University of Wisconsin Water Resources Institute Annual Technical Report FY 2002

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

Field Evaluation of Raingardens as a Method for Enhancing Groundwater Recharge

Basic Information

Title:	Field Evaluation of Raingardens as a Method for Enhancing Groundwater Recharge
Project Number:	2002WI3B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	WI - 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Supply, Water Quantity, Water Use
Descriptors:	
Principal Investigators:	KENNETH W POTTER, KENNETH W POTTER

Publication

Field evaluation of raingardens as a method for enhancing groundwater recharge

Kenneth Potter, Civil & Environmental Engineering, University of Wisconsin-Madison
Funding Agency: UWS Groundwater Research Program

Project duration: July 2001 – June 2003

In urbanized areas of Wisconsin that rely on groundwater as the primary source of water, groundwater withdrawals significantly exceed groundwater recharge rates. This can lead to environmental degradation, as it reduces the discharge of groundwater to springs, wetlands, streams, and lakes and their associated ecosystems. Raingardens, sunken gardens that receive stormwater runoff, appear to offer a solution to groundwater loss. In an ongoing research project, the PI has used a numerical model to demonstrate that a raingarden with area equal to 10% of the connected pervious area can double the local groundwater recharge rate. The explanation of this surprising result is that focusing of runoff to a small, highly pervious area greatly reduces losses to evapotranspiration.

Before raingardens are widely implemented, they should be tested through carefully designed demonstration projects. The goals of this project are to construct an experimental raingarden and use it to improve our understanding of, and ability to model, raingarden performance. At our experimental raingarden we will monitor precipitation, inflows, soil moisture, outflows, and seepage from the root zone. We will also numerically simulate the performance of the raingarden using a previously developed model. Comparisons of the modeling and experimental results will enable us to verify the accuracy of the former, and correct if necessary.

Project Update

We have constructed an experimental raingarden, at the Dane County Parks Lussier Family Heritage Center in Madison. The raingarden is lined so that the drainage can be collected and measured. The raingarden has an area of 5.4 m^2 and is connected to two downspouts, each draining about 55 m^2 of roof. Valves allow one or both roof areas to be connected, yielding area ratios of 0.05 and 0.10. Roof runoff is measured by means of a prerated trapezoidal flume in which a pressure transducer has been installed. Another transducer monitors the ponded depth in the raingarden. Runoff from overspill is collected in an overflow tank. To estimate soil moisture storage, Time Domain Reflectometry (TDR) probes were placed at seven depths and connected to a multiplexer, cable tester, and data logger. Seepage through the raingarden (which we take to be recharge) flows through a bottom drain to a pipe that discharges into a seepage collection tank. The tank contains a siphon that empties and triggers a switch when it accumulates 112 liters. The tank also contains a pressure transducer for monitoring changing water levels.

Full instrumentation of the experimental raingarden was achieved in the summer of 2002. Three controlled experiments were run to provide validation data for the Richards Equation model. For these experiments, a water source was used to provide a constant application rate until the raingarden ponded to 15 cm. The soil moisture data obtained from these experiments compared reasonably well with the model predictions. However, the measured drainage volumes were 13 to 27% lower than the predicted volumes. We concluded that the discrepancy was due to leakage through the openings that provide access to the TDR probes, and have taken steps to greatly reduce the leakage rates. In the spring of 2003 we took steps to eliminate the leakage.

Funding has been obtained to continue operation of the raingarden for an additional two years. This will enable long-term observations of raingarden performance, including observations during snowmelt periods.

Removal of Arsenic in Groundwater Using a Novel Mesoporous Sorbent

Basic Information

Title:	Removal of Arsenic in Groundwater Using a Novel Mesoporous Sorbent
Project Number:	2002WI4B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	WI - 2nd
Research Category:	Engineering
Focus Category:	Treatment, Toxic Substances, Water Quality
Descriptors:	arsenic, treatment
Principal Investigators:	JAE K PARK, Marc Anderson

Publication

Progress Report of WRI

Title: Removal of Arsenic in Groundwater Using Novel Mesoporous Sorbent

The highly ordered mesoporous silica media, SBA-15, was synthesized and incorporated with iron, aluminum, and zinc oxides using an incipient wetness impregnation technique. Adsorption capacities and *kinetics* of metal-impregnated SBA-15 were compared with activated alumina which is widely used for arsenic removal. Media impregnated with 10% of aluminum by weight (designated to Al_{10}SBA-15) had 1.9~2.7 times greater arsenate adsorption capacities in a wide range of initial arsenate concentrations and a 15 times greater initial sorption rate at pH 7.2 than activated alumina. According to our previous x-ray photoelectron spectroscopy (XPS) study, the oxidation phase of aluminum incorporated onto the surface of SBA-15 was assigned to Al-O, which has lower oxidation state than activated alumina (Al_2O_3). By employing the one- and two-site models, surface complexation modeling was conducted to investigate the relationship between the aluminum oxidation states in different media and adsorption behaviors such as *isotherms* and *kinetics*. Surface complexation modeling results for arsenate adsorption edges conducted with different pH showed that Al_{10}SBA-15 have a dominated monodentate complex ($SAsO_4^{2-}$) while activated alumina have bidentate complexes ($XHAsO_4$ and $XAsO_4^-$) at pH 7.2, respectively. In *kinetic* studies at pH 7.2 ± 0.02, Al_{10}SBA-15 has only a fast-rate step of initial adsorption while activated alumina has two different fast- and slow-rate steps of arsenic adsorption. Therefore, it can be inferred from Grossl *et al.* that the monodentate arsenate complex predominant in Al_{10}SBA-15 is leading to faster adsorption rates than bidentate arsenate complexes favored at activated alumina. Therefore, the overall results suggest that the arsenate adsorption behavior and arsenate surface complexation might be well explained by aluminum oxidation states and surface structural properties of media.

Using an incipient wetness impregnation, $La(NO_3)_3 \cdot xH_2O$ (where x = 3 ~ 5) was impregnated for calcined SBA-15. Through the FTIR analysis, it was found that there was no structural collapse of pore structures occurred by the attacks of lanthanum precursors for Si-O bonds. This phenomenon is different with aluminum impregnation, in which a structural collapse occurred at 30% of aluminum impregnation. As a result of arsenate *kinetic* tests, La_{20}SBA-15 had an arsenate adsorption capacity of 0.95 mmol/g or 70.8 mg/g, which is about 10-fold higher adsorption capacity than that of activated alumina. In addition, *Kinetic* trends of lanthanum impregnated SBA-15 and lanthanum oxide were very similar and have higher determination coefficients (R^2) of simple Elovich model than those of parabolic diffusion, which governed kinetics of aluminum impregnated SBA-15. Results of *isotherms* using bottled water exhibited that LaSBA-15 had a very strong selectivity for arsenate because its adsorption capacities were not deteriorated by several other anionic species, such as sulfate, nitrate, and chloride. This result agreed well with Wasay *et al.*, in which arsenate adsorptions of lanthanum impregnated silica gel were not reduced with other anions such as Cl^-, Br^-, I^-, NO_3^-, and SO_4^{2-}.

Through several characterization studies and adsorption *kinetic* or *isotherm* tests, lanthanum was found to be a good candidate of functioning chemicals to have highly active sites for arsenate adsorption. Considering higher adsorption capacity and fast sorption rate of arsenate removal, lanthanum incorporated SBA-15 may be one of prospective adsorption media for arsenic removal. A series of column tests is being performed to determine adsorption capability, minimum effluent arsenic concentration, time for regeneration, and loading rate.

References

Presentation

Jang, M., E.W. Shin, and J.K. Park. Removal of Arsenic Using Metal-Impregnated Mesoporus Media. 75th Annual Water Environment Federation Conference, Chicago, Sept. 29-Oct. 2, 2002.

Paper

Jang, M., E.W. Shin, J.K. Park, and S.I. Choi. Mechanisms of Arsenate Adsorption by Highly-Ordered Nano-Structured Silicate Media Impregnated with Metal Oxides. Submitted to *Environmental Science and Technology*, 2003.

Patent

Park J.K. and M. Jang. "Removal of Arsenic and Other Anions Using Novel Adsorbents," Patent (US Patent) Proceeding.

Development of Translators for Filterable Metals Based on Watershed Characteristics

Basic Information

Title:	Development of Translators for Filterable Metals Based on Watershed Characteristics
Project Number:	1999WI0015G
Start Date:	10/1/1999
End Date:	9/1/2001
Funding Source:	104B
Congressional District:	WI 2nd
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Surface Water, Non Point Pollution
Descriptors:	metals, GIS, land use, land cover
Principal Investigators:	David E. Armstrong, Martin M. Shafer, William C. Sonzogni

Publication

Development of Translators for Filterable Metals Based upon Watershed Characteristics

Project Number: C-04

Start Date: 09/01/1999

End Date: 08/31/2001

Research Category: Water Quality

Focus Category #1: Non Point Pollution

Focus Category #2: Toxic Substances

Focus Category #3: Models

Lead Institution: The University of Wisconsin

Principal Investigators:

David E. Armstrong, Professor, University of Wisconsin-Madison 01
James P. Hurley, Professional Staff, Water Resources Institute 02
William C. Sonzogni, Professor, Wisconsin State Laboratory of Hygiene 03
Martin M. Shafer, Professional Staff, University of Wisconsin-Madison 04

Problem and Research Objectives:

Loading of trace metals from point and nonpoint sources poses serious concerns for the water resources of the Midwest. Stream health, as measured by biodiversity and potential to support viable populations of target species, has declined markedly in many Midwest river systems. This trend can be traced to watershed disturbances and both nonpoint and point loadings. Concern over the impacts of metals on receiving waters emphasizes the need for information on both the factors controlling export and fundamental information on metal speciation in the receiving waters.

Methodology:

Our fundamental objective is to model the partitioning of a suite of trace metals to environmental solids across geochemically contrasting environments. To accomplish this we will apply two general modeling strategies to a unique and large database of reliable trace metal data: (1) multivariate regression with chemical vectors, and (2) multivariate analysis of environmental characteristics in a GIS-based format. The trace metals chosen for study (As, Cd, Cr, Cu, Pb, and Zn) are all significant environmental contaminants and reactivity with inorganic ligands, particle surfaces, and functional groups on DOC are significantly different. Therefore, we will take advantage of the contrasts in aqueous speciation of these metals to probe metal specific retention and partitioning processes in the watersheds. Geochemical characteristics of the streams and associated watersheds are defined through the measurement of major ions, dissolved organic carbon (DOC), suspended particulate matter (SPM), pH, and specific conductance. The study will draw upon data for total and filterable metals that our research group has obtain for over 80 relatively homogeneous watersheds in our study area (the complete Lake Michigan basin, the complete US Lake Superior basin, and the entire State of Wisconsin). This extant data will be supplemented by additional fieldwork designed to fill in gaps in our current database. This work will address (1) spatially significant combinations of environmental variables in under-represented ecotypes, and (2) specific combinations of DOC, SPM, and conductance missing from the current data set. GIS coverages will be assembled for regions of the Midwest incorporating our study area. The coverages will include: (1) Land Cover/Land Use (7 subclasses; (2) Surficial Deposits - Texture (5 subclasses); (3) Bedrock Geology (6 subclasses); (4) Depth to Bedrock (4 subclasses); and (5) Stream Slope. Multivariate statistics will be applied to describe the variability in metal levels. Metal descriptors used in these analyses will include: levels of total, filterable, and particulate metal; fraction dissolved; metal-partition coefficient (Kd); and amount of particles (ug/g). The multivariate models will allow us to rank the study variables as to their influence on individual metal descriptors. Modeling in explicit support of translator development will include multivariate regressions directly on the fraction dissolved (Fd), as well as examination of fundamental factors underlying the Fd, i.e., the partition coefficient, and levels and characteristics of particulate and filterable ligands. In implementing the GIS-watershed characteristic component on the study, the specific hydrologic state of each river at the time of sampling will be factored-in. We plan to focus the GIS-multivariate analyses on baseflow conditions, with a much more limited analysis at a 2-year recurring high flow condition. Regression models will be constructed for the complete data set, as well as for subsets including: (1) similar ecotype, (2) similar environmental characteristic, (3) single basin, and (4) single watershed.

Principal Findings and Significance:

Progress: Detailed GIS-based coverages of Land Use/Land Cover, Surficial Deposits, Bedrock Geology, Depth to Bedrock and Soil Characteristics for the entire study area have been assembled. A comprehensive statistical analysis of these coverages has been performed through which the representativeness of our current site database has been evaluated. In addition, all important regions of relatively homogeneous combinations of the primary GIS-coverages have been identified. The extant trace metal data has been examined for its ability to support robust statistics, and in areas where found lacking, two matrices of additional field sites were developed that would improve the statistical validity of our conclusions. One matrix was structured around homogeneous Forested watersheds, and the other around homogeneous Agricultural watersheds. In both instances the matrix axes incorporated homogeneous watershed classes of Surficial Deposits and Bedrock Geology, identified using GIS. The field sampling plan also included an enhanced study of the role of Wetlands on trace element partitioning. The influence of Wetlands was approached by identifying watersheds with increasing wetland percentage, while holding most other geospacial characteristics constant. This ambitious field sampling plan of over 35 sites was completed in mid-late Fall of 2000. Supporting analyte and trace metal measurements on these samples were completed in early Spring 2001. In assembling the GIS coverages, we developed a novel, totally automated, method of delineating watershed basin areas through the use of digital elevation models. This enhancement to traditional geospacial analysis promises to greatly increase the productivity of watershed characterizations. A subset of the 35 sites, in particular the Wetland gradients, will be resampled in July 2001, to evaluate seasonal controls. Analysis of the relationships between geospacial characteristics and both trace metal descriptors and supporting variables (DOC, SPM, I, e.g.) are underway, using statistical techniques such as ANOVA (on structured matrices) and step-wise regression.

Findings: The percentage of Wetland in a watershed is a strong predictor of both filterable metal concentrations and filterable metal export in the stream draining the watershed. This relationship is particularly strong for the species: Cd, Hg, methyl-Hg, Pb, and Zn; and is statistically more powerful in watersheds/basins with relatively low ionic strength waters. Given our observation of a highly significant relationship between Wetland percentage in the watershed and DOC levels, the implication is that DOC, either directly or indirectly, is a controlling influence on filterable metal levels and stream export. We also observe a statistically valid inverse relationship between DOC levels and the partition coefficients of certain metals (Cu, Hg, Pb, Zn), which is consistent with our modeling construct of DOC as a "dissolved" ligand in competition with functional groups on suspended particle surfaces. For total (unfiltered) metals, surficial deposit characteristics (texture and soils) appear to have the greatest influence on trace metal concentrations among all the watershed variables examined. The highest metal concentrations are observed in those watersheds producing more erodible particles, or particles with higher metal content. Specifically, soil permeability consistently accounted for the largest fraction of the variance in unfiltered trace metal concentrations. Strong negative correlations are observed between permeability and metal levels - e.g., a decrease in soil permeability results in an increase in metal concentrations. This finding is consistent with other observations that indicate that less permeable clay regions are associated with higher metal levels, and highly permeable sand and gravel regions are associated with lower trace metal levels.

Publications and Presentations:

Wieben, A.M., M.M. Shafer, and D.M. Robertson. 2001. Development of Translators for Trace Metals Based on Watershed Characteristics. Abstract for 44th Conference on Great Lakes Research, International Association for Great Lakes Research, June 10-14, 2001; Green Bay, Wis.

Wieben, Ann, Martin M. Shafer, and David E. Armstrong. 2001. Analysis of Watershed Features Influencing Trace Metal Distribution between Suspended Particles and Water Using a GIS-Based Model. Abstract for 21st International Symposium, North American Lake Management Society, November 7-9, 2001; Madison, Wis.

Wieben, Ann. 2002. Analysis of Watershed Features Influencing Trace Metal Distribution between Suspended Particles and Water Using GIS-Based Models. M.S. Thesis, Land Resources, University of Wisconsin-Madison.

Descriptors:

Trace Elements, Metals, Mathematical Models, Watershed Management, Rivers, GIS, Translators, Particle-Partitioning, Suspended Sediment, Toxic Substances, Water Quality, Geochemistry, Contaminant Transport, Organic Carbon.

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:	8/31/2003
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:	James P. Hurley, Kristofer R Rolfhus

Publication

1. 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.
2. 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.

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

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

Problem and Research Objectives

Fish consumption advisories have been issued in US 40 states 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 non-point 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 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 four-year 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 are to:

1. Provide direct information on the effects of non-point 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 near-ambient 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 (non-radioactive) isotope of mercury [e.g., $^{199}Hg(NO_3)_2$, $^{200}Hg(NO_3)_2$, $^{202}Hg(NO_3)_2$] 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 low-level 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.

Principal Findings and Significance

Continuing MEAALICUS Work during 2002 Field Year

1. **Detailed water column sampling:** We collected profiles of particulate and filtered Hg and MeHg and ancillary chemistries in both the East and West basins of L658. A basic profile of 6 depths (2m, 5m, 7m, 9m, 13m, and 5cm above the sediment water interface) was collected the day before each spike. Once a month an expanded profile (see Close interval sampling below) was collected to better define the profile above the sediment water interface.
2. **Particulate flux estimates:** We collected settling particulate matter using sediment traps (cylindrical acrylic tubes positioned at the base of the thermocline, and at a depth 1m above the sediment-water interface). Traps were changed every two weeks and particulate matter split and processed for HgT, MeHg and ancillary measurements.
3. **Close Interval Sampling**: In order to characterize the flux of dissolved constituents across the sediment-water interface, we sampled the Close Interval Sampler (CIS) device in each basin. This allowed for sampling of water at a fixed, fine scale (5, 10, 20, 40, 80 cm above the sediment-water interface). Sampling ports on the fixed sampler allowed temporal

sampling of exact depths, regardless of the surface water conditions. Conventional sampling from a boat is affected by wind and waves that change the vertical position of the sampling boat and thus the depth sampled.

4. **Characterizing colloidal transport:** In September, we isolated the colloidal phase in the water column using a tangential-flow ultrafiltration system. Filtered water samples were collected at three depths with contrasting water chemistries. The depth at 3.5m had a peak in oxygen and chlorophyll a; the depth at 7m was at the inflection point of the oxygen profile; and the depth at 11.5m was anoxic with a peak in turbidity. The specific parameters were chosen, in part, to complement the biouptake experiments (see below). As far as we know, this was the first attempt to isolate colloids under anoxic conditions. The ultrafiltration system was purged with argon prior to the separation, and the headspace above the sample was purged with argon during the separation.

