# Water Resources Institute Annual Technical Report FY 2004

# 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** 

# **Design and Evaluation of Rain Gardens for Enhancement of Groundwater Recharge**

## **Basic Information**

Title:	Design and Evaluation of Rain Gardens for Enhancement of Groundwater Recharge
Project Number:	2004WI78B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	2nd
Research Category:	None
Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Kenneth W. Potter

- 1. Dussaillant, A. R., C. Wu, and K.W. Potter, Richards equation model of a rain garden, Journal of Hydrologic Engineering, ASCE, 9(3), 219-225, 2004.
- 2. Brander, K. E., K. E. Owen, and K. W. Potter, Modeled impacts of development type on runoff volume and infiltration performance, Journal of the American Water Resources Association, 40(4), 961-970, 2004.

#### Design and Evaluation of Rain Gardens for Enhancement of Groundwater Recharge

Kenneth Potter, University of Wisconsin-Madison, Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2005

In highly urbanized and rapidly urbanizing portions of Wisconsin, groundwater depletion can and has occurred as a result of excessive pumping and reduction of groundwater recharge due to introduction of impervious surfaces. In past and ongoing research we have demonstrated that rain gardens (sunken gardens that receive surface runoff) have the potential of increasing local groundwater recharge rates well above natural rates. We have developed continuous hydrologic models and used them to evaluate the performance of various rain garden designs. We have also constructed an experimental rain garden to provide validation data and improve our understanding of rain garden performance. The objectives of the proposed research are twofold: to develop design charts and other guidelines to facilitate the design of rain gardens; and to operate the recently completed experimental rain garden for the two-year project duration to provide information on the long-term behavior and data for evaluating the ability of our models to simulate long-term performance. The design charts and other information developed in this project will greatly facilitate the use of rain gardens to enhance groundwater recharge in Wisconsin, and hence will contribute to the mitigation of aquifer depletion and groundwater degradation in highly urbanized and rapidly urbanizing portions of the state.

**Project Update:** 

We have made significant improvements to RECARGA, the model we developed for designing and evaluating bioretention facilities. Prior to these improvements, it was necessary to use RECARGA in an iterative fashion to arrive at a facility area that met a specified infiltration requirement. The revised model allows direct calculation of the required area.

We have completed a technical manual for the design of bioretention facilities. This manual explains in detail the role of each design parameter and offers general advise about the application of infiltration practices. It also includes information on the use of RECARGA. The manual is currently undergoing external peer review.

We collected data from the experimental rain garden through the spring of 2005. Late in 2004 the facility developed clogging problems that limited the usefulness of measurements of infiltration amounts. However, operation of the facility during the winter of 2004-5 demonstrated that bioretention facilities can effectively function during winter thaws.

# Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics in Subsurface Environments

## **Basic Information**

Title:	Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics in Subsurface Environments
Project Number:	2004WI79B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	2nd
Research Category:	None
Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Joel Alexander Pedersen

- 1. Gu, C.; Karthikeyan, K.G. Interaction of tetracycline with aluminum and iron hydrous oxides. Environ. Sci. Technol. 2005. 39:2660-2667.
- 2. Gao, J.; Pedersen, J.A. Adsorption of sulfonamide antimicrobial agents to clay minerals. Environ. Sci. Technol. (in revision).
- 3. Gu, C.; Karthikeyan, K.G. Sorption of the antimicrobial ciprofloxacin to aluminum and iron hydrous oxides. Environ. Sci. Technol. (in review submitted June 2005).

#### Fate Of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics In Subsurface Environments

K. G. Karthikeyan, University of Wisconsin-Madison, Biological Systems Engineering

and

J. A. Pedersen, University of Wisconsin-Madison, Soil Science Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2005

Municipal wastewater treatment plant effluent and confined animal feeding operations represent important sources of antibiotics to the environment. The last few years have witnessed an increasing number of publications documenting the occurrence of antibiotics in surface waters and groundwater, heightening concern about their presence in the environment. Compared to conventional organic contaminants, little information is available on the environmental behavior of antibiotics. Our ability to predict mobility, fate and effects of antibiotics is hampered by a lack of information on fundamental processes governing their behavior in the environment. The overall goal of this project is to determine the extent to which association of antibiotics with particle-bound and dissolved natural organic matter influences their mobility in soils and subsurface environments. We intend to focus on representative antibiotics from four major classes: fluoroquinolones, macrolides, sulfonamides and tetracyclines. The selected antibiotics have been detected in wastewater influent and effluent in Wisconsin and in streams throughout the U.S. Our specific objectives are to: (1) quantify the extent of sorption of these antibiotics to humic substances associated with hydrous iron and aluminum oxides and smectitic clays; and (2) investigate antibiotic association with dissolved and particle-bound organic matter. Our research findings will help in assessing the ability of soils to act as potential sinks for these emerging organic contaminants and increase understanding of their environmental fate and transport characteristics as influenced by particle-bound and dissolved natural organic matter.

#### 1. Year II Project Update:

This report summarizes our progress during the past year (Year II: July 2004 - June 2005) of our research project. The end date of the project is February 28, 2006.

#### I. Sorption of Antibiotics to Mineral Surfaces:

Prior to initiating sorption experiments with mineral-associated humic substances, we investigated the effect of solution chemistry on antibiotic sorption to the pure mineral phases. Association of tetracycline (TET) and ciprofloxacin (CIP) to hydrous oxides of Al (HAO) and Fe (HFO) and sorption of sulfamethazine (SMZ), sulfapyridine (SPY) and sulfamethoxazole (SMX) to smectitic and kaolinitic clays were investigated. In both the USGS national and our Wisconsin statewide surveys, TET, CIP, and SMX were among the most frequently detected antibiotic compounds.

In year I (2003-04), we completed the macroscopic experiments assessing solution chemistry (pH, ionic strength, sorbate-to-sorbent ratio) effects and reaction time on TET and CIP sorption to HAO and HFO. During the past year, complementary spectroscopic analysis (ATR-FTIR) was performed to elucidate the nature of CIP surface complexes formed on HAO and HFO. Results obtained from ATR-FTIR are indicative of the formation of different type of surface complexes with HAO and HFO; while a *monodentate mononuclear* complex (with the -COO<sup>-</sup> group) appears likely between CIP and HAO, the keto-O and one of the O from COO<sup>-</sup> seem to be involved in the formation of a *six-member ring* with Fe on HFO surface.

In year I, we determined species-specific sorption coefficients (K<sub>d</sub> values) for the association of SMZ with SWy-2, SAz-1 and GKa-1b. We also determined K<sub>d</sub> values for SMZ sorption to Pahokee peat. During the past year we extended this work to examine the influence of surface charge density and the nature of the exchangeable cation on SMZ sorption to smectitic clay The effect of surface charge density was investigated by heat treating lithium minerals. exchanged clays to effect permanent charge reduction. Montmorillonite charge density influenced adsorption of the neutral and cationic species by determining adsorption domain size. Cation exchange appeared to contribute to adsorption of the cationic sulfonamide species to smectite surfaces. We also examined the effect of sulfonamide structure on sorption by obtaining sorption parameters for two additional sulfonamide antimicrobials: SPY and SMX. The nature of the sulfonamide R group influenced the degree of adsorption of the cationic and neutral species: cationic SMZ and SPY adsorbed to Na-SWy-2 to a larger extent than SMX. Our results highlight the importance of considering sulfonamide speciation and clay surface charge density in predicting the transport of these antimicrobials.

Our results and those of others indicate that hydrous oxides and clay minerals play an important role in influencing the environmental fate and reactivity of tetracycline and fluoroquinolone antibiotics. Sorption to clay mineral surfaces appears much less important for sulfonamide antimicrobials. Our research findings will increase understanding of the environmental fate and reactivity of these emerging organic contaminants.

#### II. Association of Antibiotics with Dissolved Organic Matter:

Sorption of SMZ, the macrolide clarithromycin (CLR), and TET to Elliott soil humic acid (ESHA) was investigated using the equilibrium dialysis method. Initial results indicate that CLR association with ESHA reaches a maximum between pH 6 and 7. The pH dependence of CLR sorption was likely attributable to changes in the charge and structure of ESHA and, to a lesser extent, CLR speciation. Clarithromycin is dominantly cationic below its pKa of 8.9 - 9.0. Similar pH dependence was observed for cationic quinilone-HA association. Association of SMZ with ESHA was strongly pH-dependent with K<sub>doc</sub> increasing with decreasing pH.

Sorption equilibrium between TET and ESHA was attained in 24 h. However, a similar equilibration period was required for TET even in the absence of ESHA, which suggests that the rate-limiting step for the sorption process was antibiotic diffusion through the dialysis membrane. High compound recoveries (> 95%) were obtained indicative of negligible losses of TET due to sorption to the dialysis membrane. The experimental data will be described using the FITEQL 4.0 chemical equilibrium program to obtain complexation constants.

#### III. Association of Antibiotics with Humic-Coated Minerals:

We examined the sorption and desorption of three representative SMZ, SPY and SMX antibiotics to reference clay minerals with and without humic acid (HA) coatings. Coating clay minerals with HA enhanced sulfonamide sorption, and sorption increased with increased HA loading. Sorption of sulfonamide antimicrobials to humic-clay complexes was linear over the investigated concentration range. We are investigating the effect of HA loading and sorbent composition on sorption-desorption hysteresis.

2. Notable Achievements and Awards: Please report the title, date and description of any award, honor or recognition you or students associated with this project received related to this specific project.

3. **Publications:** Please provide us with a list of any publications resulting from this or related WRI-funded projects.

Gu, C.; Karthikeyan, K.G. Interaction of tetracycline with aluminum and iron hydrous oxides. *Environ. Sci. Technol.* **2005**. 39:2660-2667.

Gao, J.; Pedersen, J.A. Adsorption of sulfonamide antimicrobial agents to clay minerals. *Environ. Sci. Technol.* (in revision).

Gu, C.; Karthikeyan, K.G. Sorption of the antimicrobial ciprofloxacin to aluminum and iron hydrous oxides. *Environ. Sci. Technol.* (in review – submitted June 2005).

# 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

#### Project ID: 2004WI82G

Title: Groundwater sustainability in a humid climate: Groundwater pumping, groundwater consumption, and land use change. Project Type: Research Focus Categories: Water Use, Groundwater, Management and Planning Keywords: aquifer sustainability, groundwater use, hydrologic systems Start Date: 09/01/2004 End Date: 08/31/2006 Federal Funds Requested: \$69,246 Non-Federal Matching Funds Requested: \$70,230 Congressional District: 2 Principal Investigators: Madeline Beth Gotkowitz David John Hart Charles P. Dunning

#### Abstract

Integration of groundwater use trends and forecasts with an evaluation of the sustainable yields of aquifers is necessary to convey principal concepts of hydrologic systems mass balance and base flow preservation to water-resource managers. Water use is a concern even in humid "water-rich" states, such as Wisconsin, where groundwater pumping causes severe declines in groundwater levels and reduces groundwater discharge to surface water.

In the proposed research, we will address relationships between groundwater use, landuse change, population change, and the sustainability of groundwater resources in a water-rich environment. The work will advance the process of integrating water-use data collection with the "science of water use" by evaluating accounting and estimating methods within research into the economic and social components that drive patterns of water use. We will identify methods of reporting and estimating water use, with associated error analysis, that provide data of a quality sufficient to improve groundwater flow models used to forecast impacts of pumping on hydrologic systems. One objective of the proposed research is to identify causes of observed exponential

growth in groundwater pumping. This will be accomplished by developing a detailed understanding of water demand, consumption, and return for two study areas. One location is a rapidly urbanizing and suburbanizing county that has experienced a four-fold increase in population with a seven-fold increase in groundwater pumping, with significant increases in manufacturing and service sector employment. The second county is predominantly rural and has much lower rates of growth in water use, population, and economic development.

This information will allow us to integrate a detailed temporal and spatial database of groundwater withdrawal with existing groundwater flow models, yielding a tool to assess societal demands for economic growth and development in the context of water-resources planning and aquifer sustainability. Proposals for industrial, agricultural, commercial, and residential development may then be evaluated in the context of competing societal uses for groundwater. Forecasts of future water levels and baseflow may be based on realistic

scenarios of land-use change, and consequently can be used by planners and managers to assess the impacts of land-use patterns on water resources.

We will also investigate the impact of current practice in Wisconsin for tracking groundwater use on estimates of groundwater use, and propose a model for collecting (and/or estimating) groundwater pumping and discharge data in the state. Project results will be of interest to communities across the Great Lakes region, where, although there is a seemingly abundant supply of fresh water from the Cambrian sandstone aquifer and the lakes themselves, local governments actively participate in regional efforts of ecosystem preservation and water-supply planning. Project results will also be framed within a series of specific recommendations regarding water use and water discharge reporting from well owners, leading to improved strategies for compiling, estimating and reporting water use by counties and economic sectors.

1. **Project Update:** Overview of your progress on this project during the past year.

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.

# Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study

### **Basic Information**

Title:	Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study
Project Number:	2000WI8G
Start Date:	9/1/2000
End Date:	8/31/2004
Funding Source:	104G
Congressional District:	WI-2
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Toxic Substances, Non Point Pollution
Descriptors:	mercury, hydrology, dissolved organic carbon, transport, wetlands, lakes
Principal Investigators:	

- Harris, R.C., J.W.M. Rudd, M. Amyot, C. Babiarz, K. Beaty, P. Blanchfield, A. (Drew) Bodaly, B. Branfireun, C.C. Gilmour, A. Heyes, H. Hintelmann, J. Hurley, C. Kelly, D. Krabbenhoft, S. Lindberg, M. Paterson, C. Podemski, K. Rolfhus, K. Sandilands, K. Scott, G. Southworth, V. St. Louis. 2001. METAALICUS: A Study to Determine the Relationship Between Mercury Deposition and MeHg Concentrations of Fish. Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments Sponsored by the U.S. Environmental Protection Agency. West Palm Beach, Florida. May.
- Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott and V.L. St. Louis. 2002. Reactivity and mobility of new and old mercury in a boreal forest ecosystem during the first year of the METAALICUS study. Environmental Science and Technology. 36(23):5034-5040.
- 3. Babiarz C.L, J.P. Hurley, D.P. Krabbenhoft, C.C. Gilmour, and B.A. Branfireun. 2003. Application of ultrafiltration and stable isotope amendments to the partitioning of mercury in lake water and over land runoff. Science of the Total Environment. 304: 295-303
- 4. 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.
- 5. Hurley, J.P., M. Amyot, M., K. Beaty, K., P. Blanchfield, R.A. Bodaly, B. Branfireun,, C.Gilmour,

R.C. Harris, A. Heyes, H. Hintelmann, C. Kelly, D. Krabbenhoft, S. Lindberg, M. Paterson, C. Podemski, J.W.M. Rudd, K. Sandilands, G. Southworth, V. St. Louis. 2003. Watershed-level Addition of Mercury Stable Isotopes: A Tool for Understanding Processes from Deposition to Bioaccumulation. Conference on Frontiers in Assessment Methods for the Environment (FAME). Minneapolis, MN. August. (Invited).

- Babiarz, C., J. Hurley, D. Krabbenhoft, T. Trinko, M. Tate, S. Chadwick, and D. Armstrong. An overview of the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States. American Water Resources Association. Minocqua, Wisconsin. February 27 & 28, 2003.
- Babiarz, C., J. Hurley, D. Krabbenhoft, T. Trinko, M. Tate, S. Chadwick, and D. Armstrong. A Hypolimnetic Mass Balance of Mercury from a Dimictic Lake: Results from the METAALICUS Project. 12th International Conference on Heavy Metals in the Environment. Grenoble, France. May 26-30, 2003.
- 8. Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft, T. R. Trinko, M.T. Tate. Towards a Hypolimnetic Mass Balance: Results from the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS). Experimental Lakes Area, Canadian Dept of Fisheries and Oceans. June 24, 2003.
- 9. Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft. Early results from the mercury experiment to assess atmospheric loading in Canada and the United States. Environmental Chemistry & Technology Program, University of Wisconsin. September 19, 2003.
- Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft, T. R. Trinko, M.T. Tate. Towards a Hypolimnetic Mass Balance: Results from the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS). 26th Midwest Environmental Chemistry Workshop. Iowa City, Iowa. October 10-12, 2003.
- 11. Chadwick, S.P., Babiarz C.L., Hurley J.P., and Armstrong, D.E. (In Press) Biogeochemical cycling of iron, manganese and dissolved organic carbon in a seasonally anoxic lake amended with stable isotopes of mercury. Science of the Total Environment.
- 12. Babiarz, C. L., J. P. Hurley, D. P. Krabbenhoft, S. P. Chadwick, T. R. Trinko, and M. Tate. (2004) Towards a hypolimnetic mass balance of Hg in a dimictic lake: Early results from the METAALICUS project. RMZ Materials and Geoenvironment 51:778-782.
- 13. 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. In Press, Water Resources Research.

