J.; Daniel T. Feinstein, Christine D. Pint and Mary P. Anderson. 2006. The importance of diverse data types to calibrate a watershed model of the Trout Lake Basin, Northern Wisconsin, USA. Journal of Hydrology 321(2006):28696.
2. 2004WI133O ("Hydrostratigraphy of West-Central Wisconsin: A New Approach to Groundwater Management") - Other Publications - Cobb, M.; D. LePain, K. Bradbury. 2005. Hydrostratigraphic Data Resources for West-Central Wisconsin. Wisconsin Geological and Natural History Survey Open-File Report 2005-04.
3. 2004WI131O ("A Comparison of USEPA-Approved Enzyme-Based Total Coliform/E. coli Tests for Microbiological Groundwater Monitoring and Laboratory Consultation") - Articles in Refereed Scientific Journals - Olstadt, J.; J. J. Schauer, J. Standridge, and S. Kluender. A Comparison of Ten US EPA Approved Total Coliform/E. coli Tests. Submitted to Journal of Water and Health.
4. 2005WI151O ("Providing Communities with the Groundwater Information Needed for Comprehensive Planning") - Articles in Refereed Scientific Journals - Cherkauer, D.S., and S.A. Ansari. 2005. Estimating groundwater recharge from topography, hydrogeology and land cover. Ground Water 43(1).
5. 2004WI78B ("Design and Evaluation of Rain Gardens for Enhancement of Groundwater Recharge") - Other Publications - Atchison, Dustin; Ken Potter, Linda Severson. 2006. Design Guidelines for Stormwater Bioretention Facilities. Madison: University of Wisconsin Water Resources Institute. 33 pages.
6. 2004WI130O ("Delineation of Flow Paths, Capture Zones and Source Areas, Allequash Basin, Vilas County, Wisconsin") - Dissertations - Masbruch, M.D., 2005, Delineation of Source Areas and Characterization of Chemical Variability using Isotopes and Major Ion Chemistry, Allequash Basin,

Wisconsin. M.S. Thesis, Department of Geology and Geophysics, University of Wisconsin-Madison, 131 pp.