New Initiatives during 2002 Field Year

1. **Biouptake experiments:** In September, Patrick Gorski (one of our graduate students) ran a biouptake experiment using the fractions created during the ultrafiltration separation (<0.45 micron, 0.45 micron to 10 kDa, and <10 kDa). Cultures of the algae *Selenastrum* were spiked into flasks containing the different ultrafiltration fractions to assess the relative biouptake of mercury. Each flask received a spike of isotopic inorganic mercury (^{201}Hg) and methylmercury (^{199}HgMe). In addition to observing methylation and demethylation during the 24-hour incubations, the use of stable isotopes created an efficient way to compare the availability of very new mercury (the 199 and 201 spikes), recently equilibrated mercury (^{202}Hg from the regular lake spikes), and old mercury (^{198}Hg, ^{200}Hg – the terrestrial isotopes that have yet to be found in the lake above native levels).
2. **Redox controls on Hg cycling:** In July, Shawn Chadwick (one of our graduate students) began collecting data on the redox cycle of iron and manganese near the sediment water interface. Fe(II)/Fe(III) speciation samples and sulfide samples were added to the monthly expanded profiles in L658. This data will help us differentiate between two particulate mercury delivery mechanisms to the sediments: iron hydroxide precipitation and scavenging of mercury, versus that of organic carbon. Iron particulates were collected directly on filters from each depth of the CIS. In addition, a batch reactor was developed to artificially oxygenate a 5L sample of hypolimnetic water. Iron hydroxides were then isolated by centrifugation. Particles collected from all methods will be analyzed for Hg, MeHg, acid volatile sulfide (AVS), major ions, and oxalate-extractable iron and manganese. In addition, some samples were processed through four sequential extraction steps: First, 1M KOH for organic matter, then 6M HCl for the easily labile fraction, followed by two stronger acidic solutions: 12M Nitric Acid, and Aqua Regia. These experiments were repeated monthly in August and September.
3. **Sediment/water interface chemistry:** One of the most important numbers needed to determine the magnitude and direction of the mercury flux into (or out of) the sediment, is the pore-water mercury concentration right at the sediment water interface. Unfortunately this is also one of the more difficult locations in the lake to obtain a representative sample. We have

a good handle on the overlying lake water using the CIS, and a good handle on the deeper pore waters using the Janke squeezing technique. The Janke squeezer does an excellent job extracting pore water at specific depths along a core, but the samples are integrated over a 1cm interval and the sample at the top of the core (0-1cm) may be influenced by the infiltration of overlying water. Much of the sediment/water interface chemistry has been theorized to occur in the micro layer of freshly fallen sediment. To obtain an independent measure of the pore water concentration at the sediment water interface, we modified our sediment trap design to focus freshly fallen material into narrow vial. In August, we added these sediment traps in each basin, and collected material over one-month intervals. The vial was brought back to the laboratory and the pore water was extracted in a glove box.

Cooperative work

Our research group continues to work cooperatively with other researchers on the METAALICUS project. In addition to performing specialized isotopic mercury analysis with the US Geological Survey's isotope laboratory (Middleton, WI), we participated in two intercalibration exercises. One was among METAALICUS investigators and the other was coordinated through the Florida DEP that included 6 mercury labs across the US.

Microfabricated, Low Power, Inorganic Water Quality Sensor based on Direct Current Argon Plasma Emission Spectroscopy

Basic Information

Title:	Microfabricated, Low Power, Inorganic Water Quality Sensor based on Direct Current Argon Plasma Emission Spectroscopy
Project Number:	2001WI361G
Start Date:	9/1/2001
End Date:	8/31/2003
Funding Source:	104B
Congressional District:	Wisconsin, 2nd
Research Category:	Engineering
Focus Category:	Methods, Toxic Substances, Water Quality
Descriptors:	sensors, metals, in-situ
Principal Investigators:	, Marc Anderson, Yogesh B. Gianchandani

Publication

Microfabricated, Low Power, Inorganic Water Quality Sensor based on Direct Current Argon Plasma Emission Spectroscopy

Marc A Anderson Professor, The University of Wisconsin-Madison
Yogesh B. Gianchandani Associate Professor, The University of Michigan-Ann Arbor
Funding Agency: U.S. Geological Survey

Project duration: September 2001 – August 2003

Analytical water quality assessment is an extremely costly process that requires labor-intensive collection, transportation, and laboratory analyses of samples. In addition, even in the most careful of procedures, sample contamination can compromise the analysis. Clean sampling procedures, clean rooms, and super clean reagents and instruments are often required to analyze trace-level contaminants. Also, research laboratories currently employ sophisticated instruments to measure dissolved concentrations of inorganic and organic contaminants in our natural water systems. The cost associated with the purchase and maintenance of these instruments is extremely large. The development of an inexpensive multiple detector system that can routinely measure water quality parameters accurately, reliably, in situ, in real time, and at minimum cost would be an invaluable contribution to the field of environmental chemistry.

The primary objective of this project is to initiate the development of a microfabricated, low power sensor that utilizes DC argon plasma emission spectroscopy to monitor the inorganic chemical quality of water. The major components include: a sample delivery system, a DC plasma source, an argon reservoir and delivery system, optics (lenses, slits, mirrors), a diffraction grating, and a detector. The proposed microfabricated DC argon plasma emission spectrometer would significantly reduce the costs associated with environmental sampling. The labor costs for collection, transportation, and analyses mentioned above would virtually be eliminated by the proposed technology. Additional collection costs such as ship time on large sampling vessels (at a cost of thousands of dollars per day) would also be eliminated. Since the sample analysis is conducted in-situ, the sample contamination effects described above would also be greatly reduced. A long-range goal of this project might be to engineer a functional microfabricated DC plasma spectrometer (made from either non-toxic or biodegradable components) that can be deployed in a manner that provides large-scale environmental monitoring directly from research laboratories that could be continents away. Finally, in addition to deployment in natural waters, the proposed system could be used in city water treatment plants or even in households to monitor the concentration of aqueous chemical species.

Project Update

In our last report, which was filed in March 2003, we had shown a liquid electrode spectral emission chip (LEd SpEC) fabricated by a 4-mask lithography process that was used with an external spectrometer to perform the detection. A bias was applied across two electrodes immersed in separate microchannels, and a spark was ignited across them. This sputtered impurities from the cathode reservoir into the glow discharge, which enabled their spectroscopic detection. These initial measurements were made with saline samples. The concentration was calibrated by the ratio of the characteristic peak of Na to that of ambient nitrogen, and it was found to be well behaved over two orders of magnitude in concentration.

In the present report, we describe additional results that have been achieved with the same structure, which is shown in Fig. 1 for completeness. Additional measurements made with the same configuration have shown that:

a) Changing the pH of the solution (by HNO_3) can lead to significant improvements in sensitivity. As shown in Fig. 2, the ratio of the Na intensity peak in a 100 ppm NaCl sample to that of atmospheric nitrogen increases by an order of magnitude as the pH of the sample changes from roughly 6 to 1.

b) There are some benefits to using a thin-film metal anode and a liquid cathode instead of using a liquid microchannel for both electrodes: the liquid cathode is necessary to permit the sample to be sputtered into the glow discharge. However, experiments have shown that there is no detectable sputtering action at the anode. Consequently, if the liquid anode is replaced by the metal thin film, the discharge voltage required can be reduced, as shown in Fig. 3. This is accomplished without loss of chemical signal represented by the spectra, as shown in Fig. 4.

c) Samples with Pb, Cr, and Al contamination have been detected, as shown in Figs. 5, 6, and 7, respectively.

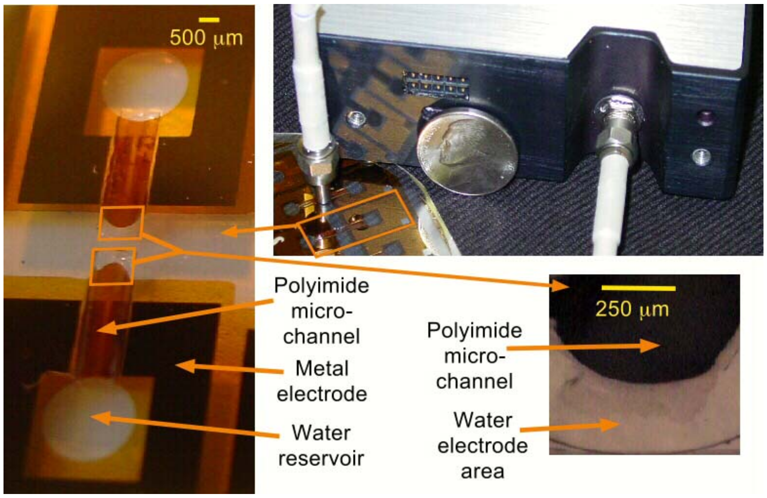

Fig. 1: Optical viewgraph of system and close-up view of the LEd-SpEC.

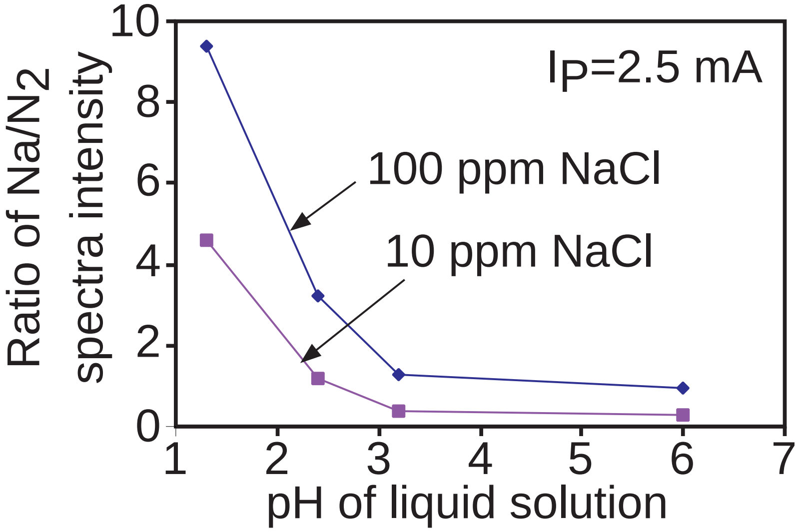

Fig. 2: Ratio of Na to N_2 spectral intensities as a function of pH of the tested solution.

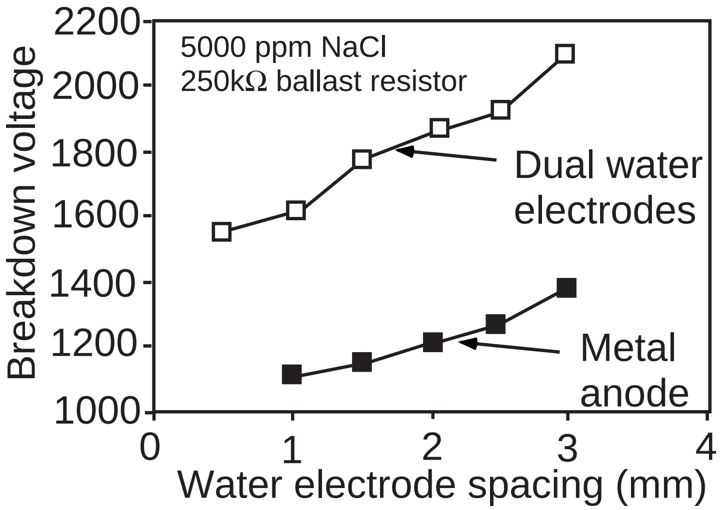

Fig. 3: Breakdown voltage dependence on interelectrode gap for 5000 ppm NaCl for dual liquid electrode device, and metal anode device.

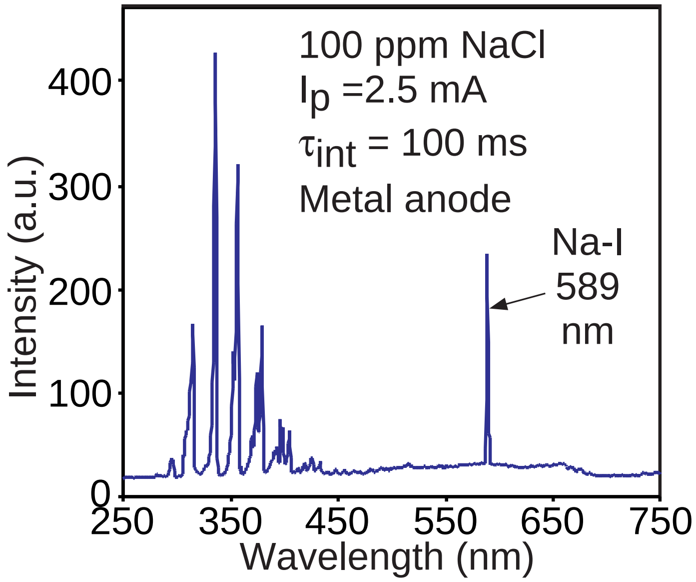

Fig. 4: Spectra generated from device with metal anode, and cathode filled with 100 ppm NaCl.

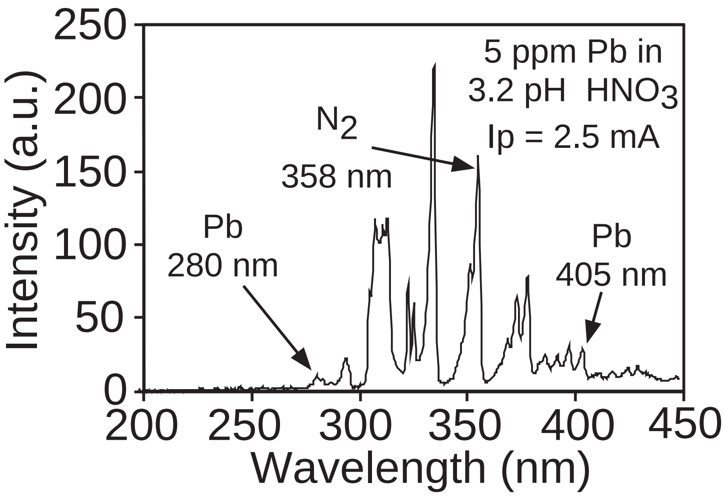

Fig. 5: Spectrum from sample containing 5 ppm Pb.

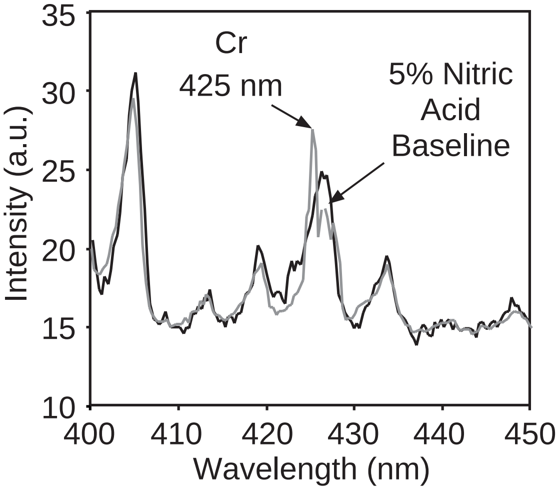

Fig. 6: Spectrum from sample containing 10 ppm chrome and 5% nitric acid, superimposed against a 5% nitric acid baseline.

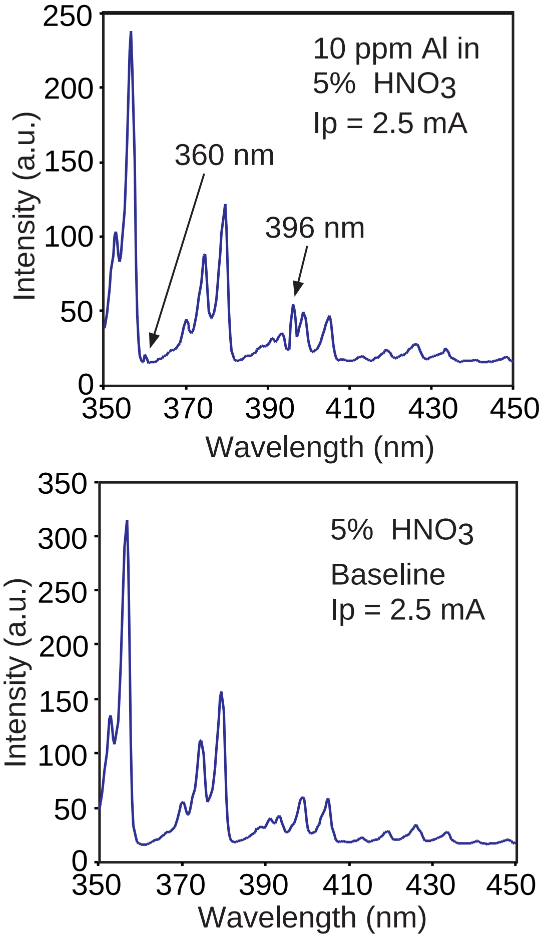

Fig. 7: (a-upper): Spectrum from sample containing 10 ppm Al in a 5% nitric acid solution and (b-lower): 5% nitric acid baseline.

We continue to be encouraged by the prospect of using the LEd-SpEC approach for the miniaturization of apparatus for detecting inorganic impurities in water. Our future work will explore ways to continue to improve the robustness, portability, and sensitivity of the device, as well as gain a better understanding of the characteristics of the microdischarges that make this device possible.

Impacts of Land Use and Groundwater Flow on the Temperature of Wisconsin Trout Streams

Basic Information

Title:	Impacts of Land Use and Groundwater Flow on the Temperature of Wisconsin Trout Streams
Project Number:	2001WI33O
Start Date:	7/1/2001
End Date:	6/30/2003
Funding Source:	Other
Congressional District:	2nd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Hydrology, Surface Water, Water Quantity
Descriptors:	trout, temperature, recharge, groundwater
Principal Investigators:	Stephen Gaffield

Publication

Impacts of land use and groundwater flow on the temperature of Wisconsin trout streams

S. Gaffield, Geological and Natural History Survey, University of Wisconsin-Extension

Funding Agency: UWS Groundwater Research Program

Project duration: July 2001 – June 2003

We are investigating the role of groundwater and surface water interactions in controlling the summer temperatures of Wisconsin trout streams. Trout require water temperatures below about 22 ^{o}C, and groundwater inflows are critical for cooling streams during hot weather. Stream channel shape and shade from riparian vegetation also influence stream temperature, and there is a lack of knowledge available for watershed managers to assess these complex interactions and predict the impact of land-use decisions on stream temperature.

Our approach combines field monitoring of several Wisconsin trout streams and model simulations of stream temperature, groundwater flow and groundwater recharge. During this project, we are adapting an existing stream temperature model developed for the Driftless Area for use in other ecoregions of Wisconsin, evaluating potential impacts of changes in management of the riparian zone on stream temperature, examining potential impacts of land use throughout a watershed on groundwater recharge and stream temperature, and determining the sensitivity of stream temperature to changes in groundwater inflow. Through these efforts, we hope to develop decision-making tools for watershed managers to predict the impact of management decisions on summer conditions in Wisconsin trout streams.

Project Update

We have applied the existing stream temperature model in 6 watersheds representing 3 Wisconsin ecoregions, and we are evaluating its ability to accurately represent conditions observed in the field. A manuscript describing this model is currently in revision after being submitted to the *Journal of the American Water Resources Association*.

In addition to testing the stream temperature model in each watershed, we are conducting a more detailed analysis for Rowan Creek. To develop a decision-making tool that provides information on the potential impacts of changing land use (in the riparian zone and throughout the watershed) on stream temperature, we are three models for groundwater recharge, groundwater flow and stream temperature. We have completed the models and have calibrated them to current conditions in this watershed. Using the recharge and groundwater models, we have tested the impact of different land use scenarios on stream base flow, and we are using this as input to the stream temperature model to assess the resulting impact on habitat.