#### Project Update: 6-15-05

#### **Project Title:**

Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study

#### **Project Investigators:**

James P. Hurley, University of Wisconsin Water Resources Institute, David P. Krabbenhoft, U.S. Geological Survey, Kristofer R. Rolfhus, University of Wisconsin

## Background

#### **Problem and Research Objectives**

Fish consumption advisories have been issued in 40 states in the U.S. and all provinces of Canada due to deleterious health effects associated with ingesting fish of high Hg concentrations. Nearly all of the mercury in fish is methylmercury (MMHg), a neurotoxin that biomagnifies to high concentrations toward the top of aquatic food webs. Small quantities of methylmercury in the diet can adversely affect wildlife and humans. Human and wildlife exposure to methylmercury is almost entirely through the consumption of fish. Thus, the greatest present research need is to further understand what drives this widespread contamination problem and to unravel the complex set of processes that link nonpoint mercury loading to bioaccumulation in fish.

There is a general consensus that, in the absence of direct point-source discharges, the primary source of Hg that bioaccumulates to upper trophic levels is atmospheric deposition. The U.S. EPA's Science Advisory Board identified in The Mercury Report to Congress (EPA 1997) several gaps regarding our current understanding of Hg cycling. In particular, they pointed to ecosystem cycling of atmospherically derived Hg, including post-depositional transport pathways, rates of transport, and biogeochemical transformation processes (methylation/demethylation and reduction/evasion).

Watershed characteristics (such as land cover patterns, soil type and glacial deposits) exert a strong influence on export, partitioning and speciation of  $Hg_T$  and MMHg from watersheds. These characteristics directly affect the types and amounts of suspended particulate matter (SPM), colloids, forms of dissolved organic compound (DOC), and other ligands transported within and from terrestrial portions of catchments to down-gradient aquatic ecosystems where bioaccumulation of Hg in the food web begins. Elucidating the connections between atmospheric Hg loading and various watershed components (forest soils and vegetation, bedrock, wetlands, streams and lakes) and bioaccumulation in the food web is the general scope of the Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S. (METAALICUS) project.

METAALICUS is a large, multidisciplinary, multi-investigator project, with an anticipated fouryear budget totaling approximately nine million dollars (including the purchase of isotopes). The project is a whole-watershed application of stable-Hg isotopes at the Experimental Lakes Area (ELA), near Kenora, Ontario. The ELA is one of the very few places where direct application of contaminants in field studies is allowable, and emphasizes the unique opportunity that this study provides.

#### **Overall Objectives of the METAALICUS Project**

1. Provide direct information on the effects of nonpoint atmospheric Hg deposition on bioaccumulation in predatory fish

2. Determine the relative importance of the watershed (including upland and wetland portions) and direct deposition in determining bioaccumulation of Hg in predatory fish of a lacustrine environment.

3. Provide (for the first time) direct measurement of ecosystem response times between Hg deposition and transport, and provide a direct comparison of the reactivity of Hg added via "new deposition" and Hg considered as the historic pool within the watershed.

4. To more definitively trace Hg processes and pathways at the ecosystem scale using nearambient levels of isotopes.

5. Provide information on rates and pathways of Hg cycling to support a watershed-based Hg cycling model

#### **Objectives for University of Wisconsin-USGS Subproject of METAALICUS**

Because METAALICUS is a large project, principal investigators have been assigned various focus areas to ensure complete coverage of the major Hg transformation and transport studies. The investigators associated with our subproject will be specifically addressing upland and wetland Hg-cycling processes and pathways that contribute to Hg accumulation in aquatic food webs. Our efforts within this subproject support overall objectives 2 through 5 above.

Our objectives for this subproject are to:

1. Determine the fraction of a watershed Hg yield that is "new" versus that derived from the historic pool of Hg in the soils and vegetation.

2. Provide direct observations of the extent of mobility of new Hg in upland soils and wetland peat.

3. Isolate and quantify transport vectors (dissolved organic carbon, colloids, particulates) leading to export from different watershed components.

4. Assess the effects of partitioning and pathway in influencing bioavailability of Hg derived from uplands and wetlands to the study lake.

5. Elucidate the contribution of new versus historic Hg to the formation and optimal locations for methylation of Hg and relative mobility for transport from the watershed to the lake.

#### Methodology

The experimental design consists of both loading and tracer experiments. Mercury has an ideal distribution of stable isotopes that are all readily available from specialized distributors. We will increase Hg loads using 95% pure stable (nonradioactive) isotope of mercury [e.g., <sup>198</sup>Hg(NO<sub>3</sub>)<sub>2</sub>, <sup>200</sup>Hg(NO<sub>3</sub>)<sub>2</sub>, <sup>202</sup>Hg(NO<sub>3</sub>)<sub>2</sub>] using the techniques in Hintelmann et al. 1995 and Hintelmann and

Evans 1997. The spike will be delivered to upland/wetland plots and mesocosms by diluting the mercury isotope into rainfall collected on site. During full-scale ecosystem addition of spike-equilibrated water, we will add separate isotopes to the upland, wetland and lake components of the watershed. The use of enriched stable isotopes of Hg allows for the analytical discrimination of new "labeled" Hg and background Hg at trace concentrations. Ratios of isotopic Hg to ambient Hg in the same samples can be analyzed to determine the relative availability of "old" versus new Hg inputs. Isotopic Hg can also be used to follow Hg through different watershed transformation and transport processes and subsequently through different compartments of the lacustrine food web.

During both pilot scale and full-scale implementation, we will use physical and chemical fractionation techniques (developed at the University of Wisconsin) to describe the composition and chemical lability of organic-Hg complexes in runoff and wetland discharge. These methods serve to separate aqueous Hg species by size and their ability to form complexes with competing solid phase ligands attached to resins, creating both concentrated ligand and ligand-free test solutions. Ultrafiltration methods will characterize the importance of sub-particulate fractions (colloids and truly dissolved species) to the transport and bioavailability of upland and wetland Hg. For example, we have observed that inorganic Hg in the <100 kD fraction of inundated ELA forest soil extracts are the most readily available for uptake to aquatic bacteria, using the *mer-lux* bioreporter assay (K. Scott, pers. comm.). The Chelex studies allow for kinetic and thermodynamic evaluation of Hg binding strength and reactivity, and directly addresses whether weakly-bound Hg complexes are biogeochemically important. The XAD treatments will further characterize the organic ligands to which Hg is bound, including hydrophobicity, acidity, and molecular weight. We will also be conducting reactive Hg measurements to operationally determine chemical lability of Hg-DOC fractions.

This project utilizes the cooperative efforts of the University of Wisconsin Water Chemistry Program (UWWCP) Mercury Laboratory and the USGS Mercury Research Laboratory (both in Madison, Wisconsin). Groups at both laboratories have specialized facilities and instrumentation for trace metal research. Each laboratory has dedicated clean room facilities developed for lowlevel Hg processing and analysis. The UWWCP facility has three Hg analytical systems (Tekran, Brooks-Rand) as well as supporting instrumentation such as a Perkin-Elmer Plasma II ICP-OES; Waters 600 HPLC with 991 Diode Array Detector; PE 5100Z GFAA; Shimadzu TOC-500 with a particulate carbon analyzer. Modern shop facilities located in our UW building allows for fabrication of specialized equipment. The USGS facility houses the main instrumentation for isotopic analyses for this study, a new Perkin-Elmer Elan 6000 that is dedicated for mercury-only isotopic analysis. In addition, the USGS lab has four Tekran Hg analytical systems, and an OI TOC-1010 carbon analyzer.

# 1. Project Update:

### 2004 Sampling Strategy and Field Campaigns

Our 2004 field-season strategy focused on the construction of a well-constrained hypolimnetic mass balance for mercury in the hypolimnion of the lake. We also committed resources to specific experiments designed to understand the underlying processes: Sediment accumulation

rates (including the historic depositional record for mercury), the kinetics of mercury partitioning to lake particles, and the retrieval of a mixed-core incubation experiment.

We completed six monthly field campaigns from May to October 2004. Our standard sampling protocol included water-column sampling and sediment-trap processing to establish the hypolimnetic mass-balance for mercury in the lake. The water column samples are used to estimate the standing pool of mercury in the hypolimnetic water column, and the sediment trap samples are used to estimate particle transport into and out of the hypolimnion. We also measured mercury in pore-waters of freshly fallen particulate matter that lies on the surface of the sediments. This pore-water data is important for calculating the flux of mercury out of the sediments from diffusion. Initial data suggests this term is large and may account for the buildup of MeHg in the hypolimnion. We also collected sediment cores on a regular basis (July, August, and October) to document the net storage of mercury in the lake sediments. This data will be combined with previous data to track seasonal changes in mercury content, and will also be combined with detailed geochronology information from Dr. Daniel Engstrom of the Science Museum of Minnesota (see collaboration section below).

In addition to the standard sampling protocol, we collected samples for specific experiments designed to look at the reactivity and biouptake of Hg in the watershed.

- In July, we collected extra surface water from the west basin to conduct a particle scavenging experiment for mercury. The kinetics of Hg sorption to particles was investigated using <sup>201</sup>Hg(II) as a tracer in a time series experiment. Additional experiments were performed to determine the role of Hg loading on the partition coefficient.
- In August we collected rain water from ELA to be used in a parallel biouptake project in collaboration with Dr. Patrick Gorski (see collaboration section below).
- Also in August, we collected hypolimnetic water to conduct an experiment on sample storage methods for DOC. Anoxic waters with high iron content can result in flocculation of DOC if the samples are frozen. Flocculation interferes with the analysis resulting in artificially low concentrations.
- In September we collected extra water at the sediment-water interface to verify and expand the experiment on sample storage methods for DOC.
- In October, we retrieved a mixed-core sediment incubation experiment that was initiated before the first addition of the lake isotope in June 2001. The goal of the incubation was to assess post-depositional migration of mercury (up or down a sediment core) and post depositional methylation/demethylation of mercury (conversion between the inorganic and organic forms). This experiment will be the first insitu experiment to test an important assumption of sedimentation models (that mercury is inactive once buried at depth). In short, sediments from Lake 658 were homogenized, spiked with <sup>201</sup>Hg and Me<sup>199</sup>Hg and placed in both the littoral and pelagic areas of the lake. Because the original cores were well mixed, any change to the native Hg profile will indicate the mobility of old Hg. Changes to the <sup>201</sup>Hg and Me<sup>199</sup>Hg profiles will either indicate methylation/demethylation or post-depositional migration of recently deposited Hg with depth. Changes in the <sup>202</sup>Hg or Me<sup>202</sup>Hg will indicate near surface recycling of new Hg. The retrieved sediments will be analyzed for isotopic Hg, MeHg and ancillaries (major ions, carbon, water content/porosity, etc...).

#### **Sample Analysis and Data Reduction**

In 2004 we completed the analysis for our standard suite of water column and sediment trap samples through the end of the 2003 field season. For the 2004 field season, approximately one third of our aqueous total-mercury samples have been analyzed and 75% of our aqueous methylmercury samples have been analyzed. Remaining mercury samples include solid-phase sediment transects from each field season and sediment samples from the mixed-core experiment. Less than 20% of all non-mercury samples remain to be analyzed. In addition, our entire data base was updated to match reporting standards set by METAALICUS principal investigators at the 2002 annual meeting. The reporting standards allow data sets to be compared across all participating METAALICUS research groups.

#### **Outside Presentations**

Our research group presented several papers on the METAALICUS project in 2004.

**7<sup>th</sup> 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.*

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

**Fall Meeting of the American Geophysical Union** in San Francisco, California, December 14-17, 2004. Dr. Christopher Babiarz was recruited to give an invited presentation on *Transport and transformation of mercury through soils from contrasting watersheds: Implications for resource management.* This was the only talk on mercury in a session entitled *Soil Retention of Atmospheric Solutes.* The session also included presentations on sulfate, nitrate, and aluminum that allowed for strong cross-disciplinary discussion.

#### **Collaboration and Outreach**

Our research group continues to collaborate with other researchers on the METAALICUS project. In addition to performing specialized isotopic mercury analysis with the USGS isotope

laboratory operated by Dr. David Krabbenhoft (Middleton, WI), we collaborated with the following scientists during the last year:

**Dr. Nives Ogrinc** of the J. Stefan Institute in Ljubljana, Slovenia. Dr. Ogrinc is an expert in carbon cycling and its sources (i.e. terrestrial vs. in-lake). In June, 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** of the Minnesota Science Museum. Dr. Engstrom is an expert on sedimentary record of freshwater lakes. He and his team joined us on a field campaign in October to collect and slice sediment cores for lead-210 analysis. The results will be 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 this project). Dr. Engstrom reports that lead-210 analysis and loss-on-ignition (LOI) analysis are both progressing smoothly. We expect the results in summer 2005 along with sub-samples of sediment for mercury analysis in our laboratory.

**Dr. Patrick Gorski** of the University of Wisconsin. Dr. Gorksi is an expert on bioaccumulation of mercury in the lower food web. In December, he conducted a bioassay on ELA rain water in cooperation with the WI State Laboratory of Hygiene Biomonitoring Group. The results of this experiment will help determine the availability of mercury in rain as it mixes with lake water.

#### We also participated in two outreach projects:

• In November, 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. 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).

#### **Project Completion Timeline**

To date we have made significant progress toward the specific goals outlined in our research plan. The field component of the project is complete, and we have strong data sets that include: a mixed sediment core experiment, seasonal lake profiles, sediment trap deployment, and experiments investigating iron and DOC controls on mercury speciation. With the exception of sediments, all samples from 2003 (and earlier) have been analyzed, and we anticipate finishing the analysis of 2004 water column samples by September 30, 2005. We expect analysis of sediment samples to be completed by December. We have one manuscript in press, and we expect to submit three more by the end of the year (not including a lake chemistry overview paper that includes our data but is being written by a colleague at the Smithsonian Institution).

- 1) Speciation controls on the partitioning of HgT and MeHg in lake amended with stable *isotopes*. Target Journal: <u>Biogeochemistry</u>
- 2) Isolation of DOM species of HgT and MeHg using diethylaminoethyl cellulose. Target Journal: Environmental Science & Technology
- 3) A Hypolimnetic mass balance of mercury in a seasonally anoxic lake amended with stable isotopes of mercury. Target Journal: Environmental Science & Technology

4) Role of iron, manganese, and organic carbon on the sedimentation of amended mercury.

Target Journal: <u>Water research</u>, <u>Biogeochemistry</u>, or <u>Canadian Journal of Fisheries and Aquatic</u> Sciences

5) *Post-depositional methylation, demethylation, and migration of mercury in carbonaceous lake sediment.* Target Journal: <u>Environmental Science & Technology</u> (To be submitted in 2006).

## 2. Notable Achievements and Awards:

Dr. Christopher Babiarz was recruited to give an invited presentation on METAALICUS results at the Fall Meeting of the American Geophysical Union (December 14-17, in San Francisco, CA). The presentation was entitled *Transport and transformation of mercury through soils from contrasting watersheds: Implications for resource management*, and 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.

## 3. Publications:

- Chadwick, S.P., Babiarz C.L., Hurley J.P., and Armstrong, D.E. (In Press) *Biogeochemical* cycling of iron, manganese and dissolved organic carbon in a seasonally anoxic lake amended with stable isotopes of mercury. Science of the Total Environment.
- Babiarz, C. L., J. P. Hurley, D. P. Krabbenhoft, S. P. Chadwick, T. R. Trinko, and M. Tate. (2004) *Towards a hypolimnetic mass balance of Hg in a dimictic lake: Early results from the METAALICUS project.* RMZ Materials and Geoenvironment **51**:778-782.

# Monitoring the Effectiveness of Phytoremediation and Hydrogeologic Response at an Agricultural Chemical Facility

# **Basic Information**

Title:	Monitoring the Effectiveness of Phytoremediation and Hydrogeologic Response at an Agricultural Chemical Facility
Project Number:	2004WI112O
Start Date:	7/1/2002
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	dinoseb, phytoremediation, poplars, groundwater
Principal Investigators:	William DeVita

#### MONITORING THE EFFECTIVENESS OF PHYTOREMEDIATION AND HYDROGEOLOGIC RESPONSE AT AN AGRICULTURAL CHEMICAL FACILITY

#### WRI#: R/UW-REM-009, GCC#:03-REM-06

William M. DeVita, Laboratory Manager, Water and Environmental Analysis Laboratory, College of Natural Resources, University of Wisconsin – Stevens Point

Mark Dawson, Environmental Engineer, Sand Creek Consultants, Inc. and Hyde Environmental, Inc., Amherst, Wisconsin

July 1, 2002 – June 30, 2004

**Background** - Phytoremediation offers the prospect of using biotechnology to degrade or sequester contaminants from soil and groundwater, and/or slow the movement of shallow groundwater. Sequestration of heavy metals and degradation of petroleum hydrocarbons and volatile organic compounds is well documented; however, the fate of many pesticides is unclear. If groundwater movement can be slowed, possibly so will the movement of contaminants off-site, and therefore, a greater likelihood they will be degraded by biotic or abiotic processes, or be sequestered by plants.

The study site, located near Bancroft, Wisconsin, has a history of soil and groundwater degradation. Dinoseb (2, sec-butyl-4,6-dinitrophenol) is the primary contaminant of concern and this soil is unacceptable for conventional landfill disposal or landspreading. Sandy soil, shallow groundwater, and other factors make this a prime site to study the effects of phytoremediation. In June 2000, a mixture of 834 hybrid poplars, willows, and cottonwoods were planted in an effort to degrade and/or retard the movement of pesticides.

**Objectives** - The objectives of this research were:

- 1) Assess mortality and biomass production of the established trees at the site as they begin tapping into the capillary fringe of groundwater.
- 2) Correlate hydrologic response to transpiration rates at various times through the project duration (both daily and seasonal changes). Calculate radius of influence based on water table observations and correlate the results with a capture-zone model.
- 3) Determine changes in groundwater contaminant profile through the plots. Perform biannual testing on select monitoring wells (12 from the current project and three from the ACCP). Analyze a total of 32 samples per year on selected wells and piezometers. Install three to four piezometers with 2-foot screens to help assess the vertical extent of contamination.

**Methods** - Mortality is assessed in the fall by visual inspection of the tree and evidence of viable leaves or leaf buds. Occasionally, determination of a viable tree is difficult as they may appear dead in the fall (as evident by a dried main stem, lack of leaves and buds) then resprout from the base the following spring.

Biomass is estimated through direct measurement of trunk diameter and height as recommended by U.S. Forest Service North Central Experimental Station. The equation for this estimation is  $d^{2}$ \*h where d = diameter breast height and h = total tree height.

Hydrologic response is monitored with the use of groundwater elevation dataloggers (Aquarod – Sequoia Scientific) in three areas of the property. Elevation is logged once every 30 minutes with 1 mm of

accuracy. Transpiration is determined with the use of thermal dissipation probes (Dynamax, Inc.). These probes are inserted into the tree and sap velocity is determined as first proposed by Granier. Volume of sap is determined and assumed to be equal to water transpired. Transpiration is correlated to weather station (Davis Instruments) data and groundwater elevation.

Groundwater modeling was performed using WELFLO and Visual MODFLOW. Hydrogeologic conditions such as hydraulic conductivity, specific yield and saturated thickness were determined in previous studies. WELFLO uses analytical equations to predict drawdown near pumping wells. Visual MODFLOW is a numeric model used to predict groundwater contours in 2 or 3 dimensions.

Three monitoring well nests with 1-foot screens were replaced with 5-foot well screens. Four piezometers were installed at select points in the site to determine vertical extent of contamination. Groundwater samples were analyzed by EPA Method 8270 which utilizes gas chromatography/mass spectrometry.

**Results and discussion** - Dinoseb concentrations in groundwater continue to fluctuate widely. Slugs of dissolved contaminants are believed to be released during changing water table elevations and large rainfall events. The steady drop in groundwater elevation throughout the summers of 2003 and 2004 is believed to be the result of extensive pumping from high capacity wells and groundwater discharge to drainage ditches in the area. Sharp rises are associated with rainfall events and correlate with rainfall data collected at the site.

Diurnal fluctuations were observed to varying degrees beginning in July 2002 and throughout 2003, but were not observed in 2004. The maximum diurnal fluctuation observed was 10 mm. Diurnal fluctuations correlate with sap flow and evapotranspiration (as determined from weather station data), suggesting the diurnal fluctuations are the result of the trees extracting groundwater. Tree sap flow is affected by humidity, solar radiation, temperature and wind. Thermal dissipation probes determined that seven to 28 liters of groundwater per day are being transpired by each of the hybrid poplars during the time period measured (Sept. 30-Oct. 10). Assuming an average sap flow of 10 liters per day (lpd), 650 trees will transpire 6,500 liters per day, or 4.5 liters per minute, of groundwater removal. Subsequent measurements in the summer of 2004 have determined up to 100 liters per day with an average within 16 measured trees of 50 lpd.

Within the hydrogeologic assumptions made, WELFLO predicts that the drawdown observed with the AquaRods could be due to trees pumping at the transpiration rate observed. The use of MODFLOW showed only a very slight effect in the water table contours near the phytoremediation plot, which suggests that the trees are not capturing the groundwater that flows beneath the plot.

**Conclusions** - Fluctuations in groundwater contaminant concentrations indicate a source of dinoseb in the upgradient zone or possibly in the zone where containers were excavated. This makes it difficult to assess the impact hybrid poplars have on degradation of the contaminant. A separate study will evaluate tree tissue to determine the presence of dinoseb and dinoseb metabolites. It is evident that the trees are utilizing groundwater, and it is expected that retardation of groundwater flow will require more time.

Groundwater modeling portrays that the effect of the trees on groundwater flow becomes significant once the rate of evapotranspiration is increased by a factor of 10, which is expected in another two to three years.

Key words - dinoseb, phytoremediation, poplars, groundwater

**Funding** - Water Resources Institute, University of Wisconsin, McIntire-Stennis Cooperative Forestry Research Program.

# **Coupled Modeling of Gravity and Aeromagnetic Data For Analysis of the Waukesha Fault, Southeastern Wisconsin**

## **Basic Information**

Title:	Coupled Modeling of Gravity and Aeromagnetic Data For Analysis of the Waukesha Fault, Southeastern Wisconsin
Project Number:	2004WI119O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	1
Research Category:	Not Applicable
Focus Category:	None, None
Descriptors:	Aeromagnetic, Gravity, Coupled Modeling, Waukesha Fault,
Principal Investigators:	John D Skalbeck

# Publication

 PRELIMINARY RESULTS FROM COUPLED MODELING OF GRAVITY AND AEROMAGNETIC DATA IN THE WAUKESHA FAULT AREA OF SOUTHEASTERN WISCONSIN John D. Skalbeck, James N. Couch, Dennis M. Roy, Department of Geosciences, University of Wisconsin-Parkside, 900 Wood Road, Kenosha, WI 53141, presented at American Geophysical Union Fall Meeting 2003 in San Francisco, California, on December 11, 2003.

# **Project Summary**

Title:	Coupled Modeling of Gravity and Aeromagnetic Data For Analysis of the Waukesha Fault, Southeastern Wisconsin
Project ID:	R/UW-HDG-007 (WR03R003)
Investigator:	John D. Skalbeck, Assistant Professor, Department of Geosciences, University of Wisconsin-Parkside
Period of Contract:	July 01, 2003 – June 30, 2004
Background/Need:	Increased concerns about groundwater resources in Wisconsin have brought about the need for better understanding of the subsurface geologic structure that lead to developing conceptual hydrogeologic models for numerical simulation of groundwater flow. Models are often based on sparse data from well logs usually located large distances apart and limited in depth. Model assumptions based on limited spatial data typically requires simplification that may add uncertainty to the simulation results and the accuracy of a groundwater model. This research provides another tool for the groundwater modeler to better constrain the conceptual model of a hydrogeologic system. The area near the Waukesha Fault in southeastern Wisconsin provides an excellent research opportunity for our proposed approach because of the strong gravity and aeromagnetic anomalies associated with the fault, the apparent complexity in fault geometry, and uncertainty in Precambrian basement depth and structure.
<b>Objectives:</b>	The objectives of this research are to improve the current understanding of the subsurface geometry (offset and fault dip) of the Waukesha Fault in southeastern Wisconsin, to improve the current understanding of the Precambrian bedrock topography of the down-thrown area southeast of the Waukesha Fault, and to demonstrate the effectiveness of coupled modeling of gravity and aeromagnetic data for delineating the hydrogeologic settings in other areas of Wisconsin. This fault appears to exhibit complex geometry that is variable along its trend. Better definition of the fault subsurface geometry obtained from this research will allow for a better understanding of the effects of this fault on the hydrogeologic system. A better-constrained estimate of the Precambrian bedrock topography will provide needed information for a regional groundwater flow model. Results from this study can be used to demonstrate the effectiveness for delineating the hydrogeologic settings in other areas of Wisconsin.

Methods:	Coupled 2.75-dimensional modeling of existing gravity and aeromagnetic data was performed along seven northwest-southeast profiles, perpendicular to the trend of the Waukesha Fault and one north-south profile (Tie Line), using the commercially-available software program GM-Sys <sup>R</sup> . Cross-sections of the geologic subsurface were constructed from existing surface and subsurface geologic information and assigned initial density and magnetic properties from literature. Adjustment to structure and properties were made to yield acceptable fits between observed and model calculated gravity and aeromagnetic anomalies. Elevations from these model sections and from well logs were used to generate a 3-dimensional representation of the top of Precambrian bedrock.
Results and Discussion:	Acceptable fits between observed and model calculated gravity and aeromagnetic anomalies were obtained from the geologic models constructed for the eight profiles in the study area. A single well reaching bedrock on the down-thrown block provided excellent vertical control for initial model calibration. Profile model data yields a 3-D representation of the Precambrian bedrock top surface with elevations that range from 168 m above mean sea level (msl) on the up-thrown block to $-1318$ m msl on the down-thrown block. The prominent southwest-northeast trending drop in bedrock surface elevation is interpreted as the Waukesha Fault scarp.
Conclusions/ Implications/ Recommendations:	The results from this study show the Waukesha Fault as a high angle normal fault dipping to the southeast. Model topography of the Precambrian bedrock surface appears complex on both sides of the fault with a maximum vertical displacement of 560 m. A reasonable estimate of top of bedrock elevations southeast of the fault has been obtained from this study. Further model refinement will be conducted to improve structure interpretations for southeast Wisconsin. Results from this study have direct application to the groundwater flow model for southeast Wisconsin (Feinstein et al., 2004). These researchers now have an additional data set for the Precambrian basement configuration that can be utilized in the flow model. Coupled modeling of gravity and aeromagnetic data can be applied to other areas in Wisconsin with groundwater management issues such as arsenic contamination and excessive drawdown.
Key Words:	Aeromagnetic, Gravity, Coupled Modeling, Waukesha Fault, Precambrian Basement, Ground Water, Wisconsin
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# **Role of the Hyporheic Zone in Methylmercury Production and Transport to Lake Superior**

# **Basic Information**

Title:	Role of the Hyporheic Zone in Methylmercury Production and Transport to Lake Superior
Project Number:	2003WI45B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	2nd
Research Category:	None
Focus Category:	Geochemical Processes, Toxic Substances, Non Point Pollution
Descriptors:	None
Principal Investigators:	David Armstrong, Christopher L. Babiarz

#### **Project Summary**

**Title:** Role of the Hyporheic Zone in Methylmercury Production and Transport to Lake Superior **(WR02R002)** 

**Investigators**: David E. Armstrong (Professor), Christopher L. Babiarz (Assistant Scientist), and Matthew M. Meyer (Research Assistant), Environmental Chemistry and Technology Program, University of Wisconsin-Madison

This investigation was conducted to explore the role of the hyporheic zone in the production and transport of methyl mercury into surface waters. We selected a field site where total Hg and methyl Hg concentrations could be measured along hydrologic flowpaths. Our investigation focused on 1) the temporal and spatial distribution of total Hg and methyl Hg in ground waters, hyporheic zone waters and sediments, and waters of surface streams, and 2) the relation of temporal and spatial patterns of total Hg and methyl Hg concentrations to environmental factors and processes potentially important in controlling transport and fate for mercury.

We selected sub-watersheds of the Trout Lake watershed the field site for investigation of hyporheic zones processes. This site, located in Vilas County, Wis., is also within the investigation areas for the UW-Madison NSF Long Term Ecosystem Research program and the USGS Water, Energy, and Biogeochemical Budgets program. This enabled collaboration with scientists from these groups and use of USGS background information and groundwater sampling sites installed at the site. We compared hyporheic zones at two sites within the Allequash Creek watershed, upper springs and middle wetland, to neary by sites at North Creek and Stevenson Creek, all within the greater Trout Lake watershed. Sampling was conducted in 2003 and 2004.

Surface stream water concentrations ranged from 0.56 to 4.44ng/L for total Hg and 0.07 to 0.73 ng/L for methyl Hg. In general, highest total Hg concentrations coincided with the spring melt period, while highest methyl Hg concentrations were observed in August and June. The proportional level of methyl Hg in stream water was highly variable, ranging from 2.3 to 51.4% of total Hg.

Total Hg concentrations in ground waters were similar to those in surface stream waters. Transects at the two in the Allequash Creek watershed sites showed that mercury (as total Hg) was present at moderate concentrations in all groundwater samples, ranging from 0.36 to 8.78 ng/L at the middle wetlands site and 0.26 to 10.76 ng/L at the upper springs site. Concentrations varied temporally, tending to be lower in October than in April, June, or August. Concentrations also varied spatially, both with depth at a given site and along the transects. However, there was not a clear distinction between concentrations in deeper ground waters beneath upland hill slopes and shallow groundwater in the riparian zones. In contrast, methyl Hg concentrations in ground waters were generally low in comparison to concentrations of 1.1 ng/L were detected, one in April and the other in June.

In pore waters within hyporheic zones, concentrations of total Hg tended to be higher than concentrations in either surface waters or ground waters, averaging about 6 ng/L, and there was not a clear trend with depth at a given site. Similarly, concentrations of methyl Hg were

typically also higher in hyporheic waters (averaging about 0.4 ng/L) than in either ground waters or surface waters.

Two hyporheic zone sites provided a contrast between upwelling and downwelling groundwater and the influence on methyl mercury concentrations. At a groundwater upwelling site (Allequash middle wetland), methyl Hg concentrations decreased with depth below the sediment water interface, while at a groundwater upwelling site (Stevenson Creek), concentrations were relatively constant with depth. Similarly, the percent of total Hg present as methyl Hg decreased with depth at the upwelling site, with typical values of about 10 % in the upper 5 cm as compared to 5% or less in the 10-15 cm region. In contrast, at the downwelling site, methyl Hg was a more constant proportion of total Hg with depth, typically around 5%. These trends indicate that net methylation rates are highest near the sediment-water interface. Furthermore, since upwelling rates of groundwater are high, net methylation rates must be high in order to maintain the relatively high methyl mercury concentrations. These results indicated that upwelling ground waters in the hyporheic zone are an important source of methyl Hg to stream waters.