We have constructed all three models and are in the process of calibrating the latter two. Once they accurately represent current conditions, we will test the impact of changing land cover, noting generalizations and techniques that can be applied to other watersheds.

The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling

Basic Information

Title:	The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling
Project Number:	2001WI34O
Start Date:	3/28/2001
End Date:	9/30/2002
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Surface Water, Non Point Pollution
Descriptors:	mercury, methylmercury
Principal Investigators:	James P. Hurley

Publication

1. 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.
2. Babiarz, C.L., J.P. Hurley, K.R. Rolfhus, D.P. Krabbenhoft, K.J. Scott and B.A. Branfireun. 2002. Colloidal phase transport of newly deposited mercury through contrasting watersheds: Insight from the METAALICUS project. Science of the Total Environment. In Press.

PROJECT SUMMARY

Title: The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling

Project ID: 2001WI34O

Principal Investigator: James P. Hurley, Associate Director for Research and Outreach, UW Aquatic Sciences Center

Background/Need: The potential consequences of Hg (Hg) contamination of aquatic food webs were first recognized in the 1950s and 1960s in Minamata and Niigata, Japan, where human consumers of contaminated fish were severely poisoned. These and other tragic incidents prompted widespread reductions in direct releases of Hg into surface waters in many countries. Hg levels in fish in affected waters typically declined during the years after point-source loads declined, leading to a widespread perception that the "Hg problem" had been solved. Since about 1985, however, widespread Hg contamination of aquatic biota has become evident in systems remote from obvious anthropogenic Hg sources. Investigations at these sites have shown that in most cases atmospheric transport and low rates of Hg deposition are responsible for the observed Hg contamination levels, and virtually any aquatic ecosystem is potentially affected. In some cases, concentrations in fishes from these remote sites have equaled or exceeded those in fishes from waters heavily contaminated by direct industrial discharges. Mercury concentrations in aquatic biota are often elevated, for example, in fish from low-alkalinity or humic freshwaters, newly flooded reservoirs, and surface waters that adjoin wetlands. However, we lack sufficient information to predict reliably which aquatic ecosystems will contain Hg-contaminated biota, and the effectiveness of recently proposed Hg emissions reduction strategies.

Unlike most contaminants, some natural processes in the environment actually increase Hg toxicity by the conversion to methylmercury (MeHg). Methylmercury comprises nearly all the Hg found in the top levels of aquatic food webs, yet it rarely exceeds 10 percent of the total mass of Hg in sediment or water. Gaps in our understanding of the processes and factors controlling exposure to MeHg (methylation, demethylation and biotic uptake) are a key challenges facing scientists investigating the Hg problem. Several information gaps currently exist in the environmental Hg science basis, including knowledge of the relative importance of factors controlling Hg methylation and bioaccumulation (Hg loading rates, Hg source type, ecosystem setting, and water and sediment chemistry.

The University of Wisconsin, Water Chemistry Program is a recognized world leader in Hg research, and has developed many of the low-level trace metal techniques used by many agencies, including the USGS. At the same time, the USGS, Wisconsin District has developed a expertise in mercury research, but the strengths of the USGS Hg Team are complimentary to the University of Wisconsin group. For example, the University of Wisconsin group has developed sophisticated methods for the isolation of specific dissolved organic carbon (DOC) fractions (Babiarz and others, 2000) that are largely responsible for the transport of Hg and MeHg in the environment. The USGS group, on the other hand, has expertise in photochemical process affecting mercury speciation and fate. Combined, the two research groups offer a complete set of research tools to examine mercury cycling in critical environments where we need a better understanding of the complex environmental mercury cycle

The USGS and University of Wisconsin have a long history of effective collaborations on mercury research, starting with the Mercury in Temperate Lakes (MTL) project in 1988, to the Mercury Accumulation Processes and Pathways (MAPP) project in 1992, to Deep Production in Lakes in 1994. More recently, the these two research groups teamed up to take on the very complex task of understanding the Everglades Hg problem from 1995 to 1999.

Objectives: For this proposal, the University of Wisconsin will provide technical assistance and leadership on the Mercury Experiment To Assess Atmospheric Loading In Canada and the United States (METAALICUS) Project. The USGS has responsibility to lead the watershed portions of this large, multi-national effort, and is in need of assistance from the University to effectively carry out this research. The overall objective of the watershed studies portion of this project is to determine the relative importance mercury derived from uplands and wetlands as it relates to mercury accumulation in fish. Assistance from the University of Wisconsin will focus on the determination of the role of DOC in the transport and speciation of Hg and MeHg. We propose to examine the pathways and transport rates of the various forms of mercury from the uplands to the lake. Depending on site conditions, various researchers have inferred that watershed mercury contributions to lakes vary from negligible to dominant. Some researchers would contend that even if we eliminate all mercury emissions to the atmosphere, long-term accumulations of mercury in soils would continue to maintain elevated levels of mercury in food webs at time scales spanning many decades. Without the ability to discriminate the mercury that originates from the watershed versus mercury from direct atmospheric deposition to the lake, the answer to this question will remain largely unresolved.

Previous work, as well as meso-scale experiment performed in the summer of 1999, lead us to conclude that watershed derived Hg can travel to the lake along surface and subsurface pathways. The primary routes to the lake include (1) transport over bedrock outcrops with overland transport; (2) infiltration and subsurface transport by groundwater flow; (3) overland or subsurface transport small streams and subsequent transport to the lake; and (4) transport from items 1-3 to wetlands, and subsequent discharge to the lake. The watershed studies will be conducted using interdisciplinary approaches toward understanding mercury transport and transformation processes and hydrological assessments. By using a geochemical and hydrological integrated approach we can calculate mass balances to assess the importance of watershed mercury to mercury added directly to the lake in a complete context. Due to the large area of the watershed, we propose to establish several monitoring locations to estimate mass fluxes of the amended isotope for each of the transport routes (1-4) listed above that will be representative of the watershed as a whole. We would then scale up our results by parsing the watershed into these four basic mercury-contributing areas. It is anticipated that the watershed studies will require 2-3 field seasons to conduct. A complete examination of the important processes will be undertaken to allow us to discriminate those driven by physical transport mechanisms (e.g., erosion, interception by bedrock outcrops) versus geochemical transport mechanisms (e.g., co-transport with dissolved and colloidal organic carbon, associations with ferric oxyhydroxides, conversion to methylmercury).

Resources allocated for this work will entirely used to fund a full time technician with the expertise and training to execute the DOC-Hg interactions research. In addition, extensive field sampling and experiments will be conducted during execution of the project.

Results:
This project is combined with 2000WI8G – progress listed under that project.

Removal of Heavy Metals and Radionuclides from Soils Using Cationic Surfactant Flushing

Basic Information

Title:	Removal of Heavy Metals and Radionuclides from Soils Using Cationic Surfactant Flushing
Project Number:	2001WI47O
Start Date:	7/1/2001
End Date:	6/30/2003
Funding Source:	Other
Congressional District:	2nd
Research Category:	Engineering
Focus Category:	Geochemical Processes, Toxic Substances, Treatment
Descriptors:	surfactants, lead, treatment, heavy metals
Principal Investigators:	Christine Evans, Zhaohui Li

Publication

Removal of heavy metals and radionuclides from soils using cationic surfactant flushing

Christine Evans and Zhaohui Li, Geology Department,
University of Wisconsin-Parkside
Funding Agency: UWS Groundwater Research Program

Project duration: July 2001 – June 2003

At some heavy industrial sites and DOE nuclear weapon manufacture and test sites, high concentrations of heavy metals and radionuclides in soils impose potential threat to groundwater. Soils with large surface areas and high cation exchange capacities may accumulate significant amounts of heavy metals and radionuclides, requiring eventual soil excavation and ex situ extraction of the heavy metals and radionuclides. Cesium and lead are two relatively common contaminants that are particularly difficult to extract from clay and oxide fractions of soils. For example, even after extensive washing with concentrated aggressive extracting agents, soils will most likely require further amelioration prior to legal disposal.

Sorption of cationic surfactant on negatively charged clay minerals and zeolites has been studied extensively in the past decade. However, the main focal points were mechanisms of sorption and the potential for using surfactant modified clays and zeolite to retard movement of organic contaminants. In fact, the strong affinity of cationic surfactants for soil particles--due to electrostatic attraction and hydrophobic bonding--makes them ideally suitable for removal of sorbed metal cations, including cesium and lead. The ultimate goal of the current proposal is to explore the feasibility and applicability of using cationic surfactant as a soil-flushing agent to desorb and extract heavy metals and radionuclides from soil. It is expected that the surfactant flushing will significantly increase the recovery of heavy metals and radionuclides from soil compared to conventional extracting agents. In addition, the cost for the surfactant-enhanced soil flushing will compare favorably to costs for traditional soil flushing.

Project Update

Cesium sorption and desorption by quaternary ammonium were tested for a kaolinite (KGa-1b) and an illite (Morris, IL). The Cs^+ sorption capacities on the kaolinite and illite were 12 and 24 mmol/kg, respectively. Desorption of Cs^+ from Cs^+-preloaded kaolinite and illite at different loading levels followed different trends. In general, Cs^+ was more readily removed from kaolinite than from illite. Surfactant chain lengths have strong influences on Cs^+ desorption from kaolinite. As the surfactant chain length increased, the percentage of Cs^+ removal from kaolinite increased. In contrast, initial surfactant concentrations have a greater influence on Cs^+ removal from illite than surfactant chain length. As the surfactant concentration increased, the percentage of Cs^+ desorption increased. For kaolinite, when surfactant concentrations were the same, a higher percentage of Cs^+ desorption was achieved when Cs^+ loading was low. As the Cs^+ loading on kaolinite increased, the percentage of Cs^+ desorption decreased. In contrast, a higher percentage of Cs^+ desorption was obtained from illite when Cs^+ loading was high. The percentage of Cs^+ desorption decreased as the Cs^+ loading on illite decreased. For kaolinite and illite with higher Cs^+ loading, the percentage of Cs^+ removal increased logarithmically with the increase in HDTMA/Cs^+. A minimum value of 30 for the HDTMA/Cs^+ ratio is required to achieve 80% Cs^+ removal from kaolinite.

The lead sorption and desorption from kaolinite and illite is currently under test.

We determined total and “plant-available” (DTPA-extractable) Pb for soils on four plots and also determined Pb content of plantain, dandelion, and clover growing on those plots. Total Pb in soils ranged from 124-440 mg kg^{-1}. DTPA-extractable Pb ranged from 18-73 mg kg^{-1}. Plant concentrations ranged from 16 mg kg^{-1} for clover to 99 mg kg^{-1} in dandelion. Concentration ratios (CRs) based on total soil Pb ranged from 0.1 to 1.7, and CRs based on “plant-available” soil Pb ranged from 0.4 to 13.

Results:

1. Plant-available (DTPA-extractable) Pb represented a consistent portion of total soil Pb ($r^2 = 0.866$, $p < 0.0196$).

2. Plant concentrations of Pb varied widely, even among plants collected from the same plots.

3. The relationship between total soil Pb and plant concentrations of Pb was also inconsistent ($r^2 = 0.046$, $p = 0.0$). Even when plant Pb concentrations were plotted vs. plant available soil Pb, there was no discernible correlation.

4. Concentration ratios based on total soil Pb also were unrelated to total soil Pb ($r^2 = 0.28$). When concentration ratios were calculated from “plant available” Pb, the relationship strengthened only slightly ($r^2 = 0.33$). Some CR’s were as high as 4 or 5, indicating that plants absorbed much more Pb than was nominally plant available.

5. Plotting CR’s based on DTPA-extracted soil Pb versus total soil Pb revealed a significant negative relationship ($r = -0.56$). This suggests that if there is a relationship between soil Pb concentrations and plant uptake of Pb, it is inverse, i.e., plant uptake decreases as soil Pb concentrations increase. Apparently plant mechanisms operate to restrict Pb uptake, perhaps to a definite threshold.

6. When CR’s are examined for individual species, a clear difference emerges. This difference is probably related to plant physiological response. Likewise, when CR’s based on “plant available” soil Pb are examined for individual species, the differences remain. Note, however, that clover CR’s are almost always ≤ 1. Mean values for dandelion and plantain are > 1, and values range as high as 4 or 5.

7. In some SE Wisconsin soils, association with the carbonate fraction effectively immobilizes approximately 30% of the total soil Pb, while a considerably smaller percentage is nominally plant available, as defined by extraction with DTPA. Presumably, the DTPA extracts the Pb adsorbed on colloid surfaces (clay, organic matter, and/or oxides). Some representative values for carbonate-bound and nominally plant-available lead are tabulated from three sites.

Site	fraction	N	Mean	S.D.	Max.	Min.
A	CO3	29	27.8	5.6	49.6	19.4
A	PA	29	7.9	7.3	22.7	0.32
B	CO3	28	29.1	9.8	46.2	0
B	PA	28	3.7	0.96	5.9	2.0
C	PA	22	17.9	5.5	23.1	8.6

CONCLUSIONS

1. The extraction protocol for nominally plant available Pb does not completely account for actual amounts of Pb that plants will absorb. This is likely because other soil processes and constituents play a role in bioavailability.

2. Plants appear to have a threshold limit for absorption of Pb that is not affected by increasing Pb concentrations in the soil.

3. Differences in plant concentrations of Pb by plant type also argue against the usefulness of a single determinant for “plant available” Pb. Data from nominally plant available extraction procedures must be interpreted in light of differences among soils and plants.

4. Application of phytoremediation to Pb-contaminated soils may be problematic. While Pb chemistry assures that natural attenuation—essentially immobilization—of Pb is usually effective, there are some situations in which it is essential to remove the Pb from the soil.

Mustard and chard were also grown in a greenhouse study, using soils that were loaded with controlled amounts of Pb. Analyses are underway to determine Pb content of plants and examine those data for correlations to various extractable fractions of Pb. The greenhouse study will be repeated this year, adding surfactant to the soils.

Co-occurrence and Removal of Arsenic and Iron in Groundwater

Basic Information

Title:	Co-occurrence and Removal of Arsenic and Iron in Groundwater
Project Number:	2001WI49O
Start Date:	7/1/2001
End Date:	6/30/2003
Funding Source:	Supplemental
Congressional District:	2nd
Research Category:	Engineering
Focus Category:	Treatment, Toxic Substances, Water Quality
Descriptors:	arsenic, iron, tratment, drinking water
Principal Investigators:	Paul McGinley

Publication

Co-occurrence and removal of arsenic and iron in groundwater

Paul McGinley, College of Natural Resources, University of Wisconsin-Stevens Point

Funding Agency: UWS Groundwater Research Program

Project duration: July 2001 – June 2003

This research is examining the co-occurrence and combined treatment opportunities for iron and arsenic in groundwater. New regulations and a greater understanding of the health effects of arsenic exposure will lead communities to consider reducing arsenic concentrations in their drinking water. If this removal can be implemented using conventional technologies while also providing other water quality benefits, communities will find the treatment more cost-effective and they will have a greater incentive to remove more arsenic from the water.

Previous research has shown that arsenic can be removed with precipitating iron, and that iron removal provides opportunities for arsenic removal. The naturally occurring arsenic in Wisconsin groundwater may co-occur with iron, suggesting iron removal may be useful for arsenic treatment. As part of this research, an iron and arsenic concentration database will be developed, and well construction records will be used to generalize relationships between arsenic and iron in Wisconsin community water systems. A group of water systems which have detected arsenic and also operate iron removal facilities have been identified. Initial testing of water from several of these facilities confirms the removal of arsenic occurs during the iron removal process. Additional testing to examine how variations in source water and treatment process impact arsenic removal is planned. The results will be evaluated to understand how overall water quality, treatment process variations, and iron/arsenic co-occurrence impact arsenic removal.

Project Update

The co-occurrence of iron and arsenic in Wisconsin municipal water supplies was examined by comparing previous arsenic testing with results reported by the water systems for iron. Most Wisconsin water systems with arsenic greater than 3 ug/l have iron concentrations greater than the secondary maximum contaminant level (0.3 mg/l). Few of these water systems currently remove the iron and many rely on chemically sequestering the iron to limit precipitation of oxidized iron. The ratio of iron to arsenic in the water typically exceeds at least 20, although several systems with detectable arsenic did report very low iron concentrations.

The project is developing a detailed evaluation of arsenic removal during iron treatment at three locations. At those locations, the groundwater contains both Arsenic (III) and Arsenic (V), with approximately 50% Arsenic (III) at two facilities and 25% Arsenic (III) at the third. Very little particulate arsenic or particulate iron (> 0.45 um) was found in samples collected using an-line filtration unit to minimize atmospheric contact prior to filtration. All three locations have influent iron between 1.0 and 1.4 mg/l and arsenic between 6 and 20 ug/l. At these facilities, 90-98% of the iron, and between 60-70% of the arsenic is removed. The results suggest the removal of both Arsenic (III) and Arsenic (V). Continuing research on the impact of arsenic speciation on removal at low iron and arsenic concentrations is the final phase of this project.

These preliminary results suggest the treatment technique presents opportunities for many water systems to improve the aesthetic quality of the water in addition to reducing the arsenic concentration.

Presentations

McGinley, P.M. Iron and Arsenic, What's the Connection? Presented at the Wisconsin Water Association Annual Meeting, Wisconsin Dells, Wisconsin, September 10, 2002.

Baumann, J. and P.M. McGinley. Arsenic Removal During Iron Treatment. Poster presented at the American Water Resources Association, Wisconsin Section, Annual Meeting, Lac du Flambeau, February 27, 2003.

Monitoring and Scaling of Water Quality in the Tomorrow-Waupaca Watershed

Basic Information

Title:	Monitoring and Scaling of Water Quality in the Tomorrow-Waupaca Watershed
Project Number:	2001WI50O
Start Date:	7/1/2001
End Date:	6/30/2003
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Surface Water, Water Quality, Groundwater
Descriptors:	nutrients, non-point pollution, groundwater-surface water interactions
Principal Investigators:	Bryant A. Browne

Publication

A water quality study was performed in the Tomorrow/Waupaca River Watershed, a first through fourth order groundwater-fed stream system located in central Wisconsin. The objectives of this study are to examine the relationship between the apparent age (number of years since the water entered the ground) and quality of groundwater discharged to streams, and to determine if a relationship exists between spatial scales (stream order and length) and surface and groundwater quality. Major field activities and water quality analyses are now complete. The project included biweekly sampling of six surface water sites conducted for a period of one year. Five synoptic surveys of up to one hundred surface water sites were conducted on a seasonal basis (summer and fall 2001, winter, spring, and fall 2002). Forty-seven of these locations were selected to evaluate the quality of groundwater entering the streams. Minipiezometers were installed approximately 60 cm below the stream to capture groundwater immediately before it entered the stream. Surface water and groundwater samples were analyzed for dissolved solutes and nutrients. Excess nitrogen gas (N_2) was measured to determine the amount of denitrification occurring. In addition, the apparent age of the groundwater samples was determined by analyzing trace gases (chlorofluorocarbons) present in the samples.

Data analysis is currently underway and is scheduled for competition in September 2003. The following observations are based on preliminary analysis of the data. Biweekly sampling revealed seasonal trends in the nitrate (NO_3^-) carried in baseflow. Highest nitrate concentrations and loads occurred in the winter. Data gained from synoptic surveys shows that water quality is sensitive to changes in land use in streams less than 10 kilometers in cumulative stream length. Past 10 kilometers there is a stabilization of the water quality caused by a lack of groundwater entry into the stream and the physical mixing of the surface water. Therefore, in order to see the effect of land use on water quality in this watershed, water must be sampled in streams less than 10 kilometers in cumulative length. Groundwater entering the stream varied in apparent age-date from 1946 to 2002 with a mean of 1973. Groundwater with apparent ages greater than 30 years (pre-1970) had little or no dissolved nitrate. Groundwater with apparent ages younger than 30 years (post-1970) had varying amounts (0.1–16.4 mg/l) of dissolved nitrate present. Measurements of excess N_2 gas in groundwater suggest aquifer denitrification (transformation of NO_3^- to N_2 gas) substantially affects the nitrate budget of the Tomorrow/Waupaca River. Reconstructed nitrate concentrations ($[NO_3^-] + 2[\text{excess-}N_2]$) reveal that on average 57% of nitrate is transformed to N_2 gas before discharging to the stream. Denitrification was nearly 100% in groundwater with apparent ages greater than 30 years. Younger water had varying degrees of denitrification ranging from 0-97%.

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:	2002WI52O
Start Date:	7/1/2002
End Date:	6/30/2003
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Geochemical Processes, Hydrogeochemistry, Toxic Substances
Descriptors:	mercury, sediment-water interface, hyporheic zone
Principal Investigators:	David Armstrong, Christopher L. Babiarz

Publication

Role of the Hyporheic Zone in Methylmercury Production and Transport to Lake Superior

D. E.Armstrong, University of Wisconsin-Madison

Funding Agency: UWS Groundwater Research Program

Project duration: July 2002 – June 2004

Project Description

This investigation focuses on the role of the hyporheic zone in the production and transport of methyl mercury into surface waters. The objectives are: (1) To measure methyl mercury levels and rates of mercury methylation and demethylation in contrasting hyporheic zones, and (2) to evaluate the potential flux of methyl mercury from these zones through measurements of hydraulic conductivities and gradients. We have selected the Allequash Creek watershed as a 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 enables collaboration with scientists from these groups and use of USGS background information and groundwater sampling sites installed at the site. Measurements will include methylation and demethylation rates, mercury and methylmercury concentrations, and water levels in hyporheic zone waters. Measurements will be made seasonally during approximately three sampling trips per year over the two-year project period.

Project Update

The investigation is being conducted by Matthew Meyer, graduate research assistant in the Environmental Chemistry and Technology Program, in collaboration with Martin Shafer, Chris Babiarz, Shawn Chadwick, and other researchers in the program.

The field component of this project commenced in March of 2003, where baseline samples and hydraulic head measurements were obtained from existing wells in the USGS WEBB network at two sites in the Allequash Creek Watershed. These sites are identified as the Upper and Middle sites. Additional samples were obtained at a nearby contrasting site located in the North Creek Watershed. In June of 2003, necessary repair and replacement of the USGS installed nested mini-piezometers located at the Upper and Middle sites commenced in order to restore the complete hydrologic sampling network. Water chemistry samples from the March 2003 excursion were also analyzed during this time and evaluated. A second sampling trip in July of 2003 focused on the Upper Allequash Creek site to fully characterize the groundwater, hyporheic/transition zone and surface water as well as to obtain sediment cores for evaluation. New sampling techniques and equipment were also field-tested during this excursion and will be fully implemented in August of 2003. Some additional repairs were also performed with a few wells requiring more extensive replacement.

Sampling will continue through Fall 2003 and Winter /Spring 2004, concluding in June of 2004. Complete excursions involving mercury methylation/demethylation studies will occur seasonally through this next year, while water chemistry sampling and hydraulic head measurements and flux determinations will be made about every 6-8 weeks. Analysis of samples is ongoing and will continue into June 2004.

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

Basic Information

Title:	Arsenic Contamination in Southeast Wisconsin: Sources of Arsenic and Mechanisms of Arsenic Release
Project Number:	2002WI53O
Start Date:	7/1/2002
End Date:	6/30/2003
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Hydrogeochemistry, Geochemical Processes, Toxic Substances
Descriptors:	arsenic, groundwater, trace metals
Principal Investigators:	Jean Bahr, Madeline Beth Gotkowitz

Publication

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

Jean Bahr, Department of Geology and Geophysics, University of Wisconsin-Madison,
and Madeline Gotkowitz, Wisconsin Geological and Natural History Survey
Funding Agency: University of Wisconsin System and Wisconsin DNR Groundwater
Management Practice Monitoring Program (DNR Project #174)
Project Duration: July 2002 - June 2004

Moderate to high levels of arsenic contamination occur in groundwater throughout eastern Wisconsin. Previous studies have shown that oxidative dissolution of arsenic-bearing sulfide minerals is the likely mechanism controlling high levels of arsenic contamination in the Fox River Valley area. Our preliminary work indicates that geologic and hydrogeologic conditions contributing to arsenic-impacted wells in southeast Wisconsin differ from those in the Fox River Valley. Thus, geochemical mechanisms of arsenic release other than sulfide oxidation, such as the reduction of arsenic-bearing iron-(hydr)oxides, may affect groundwater supplies in southeast Wisconsin. We propose to use groundwater chemistry data, lithologic, mineralogic, and well construction information to identify geologic sources of arsenic. Bench-scale leaching experiments and geochemical modeling will be used to examine the mechanisms controlling the release of arsenic to the groundwater. The objectives of this study are to identify the geologic source(s) of arsenic and the geochemical mechanism(s) and environmental conditions that cause release of arsenic to well water in southeast Wisconsin.

Project Update

Groundwater Chemistry Sampling and Analysis

To date, 17 water samples from 12 sites (1 monitoring well, 1 school supply well, 1 pond, 1 wetland, and 8 residential wells) have been collected. Additional sources of groundwater chemistry data include the Wisconsin Department of Natural Resources database and a private well sampling program conducted in cooperation with the Geneva Lake Environmental Agency. Approximately 10% of the wells in the study area have arsenic concentrations exceeding the new USEPA maximum contaminant level of 10 ppb. Maximum arsenic concentrations are on the order of 80 ppb. The groundwater chemistry data support previous observations that elevated arsenic concentrations occur in both glacial and shallow bedrock wells. The arsenic is dominantly As (III) (65%-100%), and there is a significant amount of particulate (>0.45um) arsenic in some of the wells sampled (0%-65%). In August 2002, a monitoring well was installed in an arsenic-impacted area. Four samples taken from the monitoring well over the past 11 months show relatively constant arsenic concentrations. Time-series sampling was also conducted during a pump test in an arsenic-impacted well. Very little change in water chemistry was seen in 13 samples taken over 70 well volumes during this pump test. This temporal stability suggests that processes local to the well bore have little influence on arsenic concentrations.

Collection and Analysis of Geologic Samples

Rotosonic drilling and monitoring well installation were completed in an arsenic-impacted area. During drilling, 330 ft of core were collected. A detailed description of the core has provided a valuable record of the stratigraphy in the study area. 108 samples from the core have been analyzed for whole rock geochemistry. Arsenic concentrations range from less than detection to 5 ppm in most samples. Higher concentrations of arsenic occur in an organic horizon in the glacial aquifer (21 ppm) and in residuum (weathered bedrock) (15 ppm) at the base of the glacial aquifer. The outwash and upper till units contain relatively little arsenic, while lower till units have low to moderate arsenic concentrations (less than detect to 7 ppm). Based on these data, there are three possible sources of arsenic in the core 1) organic material,

2) residuum, 3) low levels of arsenic dispersed throughout the clay and silt units in the glacial deposits. The organic horizon is more likely to be a source of arsenic for wells open to the glacial deposits, while the residuum may contribute arsenic to wells completed in shallow bedrock. The Wisconsin Geologic and Natural History Survey has provided additional funding for grain size analysis of 150 samples from the core and for carbon age dating the organic horizon (39,580 ± 800 ybp). X-ray diffraction is being used to identify potential arsenic-bearing minerals in the high-arsenic samples.

Hydrogeologic Characterization

Water levels in the monitoring well are being monitored continuously. Additionally, a pump test was conducted at the monitoring well site to evaluate hydrogeologic properties of the aquifer and to assess changes in groundwater quality related to pumping. Data from the pump test are currently being interpreted.

Laboratory Experiments

A series of chemical extractions on select arsenic-rich core samples is planned. Each extraction is designed to dissolve specific minerals. The relative amounts of arsenic released during each extraction will provide additional information about the solid phase associations of arsenic in the core samples. Method development for the extractions and analysis of the extraction samples is complete, and a trial extraction has been conducted. The extractions are expected to be finished by September 2003. The data from the sequential extractions will be used to design bench-scale leaching experiments. The goal of these experiments is to determine what environmental conditions promote the release arsenic to groundwater.

Determination of Aquitard and Crystalline Bedrock Depth Using Time Domain Electromagnetics

Basic Information

Title:	Determination of Aquitard and Crystalline Bedrock Depth Using Time Domain Electromagnetics
Project Number:	2002WI54O
Start Date:	7/1/2002
End Date:	6/30/2002
Funding Source:	Other
Congressional District:	2nd
Research Category:	Not Applicable
Focus Category:	Geomorphological Processes, Groundwater, None
Descriptors:	stratigraphy, geophysics, time domain electromagnetic method
Principal Investigators:	David J. Hart, David Alumbaugh

Publication

Determination of Aquitard and Crystalline Bedrock Depth Using Time Domain Electromagnetics

D. Hart, Wisconsin Geological and Natural History Survey; D. Alumbaugh, University of Wisconsin-Madison
Funding Agency: UWS Groundwater Research Program

Project duration: July 2002 – June 2003

As groundwater needs and concerns have increased, larger and more complex groundwater flow models have been developed to address the problems associated with the exploitation of this precious resource. One of the first steps in creating a useful groundwater flow simulation for the Wisconsin region is the development of a conceptual model that includes hydrostratigraphic units, e.g., shale aquitards, sandstone aquifers, and streambed deposits in tills. The depth, thickness, and extent of these units are usually determined from geologic logs, but in locations where the logs are sparse or nonexistent, the modeler is left with the difficult choice of deciding stratigraphic placement at depth. This crucial first step is often “set in stone.” That is, the stratigraphy of the model is unlikely to be altered unless it is later found to obviously be in error. For this reason, it is important to place the hydrostratigraphic units properly at the time of original model creation. The proposed research will provide the groundwater modeler in Wisconsin an additional tool beyond well logs for determining the placement of the hydrostratigraphic units.

We propose to use a geophysical method, the Time Domain Electromagnetic (TDEM) method, to delineate the shaley facies of the Eau Claire and Mount Simon sandstones, hereafter referred to as the Eau Claire shale, as well as to determine the depth to crystalline bedrock. This geophysical method was chosen because of its ease of deployment, and because it can be easily scaled to image the depths of interest. We chose to use the Eau Claire shale as our test formation because of its importance as a regional aquitard in much of Southern Wisconsin, and because preliminary tests and modeling indicate that the TDEM method should be successful in imaging this important aquitard.

Although an isopach map of the Eau Claire shale has been created for Dane County and portions of Sauk and Dodge counties, there has not been a compilation of all the well logs in Wisconsin to determine the statewide extent of the aquitard. Our first step in this research would be to create such a compilation. The resulting map would guide our investigation of the Eau Claire shale by providing points of known geology to calibrate our geophysical measurements. The map would also provide us with information on where a lack of data on this important regional aquitard exists. At those points we will employ our calibrated geophysical method for determination of the depth and, possibly, the thickness of the Eau Claire shale. The end product of this research will be an assessment of the TDEM method as a hydrostratigraphic mapping tool, as well as a revised map of the extent and thickness of the Eau Claire shale throughout southern Wisconsin.

Project Update

Our study of TDEM and the Eau Claire shale included the following: use of the Wisconsin Geological and Natural History Survey’s database of well records (Geobase) to delineate the shaley facies of the Eau Claire formation, borehole geophysics to measure the resistivity of the Eau Claire shale and surrounding lithologies, forward modeling of the TDEM response based on the well logs and borehole geophysics, field checking of the forward modeling at sites of know lithology and, finally, two field studies of the Eau Claire shale.

Delineation of the Eau Claire shale

We found that the northern boundary of the shaley facies of the Eau Claire shale follows the Wisconsin Arch as it appears in well logs in an arc extending from Hudson in west-central Wisconsin, southward to LaCrosse, through Sauk County and then over to Milwaukee to the east. In general, the shale facies thickens as the distance from the arch increases. However, there are isolated areas where the shale also thickens from its nominal thickness of 15 feet to over 100 feet. An example of this local thickening is found to the southwest of the Baraboo Hills.

Borehole Geophysics and Forward Modeling

We used borehole geophysics to more directly measure the resistivity of the Eau Claire shale and the lithologies surrounding the shale. The borehole geophysics also showed the presence of a shaley facies in the Mount Simon sandstone. Those resistivity measurements were then used to conduct forward modeling so that we could determine under what conditions the shale could be delineated by TEM. The results of the forward modeling showed that we could expect to clearly see the Eau Claire shale when it was 100 feet thick and at a depth of several hundred feet. The shale could also be imaged when it was only 15 feet thick and 300 feet deep as is the case in much of Dane County. However, this simple model is complicated in Dane County by the presence of a second shale unit, found in the Mount Simon with a thickness of about 30 feet and a depth of 600-800 feet. That additional conductor makes delineation of the Eau Claire shale less certain in Dane County.

Geological Studies

After testing the method on known lithologies in Trempeleau, Sauk, and Dane counties, we applied the method to two geological questions: Is the Eau Claire shale present beneath the Madison chain of lakes and how does the lateral transition from shale to sandstone occur in Iowa and Sauk counties?

The Eau Claire shale is an important aquitard in the Madison area. In the current geological model, the shale has been eroded away by glaciers, producing holes in the aquitard. To confirm this model we conducted TDEM surveys after the lakes froze on and near Lake Mendota, Monona Bay, Lake Farms County Park wetland, and Lake Waubesa. Our results suggest that the Eau Claire shale is not always present beneath the lakes. We plan to conduct further surveys on the lakes this coming winter to better determine the edge of the Eau Claire shale beneath the lakes.

We investigated how the Eau Claire formation transitioned from containing a 100-foot-thick shale to no shale on an east-west line from Arena to Spring Green, Wisconsin. We wanted to understand whether the transition was abrupt and probably erosional, or whether it was a gradational facies change. Geological logs show that the Eau Claire shale is present beneath Arena at a depth of 200 feet and is 100 feet thick and that there is no shale present in the Eau Claire formation 10 miles to the west at Spring Green. We found that the resistivity of the Eau Claire shale is only 35 ohm-meters at Arena and gradually increases to 115 ohm-meters at Spring Green, implying that the change from shale to sandstone is a gradual one, not abrupt.

Conclusions

TDEM has been shown through borehole geophysics combined with forward modeling to be useful for delineating shaley aquitards. The Eau Claire shale is likely absent beneath some areas of the Madison chain of lakes providing windows through that aquitard. The Eau Claire shale also makes a gradual transition to a sandstone from Arena to Spring Green, Wisconsin. This has implications for groundwater flow in Sauk and Iowa counties where similar transitions are likely occurring.

F Test for Natural Attenuation in Groundwater: Application on Benzene

Basic Information

Title:	F Test for Natural Attenuation in Groundwater: Application on Benzene
Project Number:	2002WI55O
Start Date:	7/1/2002
End Date:	6/30/2002
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Solute Transport, Models, None
Descriptors:	natural attenuation, model
Principal Investigators:	Fe Evangelista

Publication

F Test for Natural Attenuation in Groundwater: Application on Benzene

F. Evangelista, University of Wisconsin-Whitewater

Funding Agency: UWS Groundwater Research Program

Project duration: July 2002 – June 2003

Chapter NR 726, Wis. Adm. Code, and, more recently, ch. NR 746, allow closure of a petroleum case where ch. NR 140 groundwater enforcement standards are exceeded upon the demonstration that natural attenuation (NA) is an effective remedial option at the site. However, the demonstration of NA's effectiveness may rely on only a few monitoring wells that may not be optimally placed at a site. So closure decisions may be based on analysis of inadequate or inappropriate data, inappropriate especially because the contaminant concentration data from monitoring wells, which are the primary evidence on NA, can be compromised by the fluctuation of the water table. The history of the water-table fluctuations can track changes in important physical NA factors (e.g. recharge, groundwater flow direction), as well as non-NA factors like volume of water purged from the well before a sample is collected. When the contaminant concentration is affected by the rise or fall of the water table, any conclusion about rates of degradation (and hence NA's effectiveness) may be premature. We have developed an F test to statistically look into the importance of fluctuation in the water table. We propose to apply the test to petroleum sites in Wisconsin with adequate benzene and water-elevation data for analysis. We will look into the utility of the technique to screen sites where the statistical procedures required by rule to demonstrate NA may be inappropriate.

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:	2002WI56O
Start Date:	7/1/2002
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Agriculture, Groundwater, Solute Transport
Descriptors:	phytoremediation, pesticides
Principal Investigators:	William DeVita

Publication

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

W. DeVita, University of Wisconsin-Stevens Point
Funding Agency: UWS Groundwater Research Program

Project duration: July 2002 – June 2004

Phytoremediation as an alternative to traditional cleanup methods holds great promise for returning contaminated land and water to a usable state. This technology has been used for a wide array of contaminants and has demonstrated usefulness in laboratory and field settings. This proposed study intends to examine the effectiveness of phytoremediation at a site that has experienced severe environmental degradation, and now has the necessary infrastructure to test phytoremediation theories. The site is located in Bancroft, Wisconsin and is located at an agricultural chemical facility that has several pesticides in groundwater. The main chemical of concern is dinoseb – an acid herbicide that has been banned since 1987. Groundwater concentrations of dinoseb exceed 2000 µg/L. This research will: 1) examine the viability of the established, 2-year-old plantation as the trees begin tapping into the water table that exists at approximately 6 feet, 2) examine hydrogeologic response and correlate that response with respiration to evaluate the influence the trees have on controlling groundwater movement, and 3) determine changes in groundwater contaminant profile through the plots.

The project will address tree viability by tracking mortality and biomass production on an annual basis. Biomass production is determined by measurement of diameter, height and number of shoots produced. Mortality will consist of simple examination of the tree for signs of life – green shoots, buds, and leaves.

Hydrogeologic response will be evaluated with the use of groundwater elevation data loggers that can record elevation at timed intervals (as frequent as every 15 minutes) or changes in elevation (as little as a 1 mm change). This information will be used in conjunction with hydraulic conductivity data (previously calculated by conducting slug tests) to calculate the zone of influence and correlate these results with a capture zone model. Hydrogeologic response and groundwater chemistry profiles will utilize the current network of monitoring wells, which consists of three, 2-inch wells with 5-foot screens that hold the groundwater elevation data loggers, 12 well nests consisting of three wells per nest each with a 1-foot screen, two monitoring wells used by DATCP's Agricultural Chemical Cleanup Program (ACCP), and one piezometer also used by the ACCP. In addition, we propose to install three to four more piezometers to aid in determining vertical extent of contamination. Three of the well nests will be replaced with wells constructed with 5-foot screens to integrate the vertical profile to reduce seasonal differences in groundwater chemistry. Groundwater will be analyzed for dinoseb and various other chemicals (listed below) using EPA Method 8270 utilizing gas chromatography/mass spectrometry.