Concentrations of total and methyl Hg in sediment cores were also measured. At the middle wetland site, concentrations of total Hg were relatively constant over the upper eight cm, ranging between 81 and 105 ng/gdw and similar for cores taken at two different times. However, methyl Hg concentrations varied with time. Concentrations in an August, 2003 core increased from about 1.6 ng/gdw at 8 cm to about 7 ng/gdw in the upper 3 cm, corresponding to an increase of percent methyl Hg from < 2% at 8 cm to 9 % near the surface. However, a second core taken in October 2003 showed lower and relatively uniform methyl Hg concentrations and percentages over the 8 cm depth. Cores taken in August 2003 at other hyporheic zone sites showed increases in both the concentration and proportion of methyl Hg near the sediment water interface.

The results of this investigation show that the hyporheic zone is a region of mercury accumulation, providing a reservoir of inorganic Hg(II) for methylation. High concentrations of methyl Hg in the hyporheic zone are more likely a result of production within the hyporheic zone rather than transport to the hyporheic zone by upgradient ground water. Methylation rates are often sufficiently high to maintain high methyl Hg concentrations in rapidly upwelling ground waters, providing a source of methyl Hg to stream waters. The temporal and spatial variation in both concentrations and proportions of methyl Hg likely reflect corresponding variations in the activity of sulfate-reducing bacteria believed to be responsible for the production of methyl Hg or in the bioavailability of Hg(II) for methylation. Methylation rates may be influenced by the availability of organic substrates for microbial respiration, the concentration of sulfate available to serve as an electron acceptor for sulfate reducers, the formation of organic and sulfide complexes of Hg(II) which reduce the bioavailability of Hg(II) for methylation, and high concentrations and the concentration of Hg(II) sulfide neutral complexes believed to be important species of Hg(II) for methylation.

# Arsenic Contamination in Groundwater in Southeast Wisconsin

## **Basic Information**

Title:	Arsenic Contamination in Groundwater in Southeast Wisconsin
Project Number:	2003WI47B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	2nd
Research Category:	None
Focus Category:	Hydrogeochemistry, Toxic Substances, Water Quality
Descriptors:	None
Principal Investigators:	Jean Bahr, Madeline Beth Gotkowitz

- 1. Root, T.L., expected spring 2005. Arsenic in Groundwater in Southeastern Wisconsin: Sources of Arsenic and Mechanisms of Arsenic Mobilization. Ph.D. thesis, University of Wisconsin Madison, Department of Geology and Geophysics.
- Root, T.L., Bahr, J.M., and Gotkowitz, M.B., 2005. Controls on Arsenic in Groundwater in Southeastern Wisconsin, in Vlassopoulos, D., Benning, L., Meng, X., and ODay, P., Advances in Arsenic Research, American Chemical Society Symposium Series. (In press)

#### **PROJECT SUMMARY**

**Title:** Arsenic Contamination in Southeast Wisconsin: Sources of Arsenic and Mechanisms of Arsenic Release

Project ID: WR02R003

**Principal Investigators:** Dr. Jean Bahr, Professor, Department of Geology and Geophysics, University of Wisconsin - Madison; Madeline Gotkowitz, Associate Professor, Wisconsin Geological and Natural History Survey

**Research Assistant:** Tara Root, Department of Geology and Geophysics, University of Wisconsin - Madison

**Period of Contract:** 6/30/2002 – 6/30/2004

**Background/Need:** Groundwater in about 10 percent of wells open to Quaternary glacial and shallow bedrock aquifers in southeastern Wisconsin has arsenic concentrations greater than the U.S. Environmental Protection Agency's standard of 10 µg/l. Denser clusters of arsenic-impacted wells ([As]<sub>aq</sub>  $\geq$  10 µg/l) occur in localized areas. The lack of anthropogenic sources in these areas indicates that the arsenic is naturally occurring. Improved understanding of the controls on arsenic concentrations in groundwater is needed to inform efforts to prevent or reduce arsenic contamination in drinking water wells in southeastern Wisconsin.

**Objectives:** The objectives of this study were to characterize the source(s) of arsenic and the controls on arsenic concentrations in groundwater from the Quaternary and Silurian aquifers in southeastern Wisconsin.

**Methods:** We reviewed existing data to estimate the magnitude and spatial distribution of arsenic concentrations in groundwater from the Quaternary and Silurian aquifers in southeastern Wisconsin. Detailed field investigations were conducted near the city of Lake Geneva in Walworth County.

Using core samples from a borehole at Woods Elementary, geologic sources of arsenic were identified using X-ray diffraction and chemical extractions. We collected groundwater samples from private wells and a monitoring well installed in the borehole at Woods School. We also organized a private well sampling program in the Lake Geneva area. We examined water chemistry data for trends indicative of water-rock interactions that may mobilize arsenic. We conducted a pumping test at the Woods School monitoring well to evaluate the hydrogeology of the study area. Time series sampling during the pumping test provided information about the effect of pumping on arsenic concentrations.

**Results and Discussion:** The hydrostratigraphy in the Lake Geneva area includes a shallow aquifer consisting of glacially deposited sand and gravel. This aquifer is underlain by a confining unit of low-conductivity clayey till. A deeper discontinuous sand and gravel aquifer occurs beneath this confining unit on top of the Silurian dolomite. Pumping test results indicate that there is little hydraulic connection between the shallow Quaternary aquifer and the deeper Quaternary and shallow Silurian aquifers.

8 % of wells open to the Quaternary and/or Silurian aquifers in the study area have arsenic concentrations greater than 10  $\mu$ g/l. Near the city of Lake Geneva, more than 20 % of Quaternary and Silurian wells have arsenic concentrations greater than the E.P.A. standard. The highest arsenic concentrations (85  $\mu$ g/l) occur

in wells open to the Silurian dolomite. The maximum arsenic concentrations in wells open to Quaternary deposits are around  $30 \mu g/l$ .

Low to moderate solid-phase concentrations of arsenic (2 mg/kg to 20 mg/kg) occur throughout the entire thickness of Quaternary sediments in the study area. From a mass balance perspective, such low to moderate solid-phase arsenic concentrations, under geochemical conditions that release arsenic to groundwater, are sufficient to lead to aqueous arsenic concentrations that exceed the 10 µg/l standard. Arsenic is released from aquifer sediments during laboratory experiments designed to dissolve (hydr)oxide minerals. These results, combined with groundwater chemistry data suggest that arsenic is released to the groundwater via reductive dissolution of (hydr)oxides. In the Lake Geneva area, hydrogeologic, and geochemical factors create reducing conditions that lead to arsenic mobilization in the deep Quaternary and upper Silurian aquifers. Groundwater in shallow Quaternary sediments is not as reducing as in the deeper system and is largely unaffected by arsenic.

#### Conclusions/Implications/Recommendations:

- Where geochemical conditions are sufficiently reducing, low solid-phase arsenic concentrations associated with (hydr)oxide minerals (on the order of a few parts per million) are sufficient to sustain groundwater arsenic concentrations greater than the 10 µg/l standard.
- All well owners in southeastern Wisconsin should test well water for arsenic because of the potential for even low levels of solid phase arsenic in glacial deposits to impact groundwater in glacial and shallow bedrock aquifers.
- New wells in the Lake Geneva area should not be completed in the deep Quaternary aquifer. The only viable alternative for existing arsenic-impacted wells is treatment to remove arsenic from drinking water.
- A single model of arsenic release is not adequate to account for the occurrence of arsenic in groundwater across the state. Oxidizing conditions cause arsenic release from sulfide minerals in the St. Peter aquifer in the Fox River Valley, but reducing conditions release arsenic to parts of the Quaternary and Silurian aquifers in southeastern Wisconsin. While the findings of this work are limited to the study area, similar geologic and geochemical conditions may be present in the Quaternary aquifer in other areas of Wisconsin.

#### **Related Publications:**

Root, T.L., expected spring 2005. Arsenic in Groundwater in Southeastern Wisconsin: Sources of Arsenic and Mechanisms of Arsenic Mobilization. Ph.D. thesis, University of Wisconsin –Madison, Department of Geology and Geophysics.

Root, T.L., Bahr, J.M., and Gotkowitz, M.B., 2005. Controls on Arsenic in Groundwater in Southeastern Wisconsin, *in* Vlassopoulos, D., Benning, L., Meng, X., and O'Day, P., Advances in Arsenic Research, American Chemical Society Symposium Series. (*In press*)

Tara Root received a student research award from the Hydrogeology Division of the Geological Society of America for work on this project (2002).

Key Words: Arsenic, groundwater, Quaternary and Silurian aquifers, southeastern Wisconsin

**Funding:** University of Wisconsin System and the Wisconsin Department of Natural Resources with additional support from the United States Geological Survey, the Geological Society of America, the Wisconsin Geological and Natural History Survey, and the United States Department of Energy Office of Civilian Radioactive Waste Management.

# **Evaluation of Contamination of Groundwater around Landfills**

# **Basic Information**

Title:	Evaluation of Contamination of Groundwater around Landfills
Project Number:	2003WI59O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Water Quality
Focus Category:	Groundwater, Non Point Pollution, Water Quality
Descriptors:	contamination, landfills
Principal Investigators:	Tuncer B. Edil

#### **Evaluation of Contamination of Groundwater Around Landfills**

T. B. Edil, University of Wisconsin-Madison, Civil and Environmental Engineering; C. H. Benson, University of Wisconsin-Madison, Civil and Environmental Engineering; and

J. Connelly, Wisconsin Department of Natural Resources, Bureau of Waste Management Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2005

Wisconsin relies on groundwater as a primary source of drinking water. Therefore, protecting groundwater is essential to the health and welfare of Wisconsin's residents. A variety of threats to groundwater quality exist. Solid waste landfills constitute a potential major threat, because more than 10 million tons of solid waste is landfilled in Wisconsin annually. Accordingly, assessing the level and pervasiveness of contamination of groundwater associated with engineered landfills in Wisconsin is imperative. The study being proposed will make this assessment through a two-phase investigation. The first phase consists of a comprehensive evaluation of data collected by the Wisconsin Department of Natural Resources (WDNR) characterizing the chemical constituents in leachate, pan lysimeters, gradient control layers, and monitoring wells associated with engineered landfills in Wisconsin. The second phase will evaluate the causes and mechanisms of contaminant transport in engineered landfills, and, if necessary, develop plans to prevent future contamination. This second phase will also take advantage of recent advances in understanding and modeling contaminant transport through liner systems, including composite liner systems. This project would be conducted jointly by investigators from the University of Wisconsin-Madison and staff from WDNR.

#### **Project Update:**

Analysis of the data presented in the WDNR Groundwater Environmental Management System (GEMS) database indicates that more than half of the 675 licensed landfills in the state show some presence of volatile organic compounds (VOCs) in the landfill leachate, lysimeters, or monitoring wells. Landfill sites constructed with a lysimeter as one of the components were selected for further analysis. These sites were selected to maintain a representative, yet manageable data set and to provide chemical constituent data directly above (leachate) and beneath (lysimeter) the liner system. All 675 sites were examined to determine that 88 sites were constructed with one or more lysimeter(s) as a component of the landfill and were thus further analyzed for VOC concentrations. Thirty-eight of the 88 sites had detects of one or more VOC at or above the limit of detection in the lysimeter. Concentrations of each of the 47 VOC monitored for by the WDNR were examined in the leachate and lysimeter at 91 landfill cells to determine which VOC's were most prevalent. The aforementioned analysis indicated there were approximately 4,900 VOC detects in leachate and 1,800 VOC detects in lysimeters above the limit of detection. There were 1330 leachate samples and 215 lysimeter samples above the DNR enforceable standard. The concentration of detects above the enforceable standard ranged from being at the enforceable standard to 10 or more times that of the enforceable standard. VOC concentrations found in leachate and lysimeters of Wisconsin landfills was similar to the range of concentrations found by other researchers (Kmet and McGinley 1982, Sirdharan and Didier 1988, Friedman 1988, Battista and Connelly 1989, Forst et al. 1989, Gibbons et al. 1992, Tedder 1992, Bonaparte and Gross 1990/1993, Maxson and Feeney 1993, Rowe 1995, Krug and Ham 1995, Tilkens and Svavarsson 1995, Bonaparte et al. 1996, Townsend et al. 2000, Kjeldsen et al. 2002).

Plots of concentration variation versus elapse time for each VOC detected were created for all leachate-sampling points and lysimeters with detects. The aforementioned analysis resulted in 750 plots. A linear regression on time was performed for each plot to determine if the slope of the regression line was statistically different from zero (using a significance level of 0.05). Graphical results show VOC concentrations in both leachate and lysimeters are highly variable. Regression analysis shows that in most cases (75%) there is no temporal trend. In 22% of the cases a decreasing temporal trend is exhibited and 3% show an increasing temporal trend.

Landfill sites with detects of the same VOCs, in both leachate and lysimeters, were examined to determine what type of liner each site was designed with. This information, along with the VOC concentrations in leachate, was used to determine realistic inputs for the parameters used in the van Genuchten transport equation. Other parameters used in the van Genuchten transport equation were determined from a literature review (Park and Nibras 1993, Foose 1997, Kim et al. 2001, Sangam and Rowe 2001). Results from transport analysis show that field data (e.g. VOC concentrations in lysimeters) tends to be underestimated by the van Genuchten transport equation. That is, VOC concentrations in lysimeters of landfills in Wisconsin are generally an order of magnitude (or more) higher than the concentrations determined using the van Genuchten transport equation.

Final comparisons of construction documentation and examination of some remaining literature are currently being made to help draw conclusions about what, if any, correlation can be made between VOC concentration and liner type (i.e., if there is a statistically significant difference in VOC concentrations at clay-lined versus composite-lined sites). Also, two papers, describing (1) leachate characteristics and (2) lysimeter concentrations and transport modeling are currently being revised and completed.

# An Assessment of Aquifer Storage Recovery for Selected Generic Hydrogeologic Settings in Wisconsin

## **Basic Information**

Title:	An Assessment of Aquifer Storage Recovery for Selected Generic Hydrogeologic Settings in Wisconsin
Project Number:	2003WI63O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
<b>Research Category:</b>	Ground-water Flow and Transport
Focus Category:	Models, Water Supply, Groundwater
Descriptors:	aquafer storage, aquafer recovery
Principal Investigators:	Mary Anderson

- 1. Lowry, C.S. and Anderson, M.P., 2004, Modeling Aquifer Storage Recovery for a Representative Setting in Wisconsin, (abstract), in Wisconsin Ground Water Association Annual Conference Program: Wisconsin Dells, Wis., Wisconsin Ground Water Association, p. 4. Award: Best Graduate Student Paper.
- 2. Lowry, C.S. and Anderson, M.P., 2004, Defining Controlling Factors of Aquifer Storage Recovery Using Advection and Dispersion Models, (abstract), in Understanding and Managing Water Resources for the Future: Wisconsin Rapids, Wis., Wisconsin Section of the American Water Resources Association, p. 9
- 3. Lowry, C.S. and Anderson, M.P., 2003, An Assessment of Aquifer Storage Recovery for a Generic Hydrogeologic Setting in Wisconsin using Groundwater Flow and Transport Models, (abstract), in Ground Water in Coastal Zones: Availability, Sustainability, and Protection: Orlando, Fla., Assoc. of Ground Water Scientists and Engineers, p. 68-69
- 4. Lowry, C.S. and Anderson, M.P., 2003, Assessment of Aquifer Storage Recovery for a Generic Hydrogeologic Setting in Wisconsin, in Poeter, E., et al., editors, MODFLOW and More 2003 Understanding Through Modeling: Golden, Colo., p. 824-828
- 5. Lowry, C.S., 2004, Assessment of Aquifer Storage Recovery: Defining Hydraulic Controls on Recovery Efficiency at Three Representative Sites in Wisconsin, MS Thesis, Department of Geology
and Geophysics: Madison, Wis., University of Wisconsin - Madison, 104 p.