Project Update

As of June 30, 2003, the following objectives tasks have been completed as part of the proposed activities.

- Mortality was determined and biomass was estimated in October 2002 and compared to previous annual growth.
- Three monitoring well nests (MW-3A, B, C, MW-4A, B, C and MW-5A, B, C) were replaced with single wells with 5-foot screens. This was done in an attempt to eliminate seasonal variations in contaminant concentrations.
- Four piezometers were installed and designated as MW-4P, MW-5P, DP-1PP and DP-1PPP to assess the depth of the contaminant plume.
- Seventeen water samples have been collected and analyzed for dinoseb, chlorothalonil and various nitrogen and phosphorus containing pesticides.
- Trees at the site have been mulched with compost and unmulched areas between rows are maintained by mowing.
- Groundwater data loggers were reinstalled in early spring and have been maintained monthly.

Photocatalytic Adsorption Media and Processes for Enhanced Removal of Arsenic from Groundwaters

Basic Information

Title:	Photocatalytic Adsorption Media and Processes for Enhanced Removal of Arsenic from Groundwaters
Project Number:	2002WI57O
Start Date:	7/1/2002
End Date:	6/1/2003
Funding Source:	Other
Congressional District:	2nd
Research Category:	Engineering
Focus Category:	Treatment, Toxic Substances, Water Quality
Descriptors:	arsenic, treatment, photocatalysis
Principal Investigators:	Marc Anderson

Publication

Photocatalytic Adsorption Media and Processes for Enhanced Removal of Arsenic from Groundwaters

M. Anderson, University of Wisconsin-Madison

Funding Agency: UWS Groundwater Research Program

Project duration: July 2002 – June 2003

The principal objective of this study is to develop and test an inexpensive high performance photoactive adsorption media for the simultaneous removal of arsenite, As(III), and arsenate, As(V), without the need to adjust the pH of source waters. This process will utilize UV-irradiated photoactive thin films composed of novel mixed oxides prepared by sol-gel processing. These materials will be employed in a unique photocatalytic system, which simultaneously removes both arsenic species without additional pH adjustment or further chemical addition. Initial work has been performed and currently both the methods and process design are being optimized.

Until now, adsorption technologies are likely to be the preferred method for removing arsenic in small-scale drinking water systems. This is due to the relatively low capital cost and low operating expense of the adsorption process. Because of its low cost and high surface area, activated alumina has been the adsorbent of choice. However, adsorption processes employing activated alumina have been shown to be very sensitive to pH with optimum pH for arsenic removal ranging from 5.5 to 6.0. This is outside the range of most groundwaters. Thus, water treatment plants have been required to adjust pH prior to the adsorption process. This pH effect is likely due to the adsorption of As(V) or other protolyzable anions acting to lower the iso-electric pH (IEP) of the activated alumina. Even though the IEP of activated alumina is 8.2, the pH of the IEP shifts to 5.5 when the adsorption media adsorbs protolyzable anions. This causes a significant drop in IEP to a value around 5.5 ~ 6.0. This, in turn, results in an unfavorable range for arsenic removal in most water treatment scenarios. Although this effect will occur with most adsorption media, materials having higher IEP than activated alumina have higher arsenic adsorption capacities at pH values typical of drinking water (pH = 6.0 ~ 9.0).

The second most pressing problem associated with arsenic removal is As(III), arsenite. Since this trivalent arsenic species remains uncharged at the pH of drinking water, it is difficult to remove by adsorption or ion exchange. As(III) has been found in Wisconsin groundwaters to be almost equal in concentration to As(V) (arsenate). A typical process for removing As(III) is to oxidize As(III) to As(V) followed by adsorption. While chemical oxidation is the dominant form of oxidation, a photooxidation method was introduced by Australian Nuclear Science and Technology Organization (ANSTO). Lately, a German research group found that photooxidation of As(III) was significantly accelerated when TiO_2 was used as a photo-catalyst.

By placing these TiO_2 thin-films on optical wave-guide delivery systems and by using a unique pulsed UV light source, we believe that an effective combined oxidation/adsorption process can be developed. In addition, this photooxidation process mineralizes most organics to CO_2, water, and mineral salts. Furthermore, this process removes heavy metals such as cadmium, copper and zinc through a photoplating mechanism. Lastly, this process will likely destroy pathogens such as cryptosporidium.

Project Update

In order to better understand the current state of arsenate adsorption on activated alumina, we intensively studied the processes as a function of pH and competing anions, sulfate and silicate. These anions are commonly found in groundwaters. Sulfate anions were found not to directly compete with arsenate for adsorption sites. Instead, sulfate anions lowered the surface potential and the pH_{iep} of activated alumina. Arsenate adsorption was not reduced when the pH of samples was lower than the pH_{iep}. Arsenate adsorption significantly decreased when the pH of samples was higher than pH_{iep} whether sulfate was present or not. Therefore, the pH effect and sulfate competition is strongly related. It appears that silicate adsorption is not significantly changed with pH changes. This is likely due to the fact that silica is a neutral molecule until pH values increase to above pH = 9.0 and also to the fact that this species seems to bind chemically with the surface – without effecting potential due to it´s neutral charge. The presence of silicate on the surface of activated alumina significantly reduced the removal of arsenate while arsenate did not affect the silicate adsorption on this same substrate. Magnesium increases the pH_{iep} of activated alumina significantly. This higher pH_{iep} was helpful in actually increasing arsenic removal by activated alumina. In addition, the magnesium may be present as brucite or magnesite particles which have relatively high isoelectric points. The pH effect mainly depends on the pH_{iep} of activated alumina, which is changed depending on which species of the anion or cation adsorb onto the surfaces of this or other adsorbents. Magnesium aluminate spinel ($MgAl_2O_4$) was found to have a higher pH_{iep} than activated alumina and forms a very favorable adsorbent, which can better remove arsenic in typical pH range of natural waters (6 ~ 8.5).

TiO_2 thin-film photocatlysts oxidized As(III) to As(V) successfully. Based on column tests, approximately 80% of As(III) was oxidized to As(V) within a 5-minute Empty Bed Contact Time (EBCT). Initially, most of the oxidized arsenate was adsorbed onto the glass ring media coated with a TiO_2 thin-film. The arsenate adsorption rate decreased over time as this species filled adsorption sites on the TiO_2 surface. Interestingly, in spite of the adsorption of arsenate onto the TiO_2 thin-film-coated media, the As(III) oxidation rate was not altered, perhaps indicating a different adsorption site for these two species. Differential column batch reactors were operated to study the life of the TiO_2 photooxidation system. TiO_2 photooxidation of arsenite had the same oxidation rate even after 600 hours of operation.

Removal of As(III) and As(V) in Contaminated Ground Water with Thin-Film Microporous Oxide Adsorbents

Basic Information

Title:	Removal of As(III) and As(V) in Contaminated Ground Water with Thin-Film Microporous Oxide Adsorbents
Project Number:	2001WI81B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104B
Congressional District:	Wisconsin 2nd
Research Category:	Water Quality
Focus Category:	Groundwater, Hydrogeochemistry, Treatment
Descriptors:	hydrogeochemistry, groundwater,treatment
Principal Investigators:	Marc A Anderson

Publication

Project Summary

Title:	Removal of As(III) and As(V) in Contaminated Groundwater with Thin-film Microporous Oxide Adsorbents
Project I.D.:	R/UW-REM-003
Investigators:	**Marc A. Anderson (Principal Investigator)** Professor, Environmental Chemistry and Technology Program University of Wisconsin – Madison **Walter Zeltner** Associate Scientist, Water Science and Engineering Laboratory, University of Wisconsin – Madison **Eunkyu Lee** Research Assistant, Dept. of Civil and Environmental Engineering University of Wisconsin – Madison
Period of Contract:	July 2000 – June 2002

Objectives:

The principal objective of this study is to develop and test inexpensive, high-performance photoactive adsorption media for the simultaneous removal of arsenite, As(III), and arsenate, As(V), from groundwater without pH adjustment. This process utilizes UV-irradiated photoactive thin films composed of novel mixed oxides prepared by sol-gel processing. These materials will be employed in a unique photocatalytic process, which simultaneously removes both arsenic species without additional pH adjustment or further chemical addition.

Methods:

Aluminum oxide (Al_2O_3), spinel ($MgAl_2O_4$), and titanium oxide (TiO_2) sols were synthesized by sol-gel technology and coated on glass beads. The adsorption efficiency of each coated material was determined in a batch reactor.

Results and Discussions:

The relationship between the adsorption capacity and the pH of the isoelectric point (IEP) of aluminum oxide and spinel was intensively studied. The IEP of pure aluminum oxide was 8.0, but its IEP decreases to 5.4 when it adsorbs arsenic. Pure spinel had a higher IEP of 10.2, which decreased to 6.7 after adsorption of arsenic. The adsorption capacity for arsenic significantly decreased for both materials at pH values higher than their IEP. These results confirm that (1) adsorption of anions shifts the IEP of adsorbents to lower pH values and (2) the IEP of the adsorbent is strongly related to its adsorption capacity.

During this research, we also developed a novel approach for simultaneously removing both As(III) and As(V) without a separate oxidation step. This process involves heterogeneous photocatalytic adsorption. The adsorbent acts as a photocatalyst to oxidize arsenite to arsenate with the latter species being adsorbed by the catalytic adsorbent. Our studies utilized two types of nanoparticles, TiO_2 and AlOOH. These particles were mixed as a stable suspension (sol) that was used to coat glass beads. The thin-films that were deposited on the beads served as both the photocatalyst and the adsorbent. Test solutions at pH 7.0 contained 0.01 M $NaNO_3$ as a background electrolyte and initial concentrations of arsenite and arsenate of 3 mg/L in separate studies of adsorption in the presence and absence of UV light. Based on the batch tests, the amount of As (III) adsorbed onto the mixed Al+Ti medium was almost identical to that of As (V). These results suggest that almost 100% of arsenite is oxidized to arsenate with this latter species being adsorbed by the film.

Conclusions/Implications/Recommendations:

Adsorption processes that employ activated alumina require a pH between 5.5 and 6.0 for optimum arsenic removal. Because these pH values are outside the pH range at which most water treatment plants operate (pH = 6.0 ~ 9.0), most plants install a separate pH adjustment unit before the adsorption process. Results of this study indicate that the IEP of pure aluminum oxide, which is the main component of activated alumina, is 8.0. This IEP decreases to 5.4 when the aluminum oxide adsorbs arsenate. This result confirms that the pH effect noted above is likely due to the adsorption of arsenate or other protolyzable anions on the activated alumina, which lowers its IEP from 8.2 to 5.5 ~ 6.0. The spinel material displays the same effect. However, because spinel has a higher intrinsic IEP than aluminum oxide, the adsorption capacity of spinel for arsenate does not decrease significantly over the typical pH range of natural waters. As a result, spinel adsorbs 2.5 times more arsenate than activated alumina at pH 7.0.

Another concern with arsenic removal is treating arsenite, which is uncharged at the pH of drinking water, therefore, difficult to remove by adsorption or ion exchange. Arsenite is typically removed by oxidizing it to arsenate and then adsorbing the arsenate. The use of a TiO_2 photocatalyst has been shown to significantly accelerate the photooxidation of arsenite. Initial studies demonstrate that both arsenic species can be removed in a photocatalytic adsorption process using a novel thin-film material.

Related Publications: None at present.

Key Words: Arsenite, Arsenate, Adsorption, Surface Charge, Photooxidation, Arsenic Remediation

Funding: University of Wisconsin Water Resources Institute

Importance of Groundwater in Production and Transport of Methyl Mercury

Basic Information

Title:	Importance of Groundwater in Production and Transport of Methyl Mercury
Project Number:	2001WI101B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104B
Congressional District:	Wisconsin 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Hydrogeochemistry, Toxic Substances
Descriptors:	hydrogeochemstry,groundwater
Principal Investigators:	David E. Armstrong

Publication

PROJECT SUMMARY

Title: Importance of Groundwater in Production and Transport of Methylmercury in Lake Superior Tributaries

Project I.D. R/UW-GSI-001

Investigators: D.E. Armstrong, Professor, Department of Civil & Environmental Engineering, UW-Madison; Principal Investigator

R.W. Stoor, Graduate Student, Environmental Chemistry & Technology Program, UW-Madison; Research Assistant

D. P. Krabbenhoft, Research Scientist, U.S. Geological Survey, Middleton, WI; Co-Investigator

K. Rolfhus, Research Associate, Water Science & Engineering Laboratory, UW-Madison; Co-Investigator

L. Cleckner, Associate Researcher, Water Science & Engineering Laboratory, UW-Madison; Co-Investigator

Project Period: March 1, 2002 to June 30, 2002

Background and Need: Methylmercury accumulation in food chains of streams and lakes presents a health hazard to wildlife and humans. Although production of methylmercury occurs in anoxic zones, little is known about production of methylmercury in groundwaters or the factors that govern its transport and fate.

Objectives: We determined the spatial and temporal patterns in mercury (Hg) and methylmercury concentrations in groundwaters and hyporheic zone waters at two contrasting sites and examined relationships to land cover, biogeochemical conditions, and local hydrology.

Procedures and Methods: We compared groundwaters at two sites, one near the headwaters of the Tahquamenon in a deciduous forest near East Creek, a tributary to the Tahquamenon, and the other in a coniferous forest near the mouth of the Tahquamenon. In addition, we sampled hyporheic zone waters at three sites along East Creek. Samples were collected at selected intervals from spring 2000 to late fall 2001 using mercury-clean techniques and analyzed using clean, sensitive methods. Water chemistry, groundwater elevation, and soil properties were also measured.

Results and Discussion: Groundwater at both sites contained moderate to relatively high concentrations of both total mercury (0.1 to 15 ng/L) and methylmercury (0.04 to 0.6 ng/L), indicating that groundwater may be a significant source of mercury to surface waters. Spatial differences were observed in both total mercury and methylmercury concentrations. Total mercury concentrations were higher at the East Creek sites. In contrast, methylmercury concentrations were higher at the Tahquamenon Mouth sites, and higher at one site than the other. Temporal patterns in methylmercury concentrations, especially at the Tahquamenon Mouth sites, appeared to be related to the hydrography of the river. Concentrations tended to increase during the summer (May to September of 2001) and were also high in November 2001. However, concentrations were low in April 2001, following the spring melt period. We believe this pattern reflects a build up of methylmercury in groundwater during periods of relatively low flow and flushing of methylmercury-enriched ground water into surface waters during high recharge events, especially spring melt. This pattern is supported by the variations in MeHg observed in the Tahquamenon River during 1997. Concentrations increased with the rise in the hydrography during spring melt, reaching the highest concentration as the hydrography began to fall.

At three sites along East Creek, mini-piezometers were installed in close proximity to the creek to examine mercury concentrations in the hyporheic zone. The mini-piezometers were positioned to sample the saturated zone within a few meters of the creek and below the creek bed. Methylmercury concentrations were relatively low (nondetectable to 1.5 ng/L) in the subsurface zone adjacent to the stream, but concentrations were relatively high in porewaters beneath the creek (up to 12 ng/L), although highly variable both spatially and temporally. Concentrations in pore waters were generally high relative to concentrations in East Creek, indicating that this region of the hyporheic zone could be an important source of methylmercury to East Creek. Concentrations of methylmercury in groundwaters and pore waters were higher in the wetland site than at the forested site, consistent with observations that wetlands are important contributors of MeHg to surface waters. Concentrations of Fe and Mn were elevated in the hyporheic zone, indicative of anoxic conditions and a favorable environment for methylmercury formation.

Conclusions and Recommendations: Groundwater, containing up to 0.6 ng/L of methylmercury, is a potentially important source of methylmercury to streams in the Tahquamenon River watershed. Hydrologic and chemical data indicate a pattern of buildup of methylmercury in groundwater during low flow periods and flushing into streams during recharge events, especially spring melt. The hyporheic zone of East Creek, a tributary to the Tahquamenon River, is also a potentially important source of methylmercury. The porewaters below the stream contained up to 12 ng/L of methylmercury. Concentrations of methylmercury in both groundwaters and hyporheic zone waters are highly variable, both spatially and temporally. In assessments of methylmercury sources to surface waters, fluxes from groundwater and the hyporheic zone should be considered.

Related Publications:

Stoor, R.W. 2002. Groundwater contributions of methylmercury to a Lake Superior Watershed. M.S. Thesis, Environmental Chemistry and Technology Program, University of Wisconsin-Madison.

Key Words: groundwater, hyporheic zone, mercury, methylmercury

Funding: Wisconsin Groundwater Research Program; US Geological Survey.

A Basin-Scale Denitrification Budget for a Nitrate Contaminated Wisconsin Aquifer:

Basic Information

Title:	A Basin-Scale Denitrification Budget for a Nitrate Contaminated Wisconsin Aquifer:
Project Number:	2001WI102B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104B
Congressional District:	Wisconsin 2nd
Research Category:	Water Quality
Focus Category:	Nitrate Contamination, Non Point Pollution, Water Quality
Descriptors:	non-point pollution, water quality,nitrate contamination
Principal Investigators:	Bryant A. Browne

Publication

PROJECT SUMMARY

Title: A Basin-Scale Denitrification Budget for a Nitrate Contaminated Wisconsin Aquifer: A Study at the Groundwater/Surface Water Interface

Project ID: R/UW-GSI-002

Investigators:
Bryant A. Browne, Associate Professor of Water & Soil Resources, University of Wisconsin – Stevens Point; George J. Kraft, Director and Professor, Central Wisconsin Groundwater Center, University of Wisconsin – Stevens Point; David Saad, United States Geological Survey, Water Resources Division, Madison, Wis.

Period of Contract: July 1, 2000 to June 30, 2002

Background/Need:
Nitrate is a pervasive and increasing groundwater contaminant in Wisconsin. Many studies have found that nitrate is relatively conservative in groundwater. However, others have shown that nitrate can be transformed to nitrogen gas (denitrified) when reducing conditions are encountered along a groundwater flowpath (e.g., within riparian soil). Inadequate knowledge of groundwater denitrification hinders the development and application of accurate mass balance models for management of nitrate pollution.

Objectives:
The goal of this study was to achieve a better understanding of groundwater denitrification as a basin-scale control of nitrate concentrations and export from Wisconsin basins.

Methods:
The quantity and quality of groundwater discharging to the Little Plover River in Central Wisconsin was measured using a network of miniature wells at the groundwater/surface water interface (0.6 m beneath the streambed, distributed at 60-meter intervals over 10 km of headwater stream channel). Sampling surveys of all sites (n=160) were conducted in the summers of 2000 and 2001. A subset of sites (n=30) comprising a downwelling/upwelling sequence was sampled periodically. The concentration and load of denitrified-N carried into each 60-m stream segment via groundwater were quantified from the concentration of dissolved nitrogen gas (N_2) in excess of atmospheric equilibrium. Total groundwater nitrate was estimated from the sum of dissolved nitrate-N and excess N_2-N gas.

Results and Discussion:
For the average stream segment, 35% of groundwater nitrate-N (nitrate-N + denitrified-N) was discharged to surface water as excess N_2 gas (denitrified N). Higher denitrified N percentages were associated with one or more potential indicators (e.g., low dissolved oxygen, high dissolved organic carbon, low discharge per unit stream width) of shallow (e.g., riparian soil) groundwater flowpaths. Lower denitrified N percentages were

associated with indicators of deeper groundwater flowpaths (low DOC, high discharge per unit stream width). Summed across all stream segments, the cumulative loads of denitrified N and nitrate-N were 45 kg/day and 145 kg/day, respectively, representing a basin-wide denitrification rate of 24 percent. Extrapolated to an annual basis and expressed in terms of basin yield, these data indicate that approximately 54 kg/ha/yr were leached to groundwater as nitrate-N, of which 41 kg/ha/yr were released to surface water as nitrate-N. The remaining 13 kg/ha/yr were released to surface water as excess N_2-N (10 kg/ha/yr) or were transformed to excess N_2-N as surface water recharged groundwater in downwelling stream segments (3 kg/ha/yr).

Conclusions/Implications/Recommendations:
Though point estimates of denitrification have been routinely measured in soils and groundwater, estimates of denitrification on the scale of a small basin have been lacking. This study provides a basin-scale estimate of groundwater denitrification in a moderately thick (50-200 ft) surficial aquifer typical of many glacial/alluvial aquifers in Wisconsin. Because the annual recharge of the LPR aquifer is mostly derived during the rapid infiltration of coarse texture upland soils (which dominate the landscape), groundwater carries less DOC to fuel the respiratory consumption of O_2 and NO_3^- by microorganism than might be typical of other basins. Thus, our finding for the Little Plover River Basin could represent a lower bound basin-scale denitrification rate. Similar studies should be performed in other basins to determine how basin characteristics (e.g., soils, geomorphology) affect groundwater denitrification and further work should be done to clarify in what flow environments most denitrified N is generated (e.g., soil solution, capillary fringe/shallow water table, intermediate and regional flowpaths, or riparian/hyporheic zones).

Our results show that groundwater denitrification can substantially affect the total load and yields nitrate-N delivered to streams, and indicate that groundwater denitrification is an important factor controlling the collective release of N to large rivers systems from small agricultural basins.

Related Publications: none yet submitted

Key Words: nitrate, denitrification, groundwater/surface water interface, nitrous oxide, excess nitrogen gas.

Funding: UWS and USGS

Groundwater-Lake Interaction: Response to Climate Change in Vilas County, Wisconsin

Basic Information

Title:	Groundwater-Lake Interaction: Response to Climate Change in Vilas County, Wisconsin
Project Number:	2001WI30O
Start Date:	7/1/2001
End Date:	6/30/2002
Funding Source:	Other
Congressional District:	2nd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Hydrology, Models
Descriptors:	groundwater-surface water
Principal Investigators:	Mary Anderson

Publication

PROJECT SUMMARY

Title: Groundwater-Lake Interaction: Response to Climate Change, Vilas County, Wisconsin

Project ID: R/UW-GSI-004

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

Research Assistant: Christine (Tina) D. Pint, Department of Geology and Geophysics, University of Wisconsin-Madison (now with Barr Engineering, Minneapolis, MN).

Period of Contract: July 1, 2001 – June 30, 2002

Background/Need: There are numerous lakes and wetlands in Wisconsin and most have some connection with the groundwater system. Groundwater fluxes, while difficult to measure, may be important to the hydrology and chemistry of lakes. Stresses on the groundwater system and changes in groundwater fluxes affect surface water levels, which in turn affect groundwater levels in a dynamic feedback process. Problems in Wisconsin that critically depend on recognition and quantification of this feedback mechanism include predicting the effects of land use and proposed mining operations on groundwater and lake levels, urbanization on groundwater/surface water systems, agricultural drainage systems on wetlands, and potential global climate change on hydrologic systems.

Standard groundwater models assume that surface water levels are known inputs, and therefore do not recognize the true nature of the connection between surface water and groundwater. Recognition of the need for improvement in the way in which groundwater models handle surface water inputs led to development of specialized software packages for MODFLOW (the industry's standard code for groundwater flow modeling) that address the dynamic exchange of groundwater with rivers and reservoirs. Watersheds containing important lake and stream systems require models that include consideration of the dynamic exchange of waters among groundwater, lakes and streams.

The Trout Lake Basin study site is ideal for addressing issues related to groundwater-surface water interaction inasmuch as long-standing and on-going hydrological research with accompanying data collection and monitoring occurs at this site through the National Science Foundation's Long Term Ecological Research (LTER) program and the U.S. Geological Survey's Water, Energy, Biogeochemical Budgets (WEBB) program.

Objectives: (1) to determine effects on water levels of potential climate change in the Trout Lake Basin, Vilas County, Wisconsin and (2) to define the contributing groundwater basins and travel times to lakes within the Trout Lake Basin.

Methods: A regional groundwater-based watershed model of the Trout Lake Basin was calibrated under both steady-state and transient conditions and used to delineate lake capture areas and to assess the effects of potential climate change on surface water and groundwater levels. The industry standard groundwater flow code, MODFLOW, including the newly developed LAK3 package for simulating groundwater exchange with lakes and a beta version of the Streamflow Routing Package for simulating groundwater exchange with streams and routing of streamflow, was used to simulate groundwater flow in the watershed. The flow model was calibrated using a parameter estimation code, UCODE. Results from the flow simulation were input to a particle tracking code, MODPATH, and used to delineate steady-state capture areas for 30 lakes in the basin as well as three streams. MODPATH also calculated travel times within the capture areas for selected lakes.

Results and Discussion: The large lakes tend to have large capture zones; Trout Lake has the largest. Many lakes receive water that underflows or flows through another lake. Travel times range from 200 years within the Trout Lake capture area to less than 20 years within the Crystal Lake capture area.

Sensitivity of the model to changed climate conditions, simulated by “wet” and “dry” recharge scenarios, showed that in general, capture zones are smaller under the “wet” conditions, corresponding to lower groundwater inflow rates for most of the lakes. All lakes had increased rates of groundwater discharge during the “wet” scenario and decreased rates during the “dry” scenario. Crystal Lake, a small lake located near the regional groundwater divide, showed the most dramatic change in capture zone size between the two scenarios. Lake levels in the large drainage lakes were insensitive to changes in recharge since lake level is controlled by the outlet streams. Seepage lakes showed, on average, a half-meter stage change under both “dry” and “wet” conditions.

Conclusions/Implications/Recommendations: Calibration of the complex three-dimensional groundwater-watershed model demonstrated the importance of using multiple calibration targets including groundwater heads and fluxes as well as additional nontraditional targets. Delineation of lake capture areas verified the importance of three-dimensional flow in this watershed; capture areas clearly show the occurrence of underflow of water beneath lakes. In effect, the system of lakes acts as a conveyor of water moving water down gradient to Trout Lake. Simulations designed to test the sensitivity of the model to potential global climate change demonstrated that lake capture areas, lake stages and groundwater fluxes to/from lakes in the Trout Lake Basin are sensitive to changes in precipitation, evaporation and recharge rates.

The results of the climate change simulations will be of interest to water managers and to scientists interested in the hydrologic effects of changes in groundwater recharge at a watershed scale. The delineation of lake capture areas will be helpful in addressing questions related to potential impacts on lakes as a result of land use change. Travel times of water flow to the lakes are needed for on-going studies of the geochemical evolution of groundwater in the Trout Lake Basin and could be used in transport studies related to possible introduction of solutes from certain kinds of land use.

Key Words: Groundwater, modeling, climate change, lake capture area, travel time, groundwater age.

Investigation of Changing Hydrologic Conditions of the Coon Creek Watershed in the Driftless Area of Wisconsin

Basic Information

Title:	Investigation of Changing Hydrologic Conditions of the Coon Creek Watershed in the Driftless Area of Wisconsin
Project Number:	2001WI32O
Start Date:	7/1/2001
End Date:	6/30/2002
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Non Point Pollution, Water Use, Hydrogeochemistry
Descriptors:	hydrology, recharge, modeling
Principal Investigators:	Randall Hunt

Publication

Investigation of Changing Hydrologic Conditions of the Coon Creek Watershed in the Driftless Area of Wisconsin

Project I.D. R/UW-GSI-003

Principal Investigator: Randal J. Hunt, Ph.D., Adjunct Associate Professor, UW-Madison, Geology and Geophysics Dept.
Project Assistant: Paul F. Juckem, Graduate Student, UW-Madison, Geology and Geophysics Dept.

Project Summary

A study to investigate controls on groundwater movement and recharge in the Coon Creek Watershed in the Driftless Area of Southwestern Wisconsin was funded by a grant from the Water Resources Institute at the University of Wisconsin-Madison. The study incorporated collection and analysis of hydrologic data, and numerical simulation of groundwater flow. Data collection included measurement of: streamflow, groundwater levels in wells, precipitation, and infiltration rates. Two numerical models were constructed to simulate groundwater flow at the individual well and catchment scales.

A historical data set of streamflow and groundwater levels in the Coon Creek Watershed was augmented by data collected during this investigation. Streamflow was measured at the site of a historical gaging station in the village of Coon Valley, and also in four tributary streams. Streamflow data collected during this investigation was compared against historical data and indicated that baseflow (approximated as the amount of streamflow equaled or exceeded during 65% of the year) increased by about 60% over early records collected from 1934 to 1940. This increase in baseflow was matched by an increase of about seven feet in the average groundwater elevation in two historical wells located in the basin. Six water table wells were installed in unconsolidated stream valley sediments to obtain groundwater elevation data and hydraulic conductivity data. Slug test data in the six valley wells provided hydraulic conductivity estimates that ranged from 0.1 feet per day (ft/d) to over 2 ft/d for unconsolidated valley sediments. A Guelph Permeameter and a Double-ring Infiltrometer were used to quantify and compare infiltration rates between ridge-tops, hillslopes, and valleys, and between land use practices including: agriculture, pastures, fallow fields, and forests. Infiltration measurements from both methods ranged between two to ten times higher on hillslopes than on ridge-tops and valleys. Infiltration rates also increased with decreased land use intensity. For example, two cultivated agricultural fields, one located on a ridge-top and the other in a stream valley, had lower measured infiltration rates than nonagricultural land in both topographic settings. All data from this investigation will be published in a thesis (Juckem, in preparation) and will be available for future research.

In addition to utilizing an existing two-dimensional analytic element groundwater flow model, two finite-difference groundwater flow models were constructed. The first model provided insight into an ambiguous data set obtained from geophysical logs and a single-packer survey of a well that was drilled adjacent to the Coon Creek Watershed. The model was used to simulate groundwater levels in three aquifers that were open to the well. Results from this model analysis

showed a steep vertical groundwater gradient near the well (a decrease of nearly 1 foot in head per 1 foot drip in elevation), and that unconfined conditions likely exist in deep aquifers below ridges around the Coon Creek Watershed. A presentation of the methods and results of this model analysis (Juckem et al. 2002) received an award for outstanding student presentation at a research conference sponsored by the Wisconsin Section of the American Water Resources Association and the Wisconsin Ground Water Association. Estimated groundwater elevations from this model analysis were utilized as calibration targets in a second numerical groundwater flow model.

The second numerical groundwater flow model was used to simulate catchment-scale groundwater flow and recharge in the upper Coon Creek Watershed to improve understanding of groundwater movement through aquifers and aquitards in the basin. An analytic element model (Juckem et al. 2001) was used to provide boundary conditions for the three-dimensional numerical model based on the methodology of Hunt el al. (1998). Results from model calibration indicated that layered stratigraphy in the Driftless Area strongly influences groundwater movement at the catchment scale. Thus, stratigraphy should be explicitly incorporated in simulations of the shallow groundwater flow in Driftless Area basins, even at the catchment scale. This work also included development of a procedure to address numerical instability inherent to a widely used finite-difference code when simulating flow in areas with steep vertical groundwater gradients, stacked water tables, and anisotropic aquifers. In this procedure, all model layers were specified as confined, while simulated transmissivity in unconfined aquifers was iteratively corrected by adjusting layer thickness based upon previous solutions. Finally, the conceptual model of groundwater flow via stacked water table aquifers developed here likely has application to other Driftless Area basins.

References:

Hunt, R.J., M.P. Anderson and V.A. Kelson. 1998. Improving a complex finite-difference groundwater flow model through the use of an analytic element screening model. *Ground Water* 36(6):1011-1017.

Juckem, P.F., R.J. Hunt, M.P. Anderson. 2001. Driftless Area Hydrogeology – Preliminary Results of Temporal Change in the Coon Creek Watershed. Proceedings – American Water Resources Association – Wisconsin state section. 41p.

Juckem, P.F., R.J. Hunt, M.P. Anderson, and D.M. Chapel. 2002. Conceptual Model of Groundwater Flow in the Coon Creek Watershed. Proceedings – American Water Resources Association - Wisconsin state section. 48p.

Juckem, P.F. Spatial Patterns and Temporal Trends in Groundwater Recharge, Upper Coon Creek Watershed, Southwestern Wisconsin. Master of Science Thesis. Dept. of Geology and Geophysics. University of Wisconsin-Madison. *In preparation*.

Effect of Clean and Polluted Groundwater on Reproduction and Development of Daphnia

Basic Information

Title:	Effect of Clean and Polluted Groundwater on Reproduction and Development of Daphnia
Project Number:	2001WI35O
Start Date:	7/1/2000
End Date:	6/30/2002
Funding Source:	Other
Congressional District:	2nd
Research Category:	Biological Sciences
Focus Category:	Toxic Substances, None, None
Descriptors:	groundwater, Daphnia, pesticide, bioassay, biomonitoring, malathion, dimilin, methoprene, ecdysone, hormones, P-450
Principal Investigators:	Stanley Ivan Dodson

Publication

Project Summary

Title:
Effect of Clean and Polluted Groundwater on Reproduction and Development of Daphnia

Project I.D.:
R/UW-BEP-001

Investigator:
Principal Investigator - Stanley Dodson, Professor
Department of Zoology
University of Wisconsin-Madison

Period of Contract:
1 July 2001 to 30 June 2002

Background/Need:

There is a need for an efficient and effective whole-animal screen for ecological effects of pollutants (see Table 1). Previous work in our lab has focused on herbicides and vertebrate hormones. Several of these chemicals changed normal *Daphnia* development and sex determination, at concentrations found in groundwater. The current proposed research focuses on laboratory assays of low-level concentrations of common-use insecticides that have been reported to be contaminants of groundwater. Information on insecticide effects will contribute toward our evaluation of the *Daphnia* reproduction assay. This assay has been developed and used successfully in the lab for a number of chemical contaminants. Preliminary results suggest that it is crucial to survey insecticides. Our assays provide information on "contamination," (whether due to parent compounds, breakdown products, and chemical mixtures) because we look at the whole-animal response. This is an important feature, because there are so few cost-effective assays that can detect sublethal effects on whole organisms.

Our ultimate goal is to establish the *Daphnia* development and reproduction assays as a surrogate, cost-effective bioassay system for risk assessment. Our results suggest these assays do have value, because *Daphnia* are sensitive to ambient concentrations of contaminant herbicides, and because *Daphnia* respond in characteristic ways to some vertebrate hormones such as thyroxine and some steroid hormones.

Objectives:

The project objective was to characterize effects of common-use insecticides classified as endocrine disruptors on development and sex determination of *Daphnia* magna, using well-established short- (six day) and long-term (30 day) life-table type assays. The endpoints include:

growth in length, molting frequency, and population growth rate
fecundity and sex ratio
deviations from normal morphology in neonates and adults.

Methods:

We exposed *Daphnia* to common-use insecticides in two kinds of assays. These assays have been developed and polished in our lab over the last few years. In the first assay, adult female *Daphnia* are grown under environmental conditions that naturally induce about 50 percent males. After six days (the equivalent of two instars or molting periods), and a renewal of culture medium, the offspring are scored as to gender, survival, and morphology, and the adult females are scored as to survival, fecundity, morphology, and size. Animals grown in uncontaminated artificial lake water, or in water contaminated with low levels (100 ppb or lower) of a common-use insecticide that occurs in groundwater. In the second assay, neonates are followed with daily observations throughout their lifetime. Animals are measured each day, and we record details of reproduction and development.

Results and Discussion:

Effects of estrogen modulating compounds

Toxaphene (polychlorinated camphenes), an insecticidal mixture of over 670 congeners and widely classified as estrogenic, was the only chemical tested that affected sexual differentiation in *D. magna* (Fig. 1). *Daphnia magna* exposed to 50 and 100 µg/L toxaphene produced 17-44 percent more male clutches compared to the control *D. magna* ($p<0.01$, Fig.1). In addition to increasing male production, toxaphene exposure (50 µg/L) decreased the average clutch size from 17 to 13 individuals ($p=0.02$). At the higher concentration of 100 µg/L toxaphene had no effect on fecundity. Toxaphene exposure concentrations below 50 µg/L had no effects on reproduction or growth (Table 2).

Another putative estrogenic insecticide o'p'-DDT, did not alter the natural sex ratio at any of the concentrations tested. However, at 100 µg/L o'p'-DDT decreased survivorship, killing the majority of the *D. magna* by day three of the assay. Di-*n*-butyl phthalate had no observable effects on the developmental or reproductive endpoints examined in *D. magna* (Table 2).

Effects of thyroid modulating pesticides

Three herbicides reported as disrupting normal thyroid function in vertebrates; acetochlor, metribuzin and alachlor, did not affect sexual differentiation, survivorship, resting egg production, or morphology in *D. magna* (Table 2). The only thyroid modulating herbicide that appeared to have any effect on *D. magna* was acetochlor, and effects were seen below the listed EC_{50} (48 hours) for *Daphnia* (16 mg/L; Tomlin 1994). An EC_{50} value represents the concentration at which 50 percent of the organisms show any toxic effect (Effective Concentration). Adult *D. magna* with a six-day exposure to 100 µg/L acetochlor were significantly smaller (4.16 mm) than their respective control (4.28 mm; $p=0.04$). However, the clutch size of the acetochlor-exposed *D. magna* was not affected by the smaller adult size, hence a smaller brood chamber.

Effects of pesticides with LH, androgenic, or insulin activity

Pesticides with reported activity in vertebrate androgen systems had no effects on *Daphnia*. The o'p'-DDT metabolite p'p-DDE, which has been shown to function as a hormone (androgen) antagonist in vertebrates, did not impair reproductive or developmental processes in *Daphnia* at sublethal concentrations; however, p'p'-DDE was toxic to *D. magna* at 100 µg/L (Table 1 and 2). Likewise, the androgenic herbicide, linuron, had no toxic effects on *D. magna* at the concentrations tested.

Amitraz an insecticide that has been shown to inhibit insulin secretion in rats (Abu-Basha *et al*. 1999) did not exert toxicity on the daphnid developmental and reproductive processes monitored in this study. The herbicide 2,4-D that has been correlated with elevated LH levels in humans (Garry *et al.* 2001) had no observable effects on the developmental or reproductive endpoints examined in *D. magna*.