#### **PROJECT SUMMARY**

**Title:** An Assessment of Aquifer Storage Recovery for Selected Representative Hydrogeologic Settings in Wisconsin

Project I.D.: WR03R005

**Principal Investigator(s):** Mary P. Anderson, Professor, Department of Geology and Geophysics, University of Wisconsin-Madison

Research Assistant: Christopher S. Lowry, Department of Geology and Geophysics, University of Wisconsin-Madison

Period of Contract: July 1, 2003 - June 30, 2004

**Background/Need:** Owing to increased demand on groundwater accompanied by increased drawdown in water levels, emerging technologies, such as aquifer storage recovery (ASR), are being used in the State of Wisconsin to optimize available water resources and reduce adverse effects of pumping. ASR is defined as the injection and storage of water in a suitable aquifer when demand is low and recovery from the aquifer when demand increases. ASR reduces the effects of peak demand on an aquifer by supplementing water in storage in the aquifer when demand is low. An ASR pilot facility in Green Bay, Wis., was recently closed owing to concerns over mobilization of arsenic. An ASR facility in Oak Creek, Wis., near Milwaukee, has gone through several test cycles and is awaiting final approval from the Wisconsin Department of Natural Resources. Another facility is contemplated for the City of Waukesha.

**Objectives:** The objectives of this research were to: (1) investigate the hydraulic controlling factors on ASR as they relate to the amount of water that can be recovered, i.e., the recovery efficiency, in selected representative hydrogeologic settings in Wisconsin; (2) develop a methodology using numerical flow and transport models whereby the hydraulics of ASR systems can be investigated.

**Methods:** Three representative settings in Wisconsin were chosen to evaluate the hydraulic controlling factors on recovery efficiency: a confined sandstone aquifer, a glacial drift system and an unconfined dolomite aquifer. Flow models were created using the groundwater flow code MODFLOW (McDonald and Harbaugh, 1988) linked to the particle tracking code MODPATH (Pollock, 1994) and transport code MT3DMS (Zheng and Wang, 1999) in order to simulate movement of injected and ambient water. The effects of regional hydraulic gradient, hydraulic conductivity, effective porosity, dispersion (mixing), volume of injected water, storage period, and rates of injection and recovery were considered.

**Results and Discussion:** Results from the three settings were qualitatively similar. Dispersion, as quantified by the dispersivity parameter, controls the mixing between injected and ambient water and is the most important control on recovery efficiency. Recovery efficiency varies inversely with dispersivity, effective porosity, regional hydraulic gradient and storage period. High values of dispersivity caused more mixing while high regional gradient and high values of

effective porosity caused high flow velocities causing water to move more quickly away from the ASR well. Under high velocities, injected water moved down gradient rapidly and out of the capture zone of the ASR well. Under long storage periods there was more time for the injected water to mix with the ambient water and move down gradient. Recovery efficiency increased asymptotically with volume of injected water. Increasing the hydraulic conductivity in a layer intersected by the ASR well caused an initial increase in recovery efficiency that leveled off and then decreased. Injection and recovery rates had little effect on recovery efficiency. Groundwater mounding and dewatering occurred in the unconfined dolomite aquifer when large volumes of water were injected and removed. Low values of transmissivity, characteristic of the dolomite aquifer, also caused significant groundwater mounding under some injection scenarios.

**Conclusions:** ASR is most suitable for confined systems such as the Sandstone Aquifer in the southeastern portion of the state and confined glacial drift systems. Groundwater mounding, which could cause flooding at the ground surface, and dewatering will limit the use of ASR systems in unconfined systems such as the Silurian Dolomite Aquifer in the northeastern portion of the state. The methodology developed in this project, in combination with site specific hydrogeologic data, will be useful to water utilities, consultants, and state agencies to determine suitable locations for ASR systems. With a clear understanding of controlling factors that affect recovery efficiency these agencies can determine if ASR potentially might meet a community's water supply needs before the initial test injection of water into the aquifer.

#### **Related Publications:**

- Lowry, C.S. and Anderson, M.P., 2004, Modeling Aquifer Storage Recovery for a Representative Setting in Wisconsin, (<u>abstract</u>), *in* Wisconsin Ground Water Association Annual Conference Program: Wisconsin Dells, Wis., Wisconsin Ground Water Association, p. 4. Award: Best Graduate Student Paper.
- Lowry, C.S. and Anderson, M.P., 2004, Defining Controlling Factors of Aquifer Storage Recovery Using Advection and Dispersion Models, (<u>abstract</u>), *in* Understanding and Managing Water Resources for the Future: Wisconsin Rapids, Wis., Wisconsin Section of the American Water Resources Association, p. 9
- Lowry, C.S. and Anderson, M.P., 2003, An Assessment of Aquifer Storage Recovery for a Generic Hydrogeologic Setting in Wisconsin using Groundwater Flow and Transport Models, (<u>abstract</u>), *in* Ground Water in Coastal Zones: Availability, Sustainability, and Protection: Orlando, Fla., Assoc. of Ground Water Scientists and Engineers, p. 68-69
- Lowry, C.S. and Anderson, M.P., 2003, Assessment of Aquifer Storage Recovery for a Generic Hydrogeologic Setting in Wisconsin, *in* Poeter, E., et al., editors, *MODFLOW and More 2003 Understanding Through Modeling*: Golden, Colo., p. 824-828
- Lowry, C.S., 2004, Assessment of Aquifer Storage Recovery: Defining Hydraulic Controls on Recovery Efficiency at Three Representative Sites in Wisconsin, <u>MS Thesis</u>, Department of Geology and Geophysics: Madison, Wis., University of Wisconsin - Madison, 104 p.

**Key Words:** aquifer storage recovery, groundwater, modeling, recovery efficiency, water resources management, Wisconsin

**Funding:** State of Wisconsin Groundwater Research Program through the University of Wisconsin Water Resources Institute, Department of Geology & Geophysics, UW-Madison.

# **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:	2003WI64O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Water Quality
Focus Category:	Treatment, Groundwater, Water Quality
Descriptors:	remediation
Principal Investigators:	Zhaohui Li

- 1. Li, Z., Reardon, C. R. and Evans, C. V. (2005) Desorption of Lead and Cesium from Kaolinite and Illite Using Cationic Surfactants, In Trends in Agriculture and Soil Pollution: New Research, Nova Science Publishers, in press.
- Li, Z. and Gallus, L. (2005) Surface Configuration of Sorbed Hexadecyltrimethylammonium on Kaolinite as Indicated by Surfactant and Counterion Sorption, Cation Desorption, and FTIR, Colloids and Surfaces A: Physicochemical and Engineering Aspects, in press.
- 3. Li, Z. (2004) Cationic surfactant in mineral surface modification and its environmental application In Recent Research Developments in Surface & Colloids, Research Signpost, Kerala, India, p. 79-95.
- 4. Willms, C., Li, Z., Allen, L., and Evans, C. V. (2004) Desorption of Cesium from Kaolinite and Illite Using Alkylammonium Salts, Appl. Clay Sci., 25, 125-133.
- 5. Li, Z. (2004) Surfactant-Enhanced Oxidation of Trichloroethylene by Permanganate Proof of Concept, Chemosphere 54, 419-423.

#### Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation

Z. Li, University of Wisconsin - Parkside, Geosciences Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2005

Remediation of dense nonaqueous phase liquids (DNAPLs) presents a great challenge to modern remediation science and technology. "Pump-and-treat," a common practice for removal of DNAPL contamination, is proven ineffective due to low aqueous solubility of the contaminants. Addition of surfactant to "pump-and-treat" operation increased the solubility of the contaminants and decreased the interfacial tension between water and DNAPL, resulting in an enhanced performance and shortened operation time. However, the water withdrawn from the "pump-and-treat" operation contains high concentrations of contaminants. Onsite treatment of the contaminated water becomes inevitable. Oxidation of DNAPLs by permanganate is another emerging technology. It has been shown that contaminant degradation rate was extremely fast with a half-life in minutes. In addition, the degradation products and intermediates are environmental innocuous. The proposed research is to combine the superior solubilization and mobilization power of surfactants with the fast contaminant degradation rate of permanganate during "pump-and-treat" operation in order to synchronize contaminant solubilization and degradation in a single step; i.e., to achieve simultaneous "pump-while-treat" for DNAPL remediation, instead of the common "pump-then-treat." This research will focus on reactivity of permanganate with DNAPLs in the presence of surfactant and the effects of concentrations of surfactants, contaminants, and permanganate on contaminant degradation rate via batch tests. Then a series of column and 2-d tank tests will be deployed to verify the batch test results and to determine parameters for future pilot scale field tests. It is expected that the simultaneous DNAPL solubilization/degradation by the proposed "pump-while-treat" system will greatly shorten the treatment time, reduce the operation cost, and speed up the cleanup of DNAPLs. It is hoped that by optimizing pumping rate with the degradation rate, the onsite treatment of contaminated water can be completely eliminated.

#### **Project Update:**

Oxidative dechlorination of chlorinated solvents by permanganate is an emerging technology for remediation of groundwater contaminated with dissolved chlorinated contaminants. During the first year, the enhancement of trichloroethylene (TCE) and perchloroethylene (PCE) degradation by permanganate in aqueous solution in the presence of surfactant was evaluated through a continuous stir batch reactor system with the presence of permanganate as the limiting reagent and free phase TCE or PCE. The TCE and PCE degradation was determined by continuously monitoring the amount of chloride produced, which was then reverted to the rate of permanganate consumption. It was found that the chloride production, an indication of TCE degradation, followed a

pseudo-first-order reaction kinetics with respect to KMnO<sub>4</sub> in the presence of free phase TCE. When no surfactants were present, the observed pseudo-first-order rate constant  $(k_{obs})$  was 0.08–0.19 min<sup>-1</sup> and the half-life  $(t_{1/2})$  was 4–9 min for MnO<sub>4</sub><sup>-</sup>. When the surfactant concentration was less then its critical micelle concentration (CMC), the  $k_{obs}$  values increased to 0.42–0.46 min<sup>-1</sup> and the  $t_{1/2}$  reduced to 1.5–1.7 min for MnO<sub>4</sub><sup>-</sup>. As the surfactant concentration was greater than the CMC, the  $k_{obs}$  values increased to 0.56–0.58 min<sup>-1</sup> and the  $t_{1/2}$  reduced to 1.2–1.3 min. The reaction rate also increased when ninate 411, another type of anionic surfactant, at concentrations of 0.1, 0.3 and 1.0% were present in the system. The results showed that combination of permanganate with a proper type of surfactant could speed up contaminant removal.

Contrast to the much greater enhancement for TCE oxidation, the enhancement of PCE oxidation by KMnO<sub>4</sub> in the presence of SDS was less obvious. The  $k_{obs}$  without SDS was 0.006 min<sup>-1</sup> compared to 0.007 – 0.008 min<sup>-1</sup> when 35 and 10.5 mM SDS were present. The  $t_{1/2}$  was 124 min when SDS was absent. The  $t_{1/2}$  was reduced to 98 – 83 min when 35 and 10.5 mM SDS were present.

Column experiments were performed with fine-grained beach sand and with coarsegrained Ottawa quartz sand. For the test with fine beach sand, 1 mL of neat TCE was placed about 10 cm above the bottom inlet in each column (30 cm long by 2.5 cm in diameter) after the columns were saturated with water. Then two columns were fed with 0.1% KMnO<sub>4</sub> and the other two 0.1% KMnO<sub>4</sub>+1% SDS. The flow rate was about 20 mL/hr and the flow was maintained for 6 hours until the columns were clogged and flow was interrupted. 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, a side effect was seen as hydraulic conductivity of the sand decreased significantly caused by precipitates of MnO<sub>2</sub>, making it essentially impermeable after 6 hours. Thus, the experiment aborted. For the Ottawa coarse sand test, the same initial conditions followed. The flow was maintained for over 72 hours. For the columns fed with SDS and permanganate, the effluent TCE concentration 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 concentration was about 1700 mg/L greater than its solubility of 1100 mg/L in pure water, indicating enhanced solubilization. While for columns fed with permanganate only, the highest effluent TCE concentration was less than 300 mg/L. In addition, when SDS was present, MnO<sub>4</sub> breakthrough occurred after 21-25 hour injection. But in the absence of SDS, MnO<sub>4</sub> didn't break through until 45-70 hours later. The earlier MnO<sub>4</sub> breakthrough also indicates exhaustion of dissolved TCE during the flushing stage. Chloride analysis revealed a slightly high chloride generation 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<sub>2</sub> zone.

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

# **Basic Information**

Title:	A Combined Hydrogeologic/Geochemical Investigation of Groundwater Conditions in the Waukesha County Area, Wisconsin
Project Number:	2003WI65O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Models, Geochemical Processes, Groundwater
Descriptors:	hydrogeology, hydrostatigraphy, geochemical, sandstone aquafer, contaminants
Principal Investigators:	Tim Grundl, Daniel Feinstein

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

T. Grundl, University of Wisconsin-Milwaukee, Geosciences; K. Bradbury, Wisconsin Geological and Natural History Survey; D. Feinstein, United States Geological Survey; and D. Hart, Wisconsin Geological and Natural History Survey Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2005

A major issue facing water managers and users in eastern Wisconsin is a high, and in certain wells, increasing concentration of TDS and radioactivity in the deep sandstone aquifer. At present, the source and movement of these contaminants is uncertain. Our current level of understanding of conditions within the deep sandstone aquifer comes from three independently collected sets of data. All of these previous research efforts (overall geochemistry, flow modeling and geophysical logging) have been performed separately by independent researchers. We propose to make use of the opportunity that now exists to coalesce these data in order to form a cohesive model of the hydrostratigraphy, the magnitude and direction of groundwater flow and the geochemical processes at work within the aquifer. Additional, more detailed numerical modeling and data collection is also proposed with the overall purpose of shedding light on the origin and underlying processes behind the occurrence of saline water and high radioactivity that is seen in the deep sandstone aquifer in this area.

1. Project Update: Overview of your progress on this project during the past year.

The project is in its final stages in spite of the fact that one of the PIs has been working on it from overseas sabbatical. The following specific tasks have been completed:

- 1 Collection and analysis of vertically discrete water samples from 3 wells
- 2 Flowmeter logging from same 3 wells (in Pewaukee)
- 3 Ultrafiltration and colloidal sampling/analysis from 2 wells (in the city of Waukesha)
- 4 Complete solids analysis (X-ray diffraction and thin section mineralogy, cation exchange capacity, extractable ferric oxide content) on 10 samples from a newly drilled well in Pewaukee
- 5 Collection of all pertinent data for Waukesha County from the WDNR database and directly from several water utilities
- 6 Collection of samples from a 15-well transect across Jefferson, Waukesha, and Milwaukee counties for stable isotope and noble gas analysis (in Switzerland)
- 7 Geochemical and flow modeling work to further refine the flow field and

geochemical reactions at work.

- 8 Analysis of available well logs to investigate a possible relationship between radium concentrations and stratigraphy.
- 9 Interpretation of well logs to quantify the number and thickness of shale beds within the wells for comparison to radium concentrations.
- 10 Collection of major ion and trace metal data from the DNR database to compare aquifer salinity and trace ion concentrations to radium levels.

Some interesting results have been obtained and the following two diagrams are illustrative of two of these results.



Figure 1. <sup>228</sup>Ra appears to have a subtle relationship to depth in the aquifer. This plot shows the average <sup>228</sup>Ra activities (from 1982 through 2005) versus length of open hole in the Mt. Simon formation (the lowermost formation). Error bars are  $\pm 1$ standard deviation. The relationship is statistically valid the 99% confidence level. By contrast, <sup>226</sup>Ra shows no such relationship.



Figure 2. Geochemical modeling, in combination with detailed solids analysis and flow modeling shows that coprecipitation of radium into sulfate minerals (primarily barite and celestite) apparently controls the activity of radium in this aquifer. Predictions of combined radium activity based on this model are shown. The three wells that do not fit contain  $\leq$  5 ppm sulfate, too little for an accurate prediction. This is an unusual situation in that sorption reactions are typically thought to control radium.

# **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:	2003WI66O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Quantity, Hydrology, Models
Descriptors:	comprehensive planning, recharge
Principal Investigators:	Douglas S. Cherkauer

#### Providing Communities with the Groundwater Information Needed for Comprehensive Planning

D. Cherkauer, University of Wisconsin-Milwaukee, Geosciences Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2005

The concept of comprehensive planning in now at the forefront in Wisconsin. While it recognizes the need for inclusion of groundwater resources in the planning process, it focuses almost entirely on water quality. Communities have little expertise and get little advice on identifying and protecting the quantity of their water supply, a particular problem in populous southeastern Wisconsin.

A compendium of groundwater information and a groundwater flow model has been developed on the regional level. Within that framework, this project will extend the process to the local level. It will work with a pilot community to develop a protocol for them to quantify and understand their groundwater budget. That information will then be coupled, via a flow model, with projected changes in land use and pumping demand to define the effects of different development approaches on the community's water supply. Once developed for the pilot community, the protocol will be publicized to other groundwater users. It will allow communities to decide how to best protect the recharge areas that supply their water and to examine how groundwater changes will effect flows and water levels in surface water bodies. Ideally it will also allow communities to recognize that groundwater resources are not infinite and need active management based on an understanding of the hydrologic system.

#### **Project Update:**

The town of Richfield in Washington County has been selected from among many candidates. It is the third largest population entity and second fastest growing community in the county. All citizens obtain water from private wells, which provides a huge array of well construction reports (WCRs) as a geologic data base. The town became an active participant in the project, providing communication routes to citizens, incorporating the study's results into their comprehensive planning process, and even placing a moratorium on new development until the ground water model can be used to test development impacts.

A call for volunteers identified 38 well owners who joined our monitoring study. We measure water levels in their wells bimonthly, producing both a series of water table maps and well hydrographs. A total of 12 sets of water levels were collected as part of the project, and stream baseflow was monitored at six sites. Richfield has already committed to continuing the bimonthly well monitoring into the future.

Over 550 WCRs have been used to generate 22 hydrogeologic cross sections through the study area. A sequence of five pairs of glacial tills and outwashes overlies dolomite

bedrock, producing a complex aquifer system of interwoven sand and gravel atop porous and fractured dolomite.

Recharge rates have been estimated using GIS information on land cover, drainage system, soil properties and hillslope. The process was developed in an earlier Joint Solicitation project. The recharge values have been verified against rates obtained by analysis of the well hydrographs at the monitoring locations. Average recharge for Richfield is about 4.5 in/yr, but has a very wide spatial range.

The hydrogeology, surface hydrology and recharge have been incorporated into a groundwater flow model for the study area. It has been calibrated to the heads observed in the monitored wells and to the fluxes measured at our stream gaging sites.

During the course of this study, Richfield completed and adopted its comprehensive plan. Information on the ground water resources and how best to protect them was actively sought from us. We identified the primary source areas (recharge areas), as well as the population density that the recharge rates could support. We also identified what we termed ground water baselevel protection areas, regions with substantial wetlands or other surface water bodies which are the primary discharge locations in the town. Reduction of water levels in these areas by drainage or other human activity, will cause similar reductions in ground-water levels upflow. The Town incorporated all these regions into their 10 and 20 year land-use plans. The baselevel protection areas have all been identified as environmental corridors for preservation. Development density has been limited so that all present and future population can be supported by the recharge to the aquifers beneath those areas. Primary recharge areas have been excluded from industrial or commercial zoning, and an attempt will be made to retain as much agriculture or natural land use in those areas as possible.

The Town has proactively gone beyond just creating a land use plan. They are now in the process of implementing an ordinance to protect ground water in the future. It will require all future developments to conduct a water resource study, similar in nature to a traffic study. Developers will be asked to identify how much water they will need, and then to craft a design to assure that sufficient water exists beneath their site. They will be encouraged to collect rainwater runoff and enhance its infiltration, to minimize ornamental use of water, and similar steps. The effects of the design will be tested using the ground-water model developed in this study.

# What Happens When The Confined Cambrian-Ordovician Aquifer In Southeastern Wisconsin Begins To Be Dewatered?

## **Basic Information**

Title:	What Happens When The Confined Cambrian-Ordovician Aquifer In Southeastern Wisconsin Begins To Be Dewatered?
Project Number:	2004WI116O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	confined aquifer, aquitard, desaturation, flow dynamics
Principal Investigators:	Timothy T. Eaton

## Publication

1. Eaton, T.T., 2004. Desaturation and flow dynamics beneath an aquitard near excessively pumped wells. Geological Society of America Abstracts with Programs, Vol. 36, No. 5.

#### **PROJECT SUMMARY**

**Title:** What Happens When The Confined Cambrian-Ordovician Aquifer In Southeastern Wisconsin Begins To Be "Dewatered"?

Project ID: WRI# R/UW-HDG-008, GCC# 04-HDG-02

**Principal Investigator:** Timothy T. Eaton, School of Earth and Environmental Sciences, Queens College-CUNY

Period of contract: July 1, 2003 – July 1, 2004

**Background/Need:** The Cambrian-Ordovician aquifer has long been an important source of municipal water supply in Wisconsin, and recent trends are of some concern for future supply. Pumping has drawn down the potentiometric surface (hydrostatic pressure) of this deep aquifer system by over 400 ft during the 20<sup>th</sup> century. Wisconsin state observation wells show that head in the deep aquifer system continues to decline at a rate of 7 ft/yr and will eventually dip into the top of the St. Peter sandstone, causing dewatering as air enters the pore space. Computer simulations cannot account for reduction in hydraulic conductivity caused by progressively developing unsaturated conditions near the well bore, which forms the principal avenue for air to reach the aquifer. It is not clear exactly what happens under these conditions in the real world because few observations have been made of this phenomenon in deep aquifers where field data are rarely available.

**Objectives:** The goal of the research reported here was to investigate possible dewatering phenomena in the Cambrian-Ordovician aquifer system in southeastern Wisconsin. The specific objectives were **1**) to investigate how unsaturated conditions might develop in a physical sand-tank model, **2**) to attempt to verify the development of such hydrogeologic conditions in the field, and **3**) to predict the long-term impact on water supply and quality by observing the evolution of head in the vicinity of model pumping wells.

**Methods:** The sand-tank model was based on a design developed by Dr. James O. Peterson and Ronald Hennings, now in widespread use across the United States. It consists of vertical Plexiglas plates mounted one inch apart containing saturated sands and clays arranged to represent generic subsurface formations in profile. Sediments used were carefully analyzed for grain size and uniformity to be able to estimate resulting hydraulic conductivity when packed. The model was customized with double-curved manometer tubes and scaled graduations on either face of the model, that enabled head to be measured as the colored water levels fell below the elevation of the piezometer openings in the model aquifer. In response to pumping of wells centered in the sediment, head data over time was recorded on video camcorders. Model runs were made with a laboratory pump connected to both well discharge tubes, with wellhead valves in closed and

open positions. Head in the pumping wells was drawn down below the top of the confined aquifer, drawdown was observed in the manometer water levels around each pumping well, and resulting cones of depression quickly merged. Data were compiled by viewing the resulting videotape and transcribing the head values, read as the water levels in each manometer passed the graduated lines on the model faces. These data were plotted in the form of graphs of head change over time. They were also plotted as contour maps of the head field in the plane of the model at successive times. A field component of this project consisted of converting and instrumenting an open borehole at a site west of Milwaukee to a monitoring well with a short screen in the Sinnipee Group dolomite below the Maquoketa Formation.

Results and Discussion: Basic drawdown data shows that heads at the monitoring points responded rapidly to the pumping well drawdown, and that there are significant variations in head with depth. Head data at the monitoring points after pumping water level stabilization indicates fluctuations over time. Close examination of these fluctuations show that they are out of sequence with changes in pumping water level, a complexity in the head field in a near-uniform model aquifer that is rarely, if ever, observed in actual monitoring wells. The effective pumping rate was uncontrolled, but monitored. As the pumping water level dropped, the instantaneous pumping rate peaked and then was reduced to stabilize at about 66% of maximum capacity. The coincidence of maximum pumping rate with drawdown stabilization suggests that the pumping reached some equilibrium where it was balanced by steady-state flow from the lateral constant-head boundaries. In the confined model aguifer, the hydraulic head was used to infer less than saturated conditions when the measured head fell below the elevation of the monitoring points. Resulting hydraulic pressure at the monitoring points decreases below atmospheric pressure, at which time air enters the pore space, and pore water drains out forming a seepage face. The data show that this desaturation phenomenon occurs relatively rapidly. Head decreased to the elevation of the top of the aquifer first near one well then the other, followed by a merging of the desaturating fronts, which advanced quickly to approximately halfway down the thickness of the aquifer. Water level measurements at the field site indicate that hydraulic head in the Sinnipee Group dolomite is just above the elevation of the monitoring screen at that location.

**Conclusions/Implications/Recommendations:** After onset, the spread of desaturating conditions is relatively rapid at first, but then slows. Simulated lateral spread from wells is also rapid, leading to a merging of zones of desaturation near the top of the aquifer, before spreading to greater depths, in contrast to expected vertical development near well bores. As pumping well head decreases level off when flow from the boundaries equals the rate of well pumpage, head at monitoring points at elevations near the pumping water level continue to fluctuate over time frames that are difficult to explain solely by pumping water level fluctuations. Pumping rates decrease as pumping water levels fall below the top of the aquifer and saturated thickness diminishes.

Without airflow down the well bore, pumping rates are much lower and head drawdown much less rapid. Measurement of hydraulic head at the field site suggests that regional drawdown in the underlying Cambrian-Ordovician aquifer is now sufficient to cause development of desaturated zones in the Sinnipee Group dolomite around open wells.

Desaturation of pore space causes decreases in hydraulic conductivity that affect flow through the desaturating zone to the well, shown by the asynchronous fluctuations in head. Such dynamics would be more complex in a fully three-dimensional system, and flow to an overpumped well may be the integration of sequential flows from different sectors around the well depending on the relative saturation of the surrounding pore space. The practical consequences could increased oxidation reactions and deterioration of water quality depending on the mineralogy of the aquifer material. These dynamics of desaturation may also seriously reduce municipal well yields for given rates of drawdown. Once such desaturation is widespread, it may be impossible for well yields to recover, even with cessation of pumping, because air becomes indefinitely trapped in the pore space.

**Related Publications:** Eaton, T.T., 2004. Desaturation and flow dynamics beneath an aquitard near excessively pumped wells. Geological Society of America *Abstracts with Programs*, Vol. 36, No. 5.

Key Words: confined aquifer, aquitard, desaturation, flow dynamics

# Mercury Speciation along a Groundwater Flowpath

## **Basic Information**

Title:	Mercury Speciation along a Groundwater Flowpath
Project Number:	2004WI126O
Start Date:	7/1/2004
End Date:	6/30/2006
Funding Source:	Other
Congressional District:	2nd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Groundwater, Toxic Substances, Solute Transport
Descriptors:	mercury, groundwater, hyporheic
Principal Investigators:	David Armstrong, David Armstrong, Christopher L. Babiarz, Martin Shafer

# **Project Number:** 05-CTP-01

03-011-01

**Project Title:** Mercury Speciation along a Groundwater Flowpath

#### **Project Investigators:**

David E. Armstrong and Christopher L. Babiarz

#### 1. Project Update:

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 at four flow regimes along instrumented and characterized flow paths: local groundwater, soil lysimeter, intermediate groundwater, and the hyporheic zone. During the first year of the project, we have focused on the hyporheic zone and have conducted five sampling campaigns (April, June, July, August, and October 2004). The dates selected were based on important season and flow-regime events, and separate samples were collected for analysis of total mercury, methyl mercury and associated parameters. The data will be used to investigate the role of Hg speciation in controlling Hg transport to zones of methylation, the bioavailability of Hg(II) to methylating bacteria, and the bioavailability of MeHg for uptake into aquatic food webs.

# **Occurrence of Estrogenic Endocrine Disruptors in Groundwater**

## **Basic Information**

Title:	Occurrence of Estrogenic Endocrine Disruptors in Groundwater
Project Number:	2004WI127O
Start Date:	7/1/2004
End Date:	6/30/2006
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Toxic Substances, Water Quality, None
Descriptors:	endocrine disruptors,
Principal Investigators:	William C. Sonzogni, Jocelyn Hemming, William C. Sonzogni

#### **Project Title:**

Occurrence of Estrogenic Endocrine Disruptors in Groundwater

#### **Project Investigators:**

William Sonzogni, Jocelyn Hemming, Miel Barman and Steven Geis

#### Abstract:

Growing populations are influencing groundwater quantity and quality causing groundwater professionals to continually monitor and deal with emerging issues. Increasing demands for groundwater, resulting in infiltration of surface water into groundwater is a classic example of one of theses issues. The drawdowns and cones of depression associated with high capacity municipal and agricultural wells placed near rivers have resulted in reversals in groundwater flows. This flow reversal then sets up a potential for contaminants from the river to be transmitted to groundwater by infiltration. Additionally, the proliferation of non-conventional small scale on site waste disposal systems in rural areas may provide another route for entrance of compounds of concern to groundwater. It is expected that such non-conventional systems will usually be installed in vulnerable groundwater settings, such as areas of shallow bedrock or high water tables, where conventional on-site septic systems would not be allowed.

Of growing concern related to these phenomena, is the potential for detrimental human health effects associated with the presence of compounds in polluted surface waters known as endocrine disrupting compounds (EDCs).

Infiltration of these EDCs into the groundwater may compromise the water quality and pose a risk to human health. The understanding of the occurrence of these compounds in Wisconsin groundwater is necessary to aid in future decision making regarding water use. A data base needs to be created regarding the occurrence of EDC's in groundwater, and more specifically the occurrence in vulnerable areas near rivers and rural developments which use non-conventional waste treatment systems. This data will then allow informed negotiations within the water supply community regarding decisions that will protect the long term health of individuals who consume groundwater.

The primary goal of this project is to determine the presence of estrogenic endocrine disrupting chemicals in groundwater by using the E-screen assay. Samples will be collected from high capacity municipal water supply wells located near surface waters impacted by industrial and municipal effluents. Wells from unsewered subdivisions that are likely under septic system influence will also be assayed for estrogenic activity. Samples that indicate estrogenic activity will by analyzed with gas chromatography to identify which estrogenic compounds are responsible for the estrogenic activity with the E-screen. This study will help provide important data that could influence future decision making regarding important groundwater issues such as land use planning, water treatment options, well placement and water use.

**Project Update:** High capacity well sampling has occurred at 5 different Wisconsin municipalities, with 3 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. Septic sampling has

occurred twice, with 1 septic influent, 10 septic effluents, 4 monitoring wells and 6 soil waters being collected. Quality assurance samples include 4 matrix spikes, 3 travel blanks, 2 lab water blanks and 2 lab water spikes. In all, 89 samples have been collected for this study. All of the samples are extracted through a C18 disk, the disk is then eluted with solvents to capture the estrogenic chemicals. The extracts are then tested for estrogenic activity using a breast cancer cell proliferation assay known as the E-Screen. To date, two of the three rounds of high capacity well sampling and all of the septic system samples have been assayed. The first round of sampling 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 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. The septic system portion of this project included sampling of a subdivision that utilizes Wisconsin mound systems. The systems are set up with lysimeters to collect soil water and monitoring wells to collect nearby groundwater. Two systems were sampled and assayed for estrogenic activity. System one showed effluent activity at 25.50 ng/L while the corresponding two soil waters and groundwater had no activity. The second system had an activity level of 19.57 ng/L in the effluent, three soil waters that ranged from 0.28-0.38 ng/L in activity and three groundwaters that showed no activity. Another sampling was done at various types of septic systems. A septic influent from a sand filtration septic system and its corresponding effluent was sampled and had an activity level of 17.60 ng/L and 0.27 ng/L, respectively. Septic effluents were collected from multi-flo aerobic systems and had an activity level that ranged from 0.07-188.85 ng/L. One effluent was collected from a biomicrobic aerobic system and had a value of 0.77 ng/L. Septic system samples are currently being analyzed by the LC/MS/MS to determine which specific chemicals are present.

High capacity wells will be sampled one more time. More septic systems are to be sampled. Active samples will be chemically analyzed on the LC/MS/MS.

# Monitoring Environmental Effects at an Established Phytoremediation Site

## **Basic Information**

Title:	Monitoring Environmental Effects at an Established Phytoremediation Site
Project Number:	2004WI128O
Start Date:	7/1/2004
End Date:	6/30/2006
Funding Source:	Other
Congressional District:	7th
Research Category:	Ground-water Flow and Transport
Focus Category:	Solute Transport, Treatment, Water Quality
Descriptors:	phytoremediation, pesticides
Principal Investigators:	William DeVita

#### **Project Title:**

Monitoring Environmental Effects at an Established Phytoremediation Site

#### **Project Investigators:**

William M. DeVita and Mark Dawson

#### Abstract:

Phytoremediation is the use of plants to accumulate or degrade environmental contaminants for soil and/or groundwater. Its use has been demonstrated for certain metals, petroleum products and some pesticides. The established phytoremediation effort, located in Bancroft, WI, was initiated in June 2000 with the planting of 768 hybrid poplars and 66 willows. It was established with expectations to 1) retard the flow of contaminated groundwater off site 2) degrade or accumulate contaminants of concern, and 3) provide a base of information regarding poplar and willow viability in a degraded environment.