Effects of pesticides with no known endocrine activity

Five pesticides were examined that currently have no known impacts on vertebrate endocrine systems: cyanazine, diflubenzuron, chlorsulfuran, diquat and metolachlor. Exposure to 100 µg/L cyanazine significantly reduced the number of *D. magna* that reproduced to 23 percent (p=0.01), while only four percent of the control daphnids failed to produce a clutch in the 12 days monitored. In addition, the average clutch size of the reproducing adult *D. magna* exposed to 100 µg/L cyanazine was significantly smaller (p=0.04) with an average clutch size of 14 individuals vs. 11 individuals in the control. Cyanazine had no effect on sex determination.

Diflubenzuron was highly toxic to *D. magna,* significantly decreasing survivorship at 0.01 µg/L (p=0.005; Fig. 2). The LC_{50} value for diflubenzuron in this six-day assay fell between 0.10 and 0.01µg/L. Lower diflubenzuron concentrations elicited no adverse effects on growth/molting or reproduction of the daphnids (Table 2).

The remaining pesticides with no known endocrine activity, chlorsulfuran, diquat and metolachlor, did not affect *D. magna* at the concentrations tested (Tables 1 and 2). The herbicide chlorsulfuran has been reported in surface waters at very low concentrations (Table 1). This study indicates that these environmentally relevant concentrations appear to have no apparent effects on *Daphnia* (Tables 1 and 2). Diquat did not affect any of the reproductive or development endpoints monitored in *D. magna* at the concentrations tested. Metolachlor, an herbicide that has been found at concentrations as high as 143 µg/L in Midwestern U.S. streams and rivers, had no effects on *Daphnia* at similar concentrations (Battaglin *et al*. 2000, Table 2).

Conclusions/Implications/Recommendations:

Applicability of Daphnia *as a screen for endocrine modulating compounds*

Several pesticides affected reproductive and developmental process in *Daphnia;* however, there does not appear to be a pattern between pesticides with particular endocrine classification (reported from vertebrate systems) and effects on specific reproductive and developmental processes in *Daphnia*. Toxaphene a common groundwater contaminant was the only estrogenic compound that affected sexual differentiation in *Daphnia.* Toxaphene exposure (50 and 100 µg/L) increased male production in *Daphnia,* and yet several known estrogenic chemicals (o'p'-DDT, and Di-*n*-butyl Phthalate) had no effect on sexual differentiation in *Daphnia* (Fig. 1, Table 2). This suggests that estrogens may not play a direct role in *Daphnia* sexual differentiation. However, data in other studies imply that weakly estrogenic compounds such as dieldren and atrazine do affect sex ratio in *Daphnia*. Dodson and colleagues found a decreased proportion of males among young produced by *Daphnia* exposed to dieldrin (1999 a), and an increased proportion of males among young produced by *Daphnia* exposed to atrazine (1999 b).

The question of whether or not pesticides elicit estrogenic activity in *D. magna* is further complicated because there is no universal "gold standard" of estrogen action among vertebrate bioassays (Coldham *et al.* 1997). Toxaphene, although commonly referred to as having estrogenic properties, has also been classified as having thyroid and antiandrogen properties (Waritzet *et al.* 1998, Arcaro *et al.* 2000). Toxaphene has also been reported as not having estrogenic properties (Table 1; Palmer *et al.* 1998). Classification of various chemicals as estrogenic or nonestrogenic is still debated in the scientific community. Therefore, to draw generalizations about all estrogenic compounds is premature.

Developmental and reproductive impairments in *D. magna* by the thyroid modulating compounds (TMC) were inconsistent. Acetochlor was the only chemical with known thyroid activity in vertebrates to have any observable effects on *D. magna*. Acetochlor reduced adult size in the six-day exposure (Table 2). Acetochlor did not decrease daphnid fecundity in this study. Therefore, it is possible that the reduction in growth rate was an endocrine related response; however, the remaining TMC's tested did not have similar affects on growth rates. Although this study did not find consistent evidence of TMC on *D. magna*, it is conceivable that *D. magna* would be affected by TMC. It is unknown if *D. magna* have a thyroid system similar to vertebrates, but other invertebrates do respond to thyroxine. Chino *et al.* (1994) isolated thyroid hormones in the sea urchin (*Hemicentrotus pulcherrimus*) and determined that thyroid hormones function in the formation of the adult rudiment. Thyroxine has also been found to accelerate larval development in the Crown of Thorns Starfish (*Acanthaster planci*; Johnson and Cartwright 1996). Based on results from this study, using *D. magna* to screen for chemicals with thyroid activity may not be effective.

Other vertebrate hormones that have affected invertebrates, such as vertebrate-type steroidal androgens,have disrupted crustacean growth and reproduction. Olmstead and LeBlanc (1998) found that exposure of female daphnids to testosterone significantly inhibited the rate of development of their abdominal process. However, *D. magna* fecundity was not reduced when exposed to the androgenic compounds linuron and DDE at concentrations tested.

Due to the lack of chemicals cited as having effects on insulin or LH activity, only one pesticide was tested from each of these categories. Lutenizing hormone is known to stimulate the crustacean Sand Shrimp (*Crangon crangon)* ovaries resulting in an increase in the number of the generative oocytes, and the number of oogonia (Zukowska-Arendarczyk 1981). Therefore, an herbicide such as 2,4-D, which elevates LH levels in humans, may have a measurable effect on *D. magna* even though the presence of LH in *D. magna* is still unknown (Garry *et al*. 2001); however, based on the reproductive and developmental endpoints examined in this study, I found no effects of 2,4-D on *D. magna*. An insulin-like immunoreactive material was found in the mussel *Mytilus edulis*; therefore, if a chemical can disrupt normal insulin function in vertebrates then it may also be possible to disrupt similar pathways in invertebrates (Fritsch *et al.* 1976). However, amitraz did not disrupt any of the reproductive or development processes examined in *D. magna*.

Many pesticides have never been tested for endocrine effects, and no chemicals have been tested against all hormone systems (Table 1). Therefore, several chemicals with no known endocrine activity were assayed. These chemicals did not elucidate any patterns regarding effects on reproductive and developmental endpoints, therefore, no conclusions can be drawn regarding their effects on the daphnid endocrine system.

Although generalization regarding endocrine classification cannot be drawn from this study, several pesticides did elicit toxic effects on developmental and reproductive processes in *D. magna*. Cyanazine is a triazine herbicide in the same family as atrazine, an herbicide which Dodson *et al.* (1999) found decreased *Daphnia* sex ratio. Although cyanazine had no effect on sex determination in this study, as atrazine did in the Dodson *et al.* (1999) study, cyanazine did lower fecundity and the number of adults that produced offspring. It is possible that *D. magna* reproduction is mediated by endocrine functions, and that 100 μg/L cyanazine disrupts normal endocrine function involved in *D. magna* reproduction.

Based on results from this study, it appears unlikely that *D. magna* would make a good screen for vertebrate endocrine modulating compounds because there was no apparent pattern between pesticides reported with estrogenic, androgenic, thyroid, insulin or LH activity in vertebrates and effects on *D. magna*. However, this *D. magna* assay which monitored sublethal effects related to endocrine-regulated processes such as growth, fecundity and sex determination consistently detected ecologically relevant effects of these pesticides on *D. magna* at environmentally relevant concentrations.

Ecological Implications (daphnid sensitivity)

Any chemical that affects an organism's fitness (i.e. survival, growth rate, fecundity, and/or sexual determination) is likely to have effects that transcend individual responses and affect the entire ecosystem. Several of the pesticides tested in this study appear to disrupt individual developmental and reproductive processes at environmentally relevant concentrations. Toxaphene is a persistent insecticide heavily used in the United States until its use was restricted in 1982. Toxaphene accumulates in ecosystems due to its lipopohilic, persistent, volatile nature and appears in regions where it has never been used (DeGeus 1999). Toxaphene has been detected in groundwater at concentrations ranging from 0.1 to 1 mg/L (Bell *et al.* 1996). These concentrations are higher than the concentrations in this study that impaired reproductive and developmental processes in *Daphnia*. Therefore, the effective levels reported in this study are realistic exposures that suggest that *Daphnia* exposed to toxaphene in the wild could be at risk of impaired reproductive development.

Toxaphene not only affected sexual differentiation, but it also decreased the average clutch size (Table 2). Sanders (1980) came to similar conclusions, finding that 0.12 μg/L toxaphene significantly reduced the production of young over a 21-day period in *D. magna*. Toxaphene may affect *Daphnia* population growth rates, since a reduction in mean clutch size (fecundity) is likely to result in a decrease in *Daphnia* population growth rate. This decrease in population growth rate may be further amplified by a reduction in asexual females, which reproduce faster than their sexual counterparts do.

Cyanazine and acetochlor had similar negative impacts on *D. magna*. This study shows reproductive impairment of *D. magna* at a concentration (100 μg/L) substantially lower than the current EC_{50} listing (42-106 mg/L; Tomlin 1994). Acetochlor disrupted the normal growth patterns of *D. magna*. Acetochlor exposed (100 μg/L) *D. magna* were, on average, 0.12 mm smaller than their respective controls. The acetochlor EC_{50} (48 hours) for *Daphnia* is currently listed as 16 mg/L (Tomlin 1994) an order of magnitude higher than the concentration that decreased *D. magna* growth in this study.

Diflubenzuron has been regarded as one of the least hazardous insecticides (to vertebrates), primarily due to its specificity to selectively affect chitin synthesis inhibitors (Marx 1977). Chitin, a polysaccharide, is a major component of insect cuticles. Chitin synthesis inhibitors inhibit molting, killing the organism before maturation and preventing reproduction. Nontarget organisms, like crustaceans, also produce chitin. Currently, the listed *Daphnia* EC_{50} for diflubenzuron (48 hours) is 7.1 μg/L, while this six-day *D. magna* assay found diflubenzuron toxic to *D. magna* at 0.01μg/L (Table 2). Similarly, Savitz and Wright (1994) found that substantially lower concentrations (0.78 μg/L) than the reported EC_{50} affected naupliar survival and development in the copepod, *Eurytemora affinis.* Decreased survivorship will have larger ecological ramifications than decreases in fecundity and growth rate.

Daphnia play a key ecological role in lakes and ponds as the dominant herbivores that aid in the transfer of energy from autotrophs to the top of the food web. Determining the vulnerability of *D. magna* to sublethal but environmentally relevant pesticide concentrations is important for the establishment of environmental health standards that will maintain ecological integrity. Pesticides have been widely broadcast and are routinely found in surface and groundwaters at concentrations ranging from 0.001 to 100 μg/l (Table 1). Based on results from this study, *D. magna* are vulnerable to many pesticides found within this range in nature. *Daphnia magna* may be particularly vulnerable to chitin synthesis inhibitors such as diflubenzuron, which reduce survivorship at very low concentrations. Reproductive and developmental processes in *D. magna* are affected by acetochlor, cyanazine, and toxaphene at concentrations found in surface waters. The *D. magna* bioassay appears to be an invaluable tool in determining sublethal but environmentally relevant toxicity of pesticides on aquatic communities and *D. magna* may serve as a useful indicator of water quality.

Related Publications:

Kashian, D.R. and S.I. Dodson. 2002. Evaluation of the use of *Daphnia* for toxicity testing of endocrine disruptors: Effects of vertebrate hormones on development and sex determination in *Daphnia magna.* In Review: submitted to *Journal of Aquatic Ecosystem stress and recovery.*

Kashian D.R., 2002. Reproduction and development in *Daphnia:* The role of hormones, pesticides and detoxification. PhD dissertation. University of Wisconsin-Madison, Wisconsin.

Kashian, D.R. 2002. An investigation of xenobiotic detoxification through P-450 induction in *Daphnia magna.* To be submitted to *Environ. Toxicol. Chem*.

Kashian, D.R. and S.I . Dodson. 2002. Disruption of developmental and sexual determination processes in *Daphnia magna*: A survey of 10 agricultural chemicals. In Review: submitted to *Environ. Toxicol. Chem.*

Key Words:
toxicity, toxaphene, Acetochlor o'p'-DDT, Di-n-butyl phthalate, p'p-DDE, linuron, alachlor, metribuzin, amitraz, 2,4-D chlorosulfuran, cyanazine, diflubenzuron, metolachlor and diquat

Remediation of Soil and Groundwater Using Effectively and Ineffectively Nodulated Alfalfa

Basic Information

Title:	Remediation of Soil and Groundwater Using Effectively and Ineffectively Nodulated Alfalfa
Project Number:	2001WI46O
Start Date:	7/1/2000
End Date:	6/30/2002
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Agriculture, Nitrate Contamination, Water Quality
Descriptors:	phytoremediation, groundwater contamination soil nutrients, alfalfa cultivars
Principal Investigators:	Nancy Turyk, Byron Shaw

Publication

Remediation of Soil and Groundwater using Effectively and Ineffectively Nodulated Alfalfa

University of Wisconsin System Project 01-REM-4 and DATCP Project 00-04

Nancy B. Turyk - Sr. Research Specialist, UWSP
Dr. Byron H. Shaw - Emeritus Professor of Water Resources, UWSP
Dr. Michael P. Russelle - Soil Scientist, USDA ARS, St. Paul, Minn.

Location of Research: University of Wisconsin-Stevens Point, University of Minnesota-St Paul and Dopp dairy farm Portage County

Duration of UWS Funding: July 1, 2000 to June 30, 2002

Project Summary

Background:

Federal drinking water standards are exceeded for nitrate-N in 10% of the private wells in Wisconsin and over 40% in some Portage County townships. In addition, P leaching is becoming a recognized concern on soils that receive large applications of livestock manure.

This study was designed to test whether normal, N_2-fixing (effectively nodulated) alfalfa or special non-N_2-fixing (ineffectively nodulated) alfalfa can remove excess N and P from an abandoned barnyard. Nutrient removal, yield, and persistence of these plants will help determine the feasibility of their use in this and other agricultural activities in medium-to-coarse textured soils common to Wisconsin and other Midwest states.

Objective:

The primary objective of this study was to monitor changes that occur in groundwater quality and soil fertility in an abandoned barnyard planted with effectively and ineffectively nodulated alfalfa cultivars (Agate and Saranac) for possible use in phytoremediation. This project consists of several components; Variables analyzed included groundwater chemistry, soil characteristics, and differences between alfalfa cultivars for yield and plant nutrient content.

Methods:

Groundwater monitoring wells (up- and down-gradient) of the 60 m-long plots were sampled monthly through the growing season, from March through October, plus a winter sampling, totaling nine sample dates per year. Analyses included NO_2+NO_3-N and Cl- on all sample dates plus two samples per year for total reactive P, K, and NH_4-N.

Spatially-referenced samples from the upper 1.5 m of soil were collected at the end of each growing season in 1998 and 2000 for analysis of NO_2+NO_3-N, NH_4-N, and extractable P. Spatially-referenced topsoil samples were obtained in spring of each year and analyzed for inorganic N and extractable P. Eight spatially referenced herbage samples were collected from each plot every harvest for determination of biomass and N and P content. Topsoil samples taken at the same locations were analyzed for inorganic N and extractable P.

Results:

Both Agate and Saranac cultivars of alfalfa are capable of taking up as much as 400 kg/ha of N from these sandy soils. The maximum uptake was 380 kg/ha by Effective Agate in 1999, whereas Ineffective Agate removed 250 kg/ha. Yield and N uptake were reduced in 2000 and 2001 due to drier conditions.

This research demonstrates that N_2 fixation uptake is facultative with less fixation occurring when N supply is large. Ineffective cultivars did not remove as much total N as their effective pairs, because available N was rapidly leached in these soils, limiting growth and yield of the non-N_2-fixing alfalfas.

Nitrate leaching to groundwater was very significant with all down-gradient wells exceeding the 10 mg/L nitrate-N standard. Values as high as 88 mg/L were found in the down-gradient wells in 2002. The average nitrate-N concentrations in the upper 1.8 m of the water table down-gradient of the plots in 2001 was 47 mg/L. This concentration of N would amount is equivalent to about 250 kg/ha in the upper 1.8 meters of the aquifer. We did not find any evidence of significant groundwater impacts from P, ammonium N or K in this study, but P leaching was apparent in the upper soil profile.

Conclusions and Recommendations:

This research has shown that in sites with sandy soils and groundwater recharge of approximately 25 cm per year leaching of N from cultivated barnyard soils is more rapid than is the establishment and N uptake alfalfa.

Further research to optimize N uptake in remediation projects should focus on companion crops to alfalfa that would provide more rapid uptake of N during alfalfa establishment. Direct seeding techniques that would not require cultivation should be used to minimize oxidation of organic N compounds. Cultivation results in the destruction of any compacted layer, which, in turn, encourages both rapid mineralization of organic N and leaching. Cultivation may be unavoidable, however, if compaction is too high to allow rapid root elongation.

Key Words: phytoremediation, nitrate leaching, ineffective alfalfa, groundwater nitrate, nitrogen fixation

Funds for this study were provided by University of Wisconsin System, Wisconsin Department of Agriculture, Trade, and Consumer Protection, USDA Agricultural Research Service, and the University of Wisconsin-Stevens Point. This project has been a cooperative venture between University of Wisconsin-Stevens Point (UWSP), USDA's Agricultural Research Service (ARS), Portage and Waupaca County Land Conservation Districts (LCD), the Tomorrow/Waupaca River Priority Watershed Project (TWRP), and the Dopp family farm.

Impacts of Privately Sewered Subdivisions on Groundwater Quality in Dane County, Wisconsin

Basic Information

Title:	Impacts of Privately Sewered Subdivisions on Groundwater Quality in Dane County, Wisconsin
Project Number:	2001WI43O
Start Date:	7/1/2001
End Date:	6/30/2003
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Non Point Pollution, Groundwater, Management and Planning
Descriptors:	non-point source pollution, groundwater, modeling, nutrients, pesticides
Principal Investigators:	Kenneth R Bradbury

Publication

Impacts of privately sewered subdivisions on groundwater quality in Dane County, Wisconsin

Kenneth Bradbury, Geology and Natural History Survey, University of Wisconsin-Extension

Funding Agency: UWS Groundwater Research Program

Project duration: July 2001 – June 2003

This project is examing and monitoring the impact of newly constructed unsewered subdivisions on local groundwater. The construction of new unsewered subdivisions in southern Wisconsin and elsewhere has become a contentious land-use issue, and one of the major concerns is that such subdivisions may contribute to groundwater contamination. This project offers the opportunity to collect groundwater quality and water-level data before, during, and after construction of a new subdivision in Dane County, Wisconsin. The sites chosen for study will use nonconventional septic systems of the types proposed under the recently approved Wisconsin Comm-83 Private Onsite Wastewater Treatment Systems Code. It is expected that such nonconventional 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.

Currently, there are few data on the effects of unsewered subdivisions on groundwater in southern Wisconsin, and essentially no field data on the potential groundwater impacts of the new-technology septic systems approved in Comm-83. This project will assess the performance of such systems under field conditions. In addition, the project will establish long-term (10 years) monitoring sites at the selected subdivisions. The resulting data should help document the environmental advantages of using new-technology systems and assist rational land-use decision-making by state and local officials.