Following 3.5 years of growth, we have some trees that exceed 7 m in height and 10 cm in diameter. We also have a region of severe tree mortality or growth impairment. Trees downgradient of this "dead zone"; appear healthy it is expected these trees will capture contaminated groundwater from the water table or capillary fringe. Groundwater monitoring wells and piezometers are in place to assess contaminant levels at the water table and deeper into the aquifer. Three groundwater elevation data loggers along with a weather station are also in place on site.

Objectives for the next 2 years of study include: semiannual groundwater sampling and analysis, maintenance of groundwater data loggers, maintenance of weather station, periodic (but less frequent) weed control, periodic operation and maintenance of irrigation system, and operation of electric fence (for deer control).

1. **Project Update:** Two rounds of groundwater sampling and analysis have been completed. Eighteen monitoring wells were sampled in October 2004 and May 2005. Overall, dinoseb levels are decreasing and it is no longer detectable in the most downgradient and deepest nest of monitoring wells. However, seasonal variations still remain as dinoseb is released from the contaminated soil.

Groundwater elevation data loggers were in place from the beginning of the study period until November 2004. They were reinstalled in April 2005 to record groundwater elevation changes throughout the growing season.

The site was surveyed for biomass production in the fall of 2004.

# Foundry Slag for Treating Arsenic in Groundwater and Drinking Water

# **Basic Information**

Title:	Foundry Slag for Treating Arsenic in Groundwater and Drinking Water
Project Number:	2004WI129O
Start Date:	7/1/2004
End Date:	6/30/2006
Funding Source:	Other
Congressional District:	2nd
Research Category:	Engineering
Focus Category:	Treatment, Groundwater, Toxic Substances
Descriptors:	arsenic, treatment, foundry slag
Principal Investigators:	Craig H Benson

#### **Project Title:**

Foundry Slag for Treating Arsenic in Ground Water and Drinking Water

#### **Project Investigators:**

Dr. Craig H. Benson and Dr. David W. Blowes Ms. Stacy Metz, Graduate Student

#### Abstract:

Recent studies have shown that slags from steel production can be very effective in removing As from ground water. This proposal focuses on evaluating a similar material that is readily available in Wisconsin, i.e., slag from gray-iron foundries. Gray-iron slag is a granular byproduct of iron casting operations that is discarded in landfills or reused as granular fill in civil engineering construction. Most gray-iron slags can be obtained for little or no cost from foundries, and in some cases foundries are willing to truck slag to a job site. The objective of this study is to determine whether slags from Wisconsin gray-iron foundries have the same reactive nature as steel slags. Both contain an appreciable quantity of iron, which is the key constituent in slags responsible for the redox reactions that remove As. A successful outcome of this study would be a low-cost reactive medium readily available to Wisconsin communities for As treatment. Moreover, use of foundry slag in this manner will foster sustainable development through beneficial reuse of a byproduct often discarded in landfills as a waste.

1. **Project Update:** Overview of your progress on this project during the past year.

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  $\mu$ g/L to less than 10 $\mu$ g/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.

# Delineation of Flow Paths, Capture Zones and Source Areas, Allequash Basin, Vilas County, Wisconsin

## **Basic Information**

Title:	Delineation of Flow Paths, Capture Zones and Source Areas, Allequash Basin, Vilas County, Wisconsin
Project Number:	2004WI130O
Start Date:	7/1/2004
End Date:	6/30/2005
Funding Source:	Other
Congressional District:	2nd
<b>Research Category:</b>	Climate and Hydrologic Processes
Focus Category:	Groundwater, Climatological Processes, Wetlands
Descriptors:	
Principal Investigators:	Mary Anderson

## **Publication**

1. Masbruch, M., Hunt, R.J., and Anderson, M.P., 2005, Delineation of Flow Paths, Capture Zones, and Source Areas, Allequash Basin, Vilas County, Wisconsin, AWRA Wiscconsin Sectional conference, Abstract.

#### **Project Title:**

Delineation of Flow Paths, Capture Zones, and Source Areas, Allequash Basin, Vilas County, Wisconsin

#### **Project Investigators:**

Mary Anderson

#### Abstract:

There are numerous interconnected lakes, streams, and wetlands in Wisconsin that are well connected to the groundwater system. Consequently, the chemistry of groundwater may greatly influence the chemistry of surface waters. Therefore, the testing of tools that can aid in identifying the source areas of recharge waters and the geologic controls on groundwater chemistry is crucial to understanding and protecting both groundwater and surface water. Groundwater flow paths along three transects within the Allequash basin, a sub-basin within the Trout Lake watershed located in Vilas County in northern Wisconsin, were delineated using isotopes of deuterium ( $\delta D$ ),  $\delta^{18}O$ , and  $\delta^{87}Sr$ , as well as major ion concentrations, iron, and dissolved carbon species. A three-dimensional groundwater flow model was used to delineate lake capture zones and to investigate seasonal and long-term chemical variability. Results show significant transience directly west of Big Muskellunge Lake. Transience here affects the discharge location of solutes in this area of the basin. Geologic controls on groundwater chemistry are evident in the results. This project is being done in cooperation with the Wisconsin Long Term Ecological Research (LTER) program and the Water, Energy, and Biogeochemical Budgets (WEBB) program of the USGS and results of this study will be used by both groups. Currently, the U. S. EPA STAR funding is investigating the effects of carbon quality on metal complexation within the basin, and the University of Wisconsin System is funding work on the importance of hyporheic processes on mercury cycling. The results of the groundwater analyses proposed in this study will provide useful data for these investigations. This study will also be useful to local and state officials in efforts to understand and mitigate the effects of development and urbanization in Northern Wisconsin's Lake District.

# A Comparison of USEPA-Approved Enzyme-Based Total Coliform/E. coli Tests for Microbiological Groundwater Monitoring and Laboratory Consultation

# **Basic Information**

Title:	A Comparison of USEPA-Approved Enzyme-Based Total Coliform/E. coli Tests for Microbiological Groundwater Monitoring and Laboratory Consultation
Project Number:	2004WI131O
Start Date:	7/1/2004
End Date:	6/30/2005
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Water Quality, None, None
Descriptors:	E. coli, coliform, methodology
Principal Investigators:	James Schauer

#### **Project Title:**

A comparison of USEPA approved enzyme-based total coliform/E. coli tests for microbiological groundwater monitoring and laboratory consultation

#### **Project Investigators:**

James Jay Schauer, Jeremy Olstadt, Jon Standridge, and Sharon Kluender

#### Abstract

Protection of Wisconsin's groundwaters from microbial contamination is a top priority not only for well owners but also for the water well industry and environmental regulators. Recent epidemiological studies clearly show that gastrointestinal disease due to ingestion of drinking water is occurring at significant levels in the United States and Canada. Furthermore, the United States Centers for Disease Control reported in their last 10 year summary of waterborne disease outbreaks that over 70% of the documented outbreaks occurring in the U.S. were associated with we ll water sources. These facts underscore the need for sensitive, reliable laboratory methods to identify microbial contamination in groundwater that might pose a potential risk of illness from consuming the water. Over the past ten years, enzyme-based methodologies for detection of total coliform and E. coli indicators of microbial contamination have become widely accepted as the industry standard for water microbiological testing. Prior to 2001 there were only three approved enzyme based methods which have all been shown to be effective for testing Wisconsin groundwaters. Over the past two years, the USEPA has approved six new products for coliform testing. The limited amount of data that is available on these new methods indicates that there are large differences in their abilities to detect and enumerate both total coliforms and E. coli. To date, there are no published studies available performing a rigorous side-by-side evaluation of the new tests. It is the intent of the research outlined in this proposal to do a thorough evaluation of all nine USEPA approved products to determine their suitability for use on Wisconsin groundwaters.

**Project Update:** The data collection phase is now complete and we are currently in the manuscript publication process. Below summarizes the presentations that have and will occur regarding this project.

# **Development of Tools to Address Groundwater in Comprehensive Planning**

## **Basic Information**

Title:	Development of Tools to Address Groundwater in Comprehensive Planning
Project Number:	2004WI132O
Start Date:	7/1/2004
End Date:	6/30/2005
Funding Source:	Other
Congressional District:	7th
Research Category:	Social Sciences
Focus Category:	None, None
Descriptors:	planning, water use, groundwater
Principal Investigators:	Lynne Markham, Charles P Dunning

#### **Project Title:**

Development of tools to address groundwater in comprehensive planning

#### **Project Investigators:**

Lynn Markham, Charles Dunning, and Chin-Chun Tang

#### Abstract:

Legislation adopted in 1999(s. 66.0295) requires all communities that make land use decisions, to base those decisions on a comprehensive plan by January 1, 2010. The legislation outlines nine elements that must be included in each comprehensive plan. Aspects of groundwater quantity or quality may be a factor in all nine elements.

A number of publications have been completed by state and university groups that provide a thorough discussion of groundwater as part of the comprehensive planning process. Absent from these publications are real-life examples illustrating how local governments have planned for groundwater protection in their community, and even more importantly, how these communities have implemented their plans. Such examples would greatly assist planners and citizens in effectively addressing groundwater in comprehensive plans.

This project will:

- Establish a network of project contributors at all levels of private and public life to advise this project and future groundwater planning projects.

- Review, summarize, and analyze the groundwater components of comprehensive plans that have been filed with the Wisconsin Department of Administration.

- Develop five case studies highlighting rural Wisconsin communities that have implemented groundwater protection measures.

- Identify the key challenges, and particularly the "showstoppers", communities are facing as they attempt to develop and implement the groundwater component of comprehensive plans.

1. **Project Update:** Overview of your progress on this project during the past year. (edit above)

The Center for Land Use Education together with a scientist from the U.S. Geological Survey launched a small project to review and evaluate adopted Wisconsin comprehensive plans to understand the extent of groundwater coverage and efforts to protect and manage groundwater in comprehensive plans. In addition, we also conducted several case studies to document exemplary efforts to protect groundwater. Our plan review consists of two phases: Phase I is a preliminary review where we broadly examine how groundwater is being covered in each of the nine comprehensive planning elements. Phase II is a detailed review where we select a small pool of plans based on the preliminary results to analyze the types of data, policies, and goals included in the plans.

We used a database of completed and in-progress comprehensive plans from the Wisconsin Department of Administration to identify 79 comprehensive plans that were completed after 2000 and submitted to the DOA. Only plans adopted by their respective communities were selected for review. The majority of plans were completed by towns, followed by villages and cities.

We conducted preliminary content analysis on the 79 plans to determine the extent to which groundwater is covered in each plan. We counted how frequently the word "groundwater" appeared in each element of the plans. Figure 1 shows the results. As expected, the agricultural, natural, and cultural resources element contains the most extensive coverage of groundwater, followed by the utilities and community facilities element. The housing and transportation elements, respectively, contain little to no mention of groundwater. In total, four plans did not mention groundwater at all. It is important to note that using the word "groundwater" as the sole code word may underestimate the extent to which groundwater is covered in these plans, since alternate language could have been used. The purpose of the detailed review in Phase II is to capture these details.



Another important point to highlight is that the communities whose plans we reviewed are "pioneer communities," meaning they committed themselves to comprehensive planning shortly after the law was enacted. Thus, many of them started preparing their comprehensive plans with limited educational materials or real-life examples to guide them in integrating groundwater into their plans. From our review process, the quality of plans is indeed wide-ranging. However, the proactive spirit and initiative of these communities should be commended.

# Hydrostratigraphy of West-Central Wisconsin: A New Approach to Groundwater Management

## **Basic Information**

Title:	Hydrostratigraphy of West-Central Wisconsin: A New Approach to Groundwater Management
Project Number:	2004WI133O
Start Date:	7/1/2004
End Date:	6/30/2005
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Geomorphological Processes, None
Descriptors:	groundwater, stratigraphy
Principal Investigators:	David LePain, Kenneth R Bradbury

#### **Project Title:**

Hydrostratigraphy of west-central Wisconsin: A new approach to groundwater management

#### **Project Investigators:**

Dr. David L. LePain and Dr. Kenneth R. Bradbury

#### Abstract:

Hydrostratigraphy of West-Central Wisconsin: A new approach to groundwater management

Recent studies in west-central Wisconsin and throughout the state, as well as in neighboring Minnesota, have highlighted the need for data relating to the hydrogeology of shallow carbonate rocks of the Trempealeau, Prairie du Chien, and Sinnipee groups in upland areas, and the effectiveness of low permeability bedrock as aquitards at shallow and deeper stratigraphic levels. These shallow stratigraphic units play an important, but poorly understood, role in controlling groundwater flow to deeper aquifers in Upper Cambrian sandstones and in sustaining baseflow to streams and springs throughout the region. Data on matrix porosity and permeability, the presence, abundance, and stratigraphic distribution of fractures and dissolution features, and the lateral continuity and hydraulic characteristics of low permeability zones are not readily available for Paleozoic bedrock in west-central Wisconsin. These types of data may be included in technical reports on file with regulatory agencies, Wisconsin DOT, and private consulting firms throughout the region. This project will compile and organize existing data from these and published sources on the geology and hydraulic properties of Cambrian-Ordovician strata throughout west-central Wisconsin into a searchable digital database. This project will also begin development of a new hydrostratigraphic framework for Cambrian-Ordovician bedrock in the region, and will serve as the starting point for development of a statewide digital database and hydrostratigraphic framework. Results of this project will be of interest to the hydrogeologic and regulatory community interested in the controls on groundwater recharge and flow, and the potential for migration of groundwater contaminants.

#### **Project Update:**

Recent studies in west-central Wisconsin and throughout the state, as well as in neighboring Minnesota, have highlighted the need for data relating to the hydrogeology of shallow carbonate rocks of the Trempealeau, Prairie du Chien, and Sinnipee groups in upland areas, and the effectiveness of low permeability bedrock as aquitards at shallow and deeper stratigraphic levels. These shallow stratigraphic units play an important, but poorly understood, role in controlling groundwater flow to deeper aquifers in Upper Cambrian sandstones and in sustaining baseflow to streams and springs throughout the region. Data on matrix porosity and permeability, the presence, abundance, and stratigraphic distribution of fractures and dissolution features, and the lateral continuity and hydraulic characteristics of low permeability zones are not readily available for Paleozoic bedrock in west-central Wisconsin. The intent of this project is twofold:

- 1.) to search the files of regulatory agencies, Wisconsin DOT, and private consulting firms throughout the region for relevant hydrogeologic and hydrostratigraphic data on Cambrian-Ordovician bedrock, and compile/organize the information in a searchable digital database.
- 2.) To use the information obtained in this search to develop a hydrostratigraphic framework for Cambrian-Ordovician bedrock in the region.

The original scope of the project included searching for information on sites in westcentral Wisconsin which broadly defined, included the area between the City of Eau Claire and the Mississippi/St. Croix rivers, and from northern Polk County south to the La Crosse County-Vernon County line. During a preliminary visit to the west-central region headquarters of the Wisconsin DNR it became apparent that their files included an enormous amount of information from sites scattered throughout the region. The volume of information necessitated restricting the area covered to include only Dunn, Pierce, and St. Croix counties. The information reviewed includes consulting reports for various contamination sites, pumping test results for municipal water supply wells, and water well construction reports. Pumping test results were also obtained from various municipalities in the redefined project area, along with borehole video logs. In addition to information in the DNR files, specific capacity data from water well construction reports, hi-cap well records, and in the Wisconsin Geological and Natural History Survey's WISCLITH database will be included in the project deliverables. Specific capacity data from these wells was used to estimate aquifer transmissivity. The quality and limited stratigraphic distribution of data obtained in this search preclude development of a preliminary hydrostratigraphic framework as part of this project. The data obtained for this project are being compiled as series of GIS shapefiles for submittal, along with a brief report, to the University of Wisconsin Water Resources Institute.
**Information Transfer Program** 

# University of Wisconsin-Water Resources Institute -Information Transfer

### **Basic Information**

Title:	University of Wisconsin-Water Resources Institute - Information Transfer			
Project Number:	2002WI2B			
Start Date:	3/1/2004			
End Date:	2/28/2005			
Funding Source:	104B			
Congressional District:	WI - 2nd			
Research Category:	Not Applicable			
Focus Category:	None, None, None			
Descriptors:				
Principal Investigators:	Anders W. Andren, JoAnn M. Savoy			

### **Publication**

- 1. Anderson, Mary P. and Christopher S. Lowry. 2004. An Assessment of Aquifer Storage Recovery for Selected Representative Hydrogeologic Settings in Wisconsin. Water Resources Institute, University of Wisconsin, Madison. 15 p.
- 2. Armstrong, David. 2005. Role of the Hyporheic Zone in Methylmercury Production and Transport to Lake Superior. Water Resources Institute, University of Wisconsin, Madison. 1 vol.
- Bahr, Jean M., Madeline B. Gotkowitz, and Tara L. Root. 2004. Arsenic Contamination in Southeast Wisconsin: Sources of Arsenic and Mechanisms of Arsenic Release. Water Resources Institute, University of Wisconsin, Madison. 18p.
- 4. DeVita, William M. and Mark Dawson. 2004. Monitoring the Effectiveness of Phytoremediation and Hydrogeologic Response at an Agricultural Chemical Facility. Water Resources Institute, University of Wisconsin, Madison. 15p.
- 5. Eaton, Timothy T. and Kenneth R. Bradbury. 2005. What Happens When the Confined Cambrian Ordovician Aquifer in Southeastern Wisconsin Begins to be Dewatered? Water Resources Institute, University of Wisconsin, Madison. 19p.
- Skalbeck, John D. 2004. Coupled Modeling of Gravity and Aeromagnetic Data for Analysis of the Waukesha Fault, Southeastern Wisconsin. Water Resources Institute, University of Wisconsin, Madison. 17p.
- 7. 2004. Water Resources 2004-06 Directory of Projects and People. Aquatic Sciences Center, University of Wisconsin, Madison. 28p.
- 8. Spring 2005. Aquatic Sciences Chronicle. Aquatic Sciences Center, University of Wisconsin,

Madison. 8p.

- 9. 2004 Annual Meeting of the Wisconsin Section of the American Water Resources Association Announcement and Abstracts; Wisconsins Waters: A Confluence of Perspectives. Water Resources Institute, University of Wisconsin, Madison. 62p.
- 2004 Annual Meeting of the Wisconsin Section of the American Water Resources Association Call for Papers; Wisconsins Waters: A Confluence of Perspectives.Water Resources Institute, University of Wisconsin, Madison. 2p.
- 11. 2004 Annual Meeting of the Wisconsin Section of the American Water Resources Association Program Highlights and Registration; Wisconsins Waters: A Confluence of Perspectives. Water Resources Institute, University of Wisconsin, Madison. 2p.
- 12. Spring 2005. Campus Librarians Take Story Hours to Community Youth. Friends of the Libraries Magazine. Page 8.
- 13. 12/21/2004. Mixing Books, Fun: UW Librarians Implement Reading Program at Allied Drive Center. Wisconsin State Journal. Section B, Page 1.
- 14. 12/7/2004. Libraries Take Story Hour to Allied Drive. Wisconsin Week. Page 5
- 15. 11/16/2004. Not Your Typical Outreach: Taking Water Resources to Allied Drive. Libraries@UW-Madison. Unpaged.
- 16. November/December 2004. Turning a New Page in Outreach; UW Water Resources Library Reaches Out to State, Local Neighborhood. Littoral Drift. Page 1.
- 17. 2/28/2004. Conference Will Examine Key Water Issues Facing Wisconsin. Media Advisory.
- 18. May/June 2004. Wisconsin Water Policy Database Now Available. Littoral Drift.
- 19. 8/10/2004. State Grant Supports Research on Water Contamination, Supplies. News Release.

Highlights of the reporting period, March 1, 2004 through February 28, 2005, include the first issue of the *Aquatic Sciences Chronicle*, planning for the Eight International Conference on Mercury as a Global Pollutant, and a new Water Resources Library outreach project, "Water Critters for Kids". In addition, WRI continued to maintain several Web sites, cosponsor the AWRA Wisconsin Section conference, support a library and issue publications.

#### Newsletter

The first issue of the *Aquatic Sciences Chronicle* was published in spring 2005 after months of planning. The eight-page, full color quarterly publication contains articles to inform the public about the Water Resources and Sea Grant institutes and to notify them about funding opportunities, conferences, and more. Articles in the inaugural issue included "A Measure of Our Thirst: Great Lakes Region Pilots National Water Use Study"; "Trouble under the Boardwalk: Mysterious Corrosion Draws Experts to Duluth-Superior Harbor"; and "River Studies Center, University of Wisconsin-LaCrosse". The response to the *Chronicle* has been very positive.

#### 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 our newly launched Web site at *mercury2006.org/Default.aspx?tabid=1435* 

The Water Resources Institute continues to cosponsor the American Water Resources Association, Wisconsin Section annual meeting. Other sponsors of the 29<sup>th</sup> annual meeting, "Wisconsin's Waters: A Confluence of Perspectives" were the Wisconsin Department of Natural Resources, UW-Stevens Point Center for Watershed Science & Education, Wisconsin Geological and Natural History Survey, and the Wisconsin District of the U.S. Geological Survey.

#### **UW Water Resources Library Outreach Activities**

The Water Resources Library continued its involvement in outreach during the past year. Wisconsin's Water Library continues to offer books and other materials to any Wisconsin resident at *aqua.wisc.edu/waterlibrary*. The library also started a story hour project, "Water Critters for Kids", in a low-income area of Madison, went on the road to the Wisconsin Lakes Convention in Green Bay, started reaching out to environmental groups, and sponsored a middle school class for a reading day with Wisconsin's first lady, Jessica Doyle.

□ Allied Drive Story Hours: "Water Critters for Kids"

Using children's books purchased with a grant from the Friends of the UW– Madison Libraries, the Water Resources Library teamed with the Boys and Girls Club of Dane County and the Madison School and Community Recreation program to hold several reading programs in the Allied Drive neighborhood. Several other campus libraries are now participating in the story hours, which have become a monthly occurrence.

□ The Water Library Goes on the Road

We took a sampling of lakes-related reading material from our collection to the 2005 Wisconsin Lakes Convention in Green Bay. Wisconsin residents could check out materials and return them at their local public libraries. The Wisconsin Association of Lakes (WAL) is a nonprofit group of citizens, organizations, and businesses working for clean, safe, healthy lakes for everyone. Each spring WAL partners with the Wisconsin Department of Natural Resources and UW Extension's lake programs to sponsor the Wisconsin Lakes Convention where more than 600 lake lovers come to learn about caring for their lakes and waterways.

□ Working with Environmental Organizations

Staff also cooperated with the River Alliance of Wisconsin to produce an annotated reading list on "Building Conservation Organizations". The list which also includes Web sites is available at *www.aqua.wisc.edu/waterlibrary/action2.asp* 

□ Reading Day with First Lady Jessica Doyle

The Water Resources Library supported Madison JASON teacher Barbara Bauer's fourth-grade Windsor Elementary class of 30 students for Reading Day at the Executive Residence on October 5, 2004. For pictures, see *seagrant.wisc.edu/MadisonJASON/Default.aspx?tabid=1307*.

#### Web Sites

WRI maintains several other Web sites in addition to the site for Eight International Conference on Mercury as a Global Pollutant described above.

The main **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 **UW Water Resources Library Web Site** (*wri.wisc.edu/library*) introduces UW-Madison faculty, staff and students to the services of the library. During the reporting period, the library cooperated with UW Steenbock Library to produce "Guide to Finding Water-Related Information" at *www.library.wisc.edu/guides/WaterResources/index.htm*.

The **Wisconsin Water Policy Inventory** (*www.aqua.wisc.edu/waterpolicy*) is a webbased 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. During the reporting period, the groundwater quantity/high capacity well law (2003 AB 926) was added to the Inventory.

The **ASC Publications Store** (*www.aqua.wisc.edu/publications*) features publications from both the Water Resources and Sea Grant Institutes. *Water Resources 2004-06 Directory of Projects and People* and the Wisconsin Water Library bookmark were added to the online store during the past year.

**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 added several special features or annotated reading lists on popular topics, including "Environmentally-Friendly Lawn and Garden Care", "Native Americans and the Environment", and "Great Lakes Travel Narratives, History and Tourism".

The Water Resources Library maintains an additional Web site at *seagrant.wisc.edu/MJ/Default.aspx?tabid=83* to make books, videos and other equipment available to teachers participating in Madison JASON, an educational science project involving teachers and students from public schools and one home school in 11 Madison-area communities. Last year's topic was "Disappearing Wetlands".

#### Publications resulting from information transfer activities are entered below.

## **Student Support**

Student Support						
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total	
Undergraduate	3	3	1	12	19	
Masters	2	1	1	3	7	
Ph.D.	2	1	0	6	9	
Post-Doc.	0	1	0	0	1	
Total	7	6	2	21	36	

### **Notable Awards and Achievements**

NIWR REVIEW. Dr. James Hurley, Assistant Director for Research and Outreach continued to coordinate the peer review process for the 2004 NIWR-USGS 104(G) Competitive Grants Program. A total of 45 proposals were submitted in 2004 through the electronic submission process. Thirty proposals were forwarded to the peer review panel in late June of 2004, which was chaired by Hurley. The panel selected 8 proposals for funding. Working closely with Dr. John Schefter of USGS, Hurley assigned reviewers, coordinated reviews, ranked proposals and interacted with principal investigators.

WISCONSINS WATER LIBRARY. During 2003, the Wisconsin WRIs Water Resources Library (WRL) partnered with the UW Sea Grant Institute to develop Wisconsins Water Library (www.aqua.wisc.edu/waterlibrary) as a special outreach project in celebration of Wisconsins Year of Water observance. Established in 1964, the WRL is unique among UW–Madisons many libraries for its collection of almost 30,000 volumes of water–related information, including a curriculum collection, educational videos, and numerous journals and newsletters. The Water Library website enables any Wisconsin resident to check out the librarys materials, which are sent free of charge to the users local public library for pick up and return. This makes the WRL the only, if not the first, academic library in Wisconsin to make its collection directly available online to residents throughout the state. This unique online resource received the South Central Library Multitype Library of the Year award for 2004. Wisconsin's Water Library was also chosen by the Great Lakes Information Network as Site of the Month for April 2004.

SMART GROWTH. 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. Each is required to have a long–range land use plan so that all future growth is consistent with the plan. Recent projects funded through the federal NIWR university–state partnership have identified specific zones in the state that are exhibiting severe drawdown from municipal groundwater supplies serving rapidly growing communities. In response, the state has mandated that drinking water supply sustainability be incorporated into comprehensive land use plans. However, many communities have little expertise on identifying and protecting the quantity of their water supply. Wisconsin Water Resources Institute (WRI) researchers are working with a pilot community to develop a protocol to quantify and understand its groundwater budget. That information will then be coupled, via a flow model, with projected changes in land use and pumping demand to define the effects of different development approaches on the communitys water supply. The protocol will be shared with other communities to help them decide how best to actively manage and protect the recharge areas that supply their water.

RAINGARDENS. In urbanized areas of Wisconsin that rely on groundwater as the primary source of water, groundwater withdrawals significantly exceed recharge rates. Besides posing a long-term urban water supply problem, this can cause environmental degradation by reducing the groundwater discharge to adjacent springs, wetlands, streams, lakes and associated ecosystems. Rain gardenssunken gardens that receive local stormwater runoffappear to offer a low-cost way to enhance urban groundwater recharge while reducing urban stormwater runoff. The Wisconsin WRI sponsored a field demonstration and evaluation project to test model predictions that a rain garden with an area equal to 10 percent of the surrounding pervious area can double the local groundwater recharge rate. As part of the project, researchers developed a user-friendly computer program that designs and evaluates the performance of bioretention facilities. The Wisconsin Department of Natural Resources has used the program to develop new rules for stormwater infiltration practices, and also makes the program available to the public via the Web. These WRI researchers have developed a technical manual and software program for bioretention facility design to enhance groundwater recharge in Wisconsin that has been submitted to the University of Wisconsin Aquatic Sciences Center for publication. The Wisconsin Department of Natural Resources has adopted RECARGA, the model we developed for designing and evaluating bioretention facilities, as an acceptable tool for the design of infiltration practices. The model is provided at the DNR website (http://www.dnr.state.wi.us/org/water/wm/nps/models/SLAMM.htm)and is a direct result of funding to Dr. Ken Potter (UW-Madison) through USGS 104B funds.

GRADUATE STUDENT AWARDS. Daniel Alessi (UW-Milwaukee)received the best poster paper award at the annual meeting of the Wisconsin Chapter of the American Water Resources Association for his presentation on the development of the studys ground water model. Tara Root (UW-Madison)received a student research award from the Hydrogeology Division of the Geological Society of America for work on this project (2002).

INTERNATIONAL WATER RESOURCES ISSUES. The City of Madison Wisconsin has established Sister City programs with nine municipalities worldwide, since the inception of the program in 1988. Criteria for selection of a sister city include mutual interest and involvement in the areas of culture, business, technology, education, agriculture, sports and humanitarian interests. The Madison-Mantova Italy program has become quite active since its official signing ceremony in December 2001. Several exchanges have taken place in both cities and the program has flourished. In May 2004, a delegation of nine representatives from Mantova, led by Mayor Gianfranco Burchiellaro visited Madison for three days with the main intent of discussing water quality issues. Dr. James Hurley, University of Wisconsin Water Resources Institute and Dr. William Sonzogni, UW Environmental Chemistry and Technology Program, organized a two-day roundtable discussion between the Mantova delegation and water quality experts from the UW-Madison, Wisconsin Department of Natural Resources, Dane County Lakes and Watershed Commission and the U.S. Geological Society. Members of the Mantova delegation represented the City of Mantova, its Environmental Department, the Italian Centre for River Restoration, Mantova Committee for Lakes Restoration, and representatives of local utilities and industry. Mantova and Madison share many concerns about natural resource issues. Both cities lie next to significant water bodies that are affected by anthropogenic stressors. Both face issues regarding population growth and land use in the surrounding area. Both show similar concerns for maintaining enhanced water quality and protecting the natural beauty of the surrounding area. It was clear from our workshop in May 2004 and subsequent visits by delegations from both cities, that these resource issues are key links between our two cities and provide unique opportunities for this Sister City relationship.

## **Publications from Prior Projects**

- 2001WI47O ("Removal of Heavy Metals and Radionuclides from Soils Using Cationic") Articles in Refereed Scientific Journals - Willms, C., Li, Z., Allen, L., and Evans, C. V. (2004) Desorption of Cesium from Kaolinite and Illite Using Alkylammonium Salts, Applied Clay Science, 25, 125-133.
- 2002WI55O ("F Test for Natural Attenuation in Groundwater: Application on Benzene") Articles in Refereed Scientific Journals - Pelayo, A.M. and F.S. Evangelista. 2003. A Statistical F Test for the Natural Attenuation of Contaminants in Groundwater. Environmental Monitoring and Assessment 83: 47-70.
- 2002WI4B ("Removal of Arsenic in Groundwater Using a Novel Mesoporous Sorbent") Articles in Refereed Scientific Journals - Jang, M, EW Shin, JK Park, SI Choi. 2003. Mechanisms of arsenate adsorption by highly-ordered nano-structured sili-cate media impregnated with metal oxides. Environmental Sci and Technol 37(21):5062-5070
- 4. 2002WI3B ("Field Evaluation of Raingardens as a Method for Enhancing Groundwater Recharge") Articles in Refereed Scientific Journals Dussaillant, A.R., C. Wu, and K.W. Potter. 2004. Richards Equation Model of a Rain Garden. Journal of Hydrologic Engineering 9(3): 219-225.