The project has the objectives of establishing a groundwater monitoring system around a new subdivision in Dane County, designed for a 10-year monitoring period and available for future projects, to determine baseline groundwater conditions (quality and groundwater levels) prior to subdivision construction, to monitor groundwater quality and levels during the period of the project, and to draw preliminary conclusions about subdivision impacts over the 2-year project period, and recommend protocols for continued monitoring up to 10 years.

Project Update

In the summer of 2001, a 78-acre parcel 4 miles east of downtown Sun Prairie, Wisconsin was chosen as the site for this pilot project. The final plat for a 30-home subdivision, Savannah Valley, was approved in summer of 2002, and the installation of stormwater drains and road grading began in early September. Lots are currently for sale, and the first home was constructed in the spring of 2003.

The site chosen for development contains both farmed and wooded areas, as well as a small wetland. The agricultural history of the site dates back at least a century. Corn, soybeans, wheat, and hay have been grown in recent years. A drain tile beneath the center of the property empties into a drainage ditch just north of the site. Overall, the site has a rolling topography, with two glacial drumlins providing the greatest relief. The site is characterized by a thin (0 - 5 feet) silt-loam soil overlying till. The till ranges in thickness from 20 to 80 feet and is composed primarily of gravel and sand, although some silt and clay are also present. The till is underlain by a clean sandstone along the western edge of the property. This sandstone is absent over the rest of the site, where the uppermost bedrock unit consists of interbedded sandy dolomite and dolomitic sandstone.

Eleven water-table monitoring wells were installed by the Wisconsin Geological and Natural History Survey in October and November 2001. A total of five bedrock wells were also installed at the subdivision site. Three of these wells will be converted to private water-supply wells as houses are built, and two will remain as nonpotable monitoring wells. Six additional piezometers were drilled by USGS in fall 2002 to further define the water table. Six of the water-table wells have been instrumented with pressure transducers to collect hourly water level and temperature data. A rain gauge has been installed to collect hourly precipitation data, and a conductivity meter has collected hourly data from the drain tile effluent.

Current Project Results to Date

Groundwater flow converges toward a swale and drainage tile near the center of the site, and groundwater movement is relatively rapid. Hydrographs constructed from water-level data in the unlithified aquifer show a recharge period from February through June, with declining water levels the rest of the year. During spring recharge, this aquifer responds rapidly to snowmelt and precipitation events. Water level rise in the shallow bedrock aquifer occurs later and over a longer time, from March through August.

Monitoring wells have been sampled regularly since late 2001 for major ion concentrations, pH, conductivity, and temperature, and, occasionally, for agricultural pesticides. In addition, 18 private residential wells near the site of the future subdivision were sampled in June 2002. A summary of selected geochemical data collected to date is shown in Table 1.

Table 1. Selected water quality data

Parameter	*Number of samples*	*Minimum*	*Maximum*	*Average*	*Standard Deviation*
			Water table wells		
Nitrate[1]	97	< 0.1	36.4	8.7	7.7
Chloride[2]	97	0.3	414.2	46.9	75.4
Atrazine[3]	11	< 0.1	0.8	0.3	0.3
Conductivity[4]	97	531	1839	904	239
			Bedrock wells		
Nitrate[1]	20	< 0.1	12.6	5.2	3.6
Chloride[2]	20	< 0.1	70.0	23.1	21.4
Atrazine[3]	5	< 0.1	0.3	0.2	0.1
Conductivity[4]	20	592	921	754	100
			Local private residential wells		
Nitrate[1]	18	< 0.1	29.6	8.7	6.6
Chloride[2]	18	0.3	76.8	26.9	18.4
Conductivity[4]	18	540	1017	786	132

* Concentrations are listed as: [1]mg/L nitrate-nitrogen, [2]mg/L, [3]ug/L, and [4]uS/cm at 25° Celsius.

Delays in subdivision construction have allowed a full year of background data to be collected. During this time, it has become apparent that groundwater chemistry is extremely variable, both spatially and temporally. For example, nitrate concentrations in one well rose from 2.3 to 21.0 mg/L NO_3-N between June and August 2002. During the same period, concentrations dropped from 6.2 to 0.3 mg/L in another well just 500 feet away. We have identified several controls on the observed variability in groundwater quality. Temporal variability is primarily caused by recharge patterns, as infiltrating precipitation and snowmelt dilute the upper aquifer. Spatial variability is caused by aquifer heterogeneities, nonuniform agricultural loading patterns, and runoff of agricultural chemicals to topographically low points in the landscape. Groundwater quality is much more variable near the water table than deeper in the aquifer, as samples collected from bedrock wells are much more consistent. Any variability in these wells seems to be controlled by well construction, particularly casing depth.

We feel we have a good understanding of the site geology and hydrogeology, and a dense monitoring well network with frequent sampling intervals have allowed us to identify the spatial distribution and temporal variability of contaminants prior to subdivision construction. The knowledge of pre-existing conditions from agricultural land use, combined with continued monitoring as new homes are constructed, should allow conclusions to be drawn about the impact of this land use change on groundwater quality.

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:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	WI - 2nd
Research Category:	None
Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Anders W. Andren, James Hurley, JoAnn M. Savoy

Publication

12. Title Information Transfer Plan

13. Statement of critical regional or State water problem Water Resources Institute (WRI) staff believe an efficient system of water information retrieval and dissemination is vital for researchers, state agency personnel, state legislators and legislative agencies, and the general public to make informed decisions on water policy and promulgate intelligent water-related regulations.

14. Statement of results or benefits It is always difficult to directly measure the impact of an information transfer program, but staff will collect and analyze statistics on Web site usage, library circulation and requests for assistance, publications distribution, WRI-sponsored conference attendance, and publications and presentations by WRI staff and Principal Investigators funded through WRI. The statistical analysis should help evaluate the program and plan future activities. For example, Web site usage can be used to determine which Web pages are most popular and where to direct future efforts. Library circulation statistics tell us which subject areas are most used, and where to direct future collection development.

15. Nature, scope, and objectives of the project The WRI's information transfer responsibilities are three-fold: to promote and coordinate water resources research; to enhance educational capability through training and public service; and to provide information to government agencies, the scientific community, the private sector, and the general public. The WRI assists researchers and the general public with their information needs by maintaining a Web site for the dissemination of water information and WRI activities; by providing a library of water-related printed and electronic materials; by offering library reference services to interested individuals; by sponsoring conferences; and by publishing and distributing technical reports, proceedings, and a monthly listing of library acquisitions and new and noteworthy water Web sites.

Timeline

- Web site update – continuous, weekly at minimum
- Final Reports resulting from WRI projects – edited and published as received
- *Library Recent Acquisitions and Web Sites of Interest* – monthly
- Finish adding Water Resources Library (WRL) holdings to University of Wisconsin Circulation System – February 2003
- WRI Program Directory – Spring 2002
- AWRA – Wisconsin Section Annual Meeting; co-sponsorship of "Careers in Water Resources" symposium – March 2002
- AWRA – Wisconsin Section 2003 Annual Meeting Preparation
    - First announcement and call for abstracts – September 2002
    - Second announcement and call for abstracts – December 2002
    - Abstracts sent to printer – Mid-February 2003

16. Methods, procedures, and facilities The Wisconsin WRI will undertake the following information transfer strategies:

WRI Web Site:

The WRI believes that Web site development and upkeep are essential for water resources information dissemination. In the coming year, staff will update Web site and make it more accessible to people with vision, hearing or other disabilities. The Web accessibility guidelines of the World Wide Web Consortium (W3C) will be followed.

The WRI home page (*http://wri.wisc.edu*) contains links to eight major subsections.

1. Projects: Summaries of projects currently funded by WRI.
2. Groundwater Research: Summaries of completed groundwater research/monitoring projects funded by the University of Wisconsin System, and the Wisconsin Departments of Natural Resources (DNR); Agriculture, Trade, and Consumer Protection (DATCP); and Industry, Labor, and Human Relations (DILHR).
3. Funding opportunities: All WRI-related funding opportunities including the base program and the national competition as well as links to other water-related funding opportunities (U.S. EPA, NSF, etc.) are provided.
4. Conferences: Each year WRI co-sponsors the American Water Resources Association-Wisconsin Section annual meeting. Full programs and individual abstracts are posted on the Web. We also provide links to announcements for other regional, national, and international water-related conferences
5. Water Resources Library (WRL): General information about the library, current and past issues of *Recent Acquisitions and Web Sites of Interest*, links to MadCat (UW-Madison online catalog), AskWater online reference service, and library online publications. Online publications include a "Guide to Finding a Water-Related Job" (http://wri.wisc.edu/library/finding_jobsall.html); a "Guide to Finding Water Related Information" (http://wri.wisc.edu/library/subject.html); and the "Water Education Place" (http://wri.wisc.edu/library/WaterCurricula/index.html).
6. Water Links: Listing of Web sites for those interested in Wisconsin water including research programs, state agency programs, and graduate education programs.
7. Publications: Listing of publications based on research supported by or through the Wisconsin Water Resources Institute covering the years 1966-2001.
8. Expert Directory: Database of over 800 experts which can be searched by area of expertise, research interest or name.

Publications

In addition to the "virtual" publications on the web site, WRI staff will produce several hard copy publications. Staff will publish final reports resulting from WRI-funded projects, the announcements and abstracts for the annual meeting of the Wisconsin

Section of the American Water Resources Association, the monthly library *Recent Acquisitions and Web Sites of Interest*, and a program directory. The WRI program directory will contain an overview of program activities as well as a detailed listing of current research projects.

Water Resources Library

The WRL contains over 23,000 titles covering all major water topics, but the collection is particularly strong in Wisconsin and Great Lakes water resources issues, groundwater protection, wetlands issues, and the impacts of agricultural chemicals. The WRL also has an extensive collection of publications from the other State Water Resources Research Institutes and subscribes to more than 30 journals and receives over 100 newsletters. All materials are in the UW-Madison online catalog, MadCat, which can be searched at *http://madcat.library.wisc.edu/*. Anyone can check out materials. The WRL has two Electronic Library workstations that provide access to hundreds of UW-Madison online databases, indexes, and electronic journals as well as the resources of the Internet. The WRL is located on the UW-Madison campus and has access to that major research collection.

The Library will provide the following services:

- *Recent Acquisitions and Web Sites of Interest* will be written and circulated monthly by mail and email to over 300 users as well as being posted on the Web. Anyone can request materials.
- WRL Web site (http://wri.wisc.edu/library) will be updated and new materials will be added.
- Instruction in the use of electronic indexes and databases, and assistance with Web searches will be given.
- Reference service to assist users in finding water-related information.
- AskWater email reference service will be continued to allow users to ask questions online.
- Loan of documents and journals through the mail or in person.
- Distribution of WRI research reports and other publications.
- Document procurement through interlibrary loan, request from sources, or purchase.

Staff will also continue adding library holdings to the new UW-Madison online circulation system so that the WRL can better serve UW-Madison and other UW System campuses. Soon UW-Madison faculty, staff and students will be able to request that WRL books be delivered to any campus library convenient to them. System faculty, staff, and students will be able to search a system-wide online catalog and directly request WRL materials. Materials will be sent to the requestor promptly through a statewide delivery system.

Conferences

The WRI will once again co-sponsor the American Water Resources Association-Wisconsin Section annual meeting. Other sponsors include the Wisconsin Ground Water Association, the Wisconsin Department of Natural Resources, and the Central Wisconsin Groundwater Association. The theme of the 2002 conference is "Sustainability of Wisconsin's Water Resources." WRI will design and distribute the program announcements, provide a Web site, and edit and print the meeting abstracts.

17. Related research N.A.

18. Training potential One to two Masters degree students will receive training working with WRL staff.

19. Investigator's qualifications See attached resume.

USGS Summer Intern Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	4	0	10	16
Masters	0	1	0	7	8
Ph.D.	2	2	0	3	7
Post-Doc.	0	1	0	1	2
Total	4	8	0	21	33

Notable Awards and Achievements

Notable Achievements

NIWR Review - Dr. James Hurley, Assistant Director for Research and Outreach was appointed coordinator of the peer review process for the 2002 NIWR-USGS 104(G) Competitive Grants Program. A total of 76 proposals were submitted in 2002 through the electronic submission process. Thirty proposals were forwarded to the peer review panel in late June of 2002, 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.

The University of Wisconsin Water Resources Institute, together with its university researchers, have made a number of impacts from March 1, 2002 through February 28, 2003 These include the following topics:

ARSENIC. Arsenic contaminates public and private groundwater supplies in high concentrations in 23 of Wisconsins 72 counties, particularly those in southeastern Wisconsin and the Fox River Valley. The Wisconsin Water Resources Institute (WRI) supports a comprehensive package of university and state agency projects that address the sources of arsenic, the mechanisms of its release to groundwater, public health effects of arsenic, and specific treatment and removal strategies. To comply with new arsenic reduction standards set by the U.S. Environmental Protection Agency, many groundwater pumping stations need to install treatment units to remove excess arsenic. The American Water Works Association estimates the cost of meeting the new arsenic standard nationwide at $6 billion in initial capital costs and about $600 million annually thereafter. Clearly, cost-effective arsenic removal techniques are urgently needed. A Wisconsin WRI project completed in 2002 developed and tested an inexpensive, high-performance photoactive adsorption media for the simultaneous removal of two toxic species of arsenic (arsenite and arsenate) from groundwater without adjusting for pH nor adding other chemicals. This study indicated that photocatalytic adsorption may offer an effective single-step method for removing both species of arsenic without requiring separate oxidation and adsorption processes.

CLIMATE CHANGE. Most lakes, rivers and wetlands in Wisconsin have some direct connection with the groundwater system. Long-term climate change could have a profound effect on surface water-groundwater interactions and thus have major impacts on water quality, supply and management issues throughout Wisconsin. Anticipating the effects of climate change are important for addressing its potential effects on aquatic ecosystems and the recreational and tourist industries that depend on them. A recently completed WRI-supported study developed and calibrated models of groundwater-surface water interaction in the Trout Lake Basin to assess the effects of changes in precipitation, evaporation and recharge rates that might occur as a result of global climate change. Model simulations indicated that 28 of 30 lakes in the Trout Lake Basin would experience, on average, a half-meter change in water level under both dry and wet conditions, and all 30 lakes had increased rates of groundwater discharge during the wet scenario and decreased rates during the dry scenario. Another WRI project involving a Wisconsin Geological and Natural History Survey research is examining the impacts of land use and groundwater flow on trout stream temperatures.

METHYLMERCURY. WRI-supported investigators are continuing to participate in a landmark international study at the Experimental Lakes Area in Ontario, Canada, that is adding trace amounts of mercury to an ecosystem in order to determine its transport, methylation processes and bioaccumulation. The results of this study could have direct, major impacts on the development of mercury emission strategies and their effects on protection of biota in remote regions. A Wisconsin mercury study completed in 2002 evaluated the importance of groundwater in the production and transport of methylmercury in relatively remote Lake Superior tributaries, the results of which indicate that local groundwater may be a significant source of mercury to surface waters. A related new study is focusing on the role of the streambed-groundwater interface zone in the production and transport of methylmercury to Lake Superior via its tributaries.

NITRATE. Nitratemost of it from commercial fertilizers and manureis by far the most common chemical contaminant found in Wisconsin groundwater. Nitrate levels exceed federal drinking water standards in 10 percent of the private wells in Wisconsin and more than 40 percent of the wells in some areas. Human health risks posed by high nitrate levels include lymphnoma, gastric cancer, hyptertension, thyroid disorder, birth defects and possibly miscarriages. The Wisconsin WRI supports a wide range of studies on groundwater nitrate loading history, sources, movement, fate and remediation strategies. A WRI-funded study completed in 2002, for example, demonstrated the effectiveness of using nitrate-fixing alfalfa as an economical alternative to active remediation techniques for preventing or greatly diminishing nitrate leaching from topsoil to the groundwater below in soils with relatively low hydraulic conductivity. The study showed that, while there are limits to how much nitrogen can be absorbed by alfalfa, removal rates are typically two to four times higher than with most annual crops, like corn, and there generally is little worry about high nitrate concentrations in the resulting alfalfa forage in contrast to forage grasses.

PESTICIDES. Wisconsins WRI has helped guide efforts to control groundwater contamination by atrazine, a pesticide used in corn and vegetable production. A series of studies, funded by state and federal sources through WRI, have identified atrazine and its toxic metabolites in groundwater and traced their flow. In response to these findings, the State of Wisconsin has restricted atrazine use throughout the state and banned it entirely in some areas. Currently, a WRI study funded through the state Department of Agriculture, Trade & Consumer Protection is investigating and comparing atrazine residue penetration and accumulation in two groundwater basins in the state.

RAINGARDENS. In urbanized areas of Wisconsin that rely on groundwater as the primary source of water, groundwater withdrawals significantly exceed recharge rates. In addition to posing a long-term urban water supply problem, this can cause environmental degradation by reducing the groundwater discharge to adjacent springs, wetlands, streams and lakes and associated ecosystems. Raingardenssunken gardens that receive local stormwater runoffappear to offer a way to enhance urban groundwater recharge while reducing urban stormwater runoff. In a continuing project, WRI is sponsoring a field demonstration and evaluation project to test model predictions that a raingarden with an area equal to 10 percent of the surrounding pervious area can double the local groundwater recharge rate.

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 water supplies serving rapidly growing communities. In response, the state has mandated that drinking water supply sustainability be incorporated into comprehensive land use plans. One of these studies examined the causes of historical changes in groundwater recharge rates in southeastern Wisconsin, and this work is now being used to develop groundwater recharge estimates for a groundwater flow model for that region being developed by the U.S. Geological Survey, Wisconsin Geological & Natural History Survey and Southeast Wisconsin Regional Planning Commission.

WATERS OF WISCONSIN During the past year, the Wisconsin WRI has been a strong supporter and active participant in Waters of Wisconsin: The Future of Our Aquatic Ecosystems and Resources, a statewide initiative to examine how best to use and conserve the states water resources and aquatic ecosystems. Spearheaded by the Wisconsin Academy of Sciences, Arts and Letters (WASAL), the Waters of Wisconsin (WOW) project seeks to identify the challenges, demands and needs related to the sustainability of Wisconsins water resources. It has engaged hundreds of representatives from the academic, scientific, governmental, business, and non-governmental sectors in a series of public forums held at locations around the state, culminating in a statewide forum in October 2002 in Madison and a Governors Declaration of 2003 as the Year of Water in Wisconsin. The Wisconsin WRI will help support a full-time WOW associate position at WASAL to coordinate activities around the state during the Year of Water, work with key members of the WOW committee to conduct research on water policies, improve access to water-related information, and initiate a review of water education curricula.

Publications from Prior Projects

1. 2001WI81B ("Removal of As(III) and As(V) in Contaminated Ground Water with Thin-Film Microporous Oxide Adsorbents") - Water Resources Research Institute Reports - Anderson, M. A., Zeltner, W. and Lee, E. 2002. Removal of As(III) and As(V) in contaminated groundwater with thin-film microporous oxide adsorbents. Water Resources Institute, University of Wisconsin-Madison.
2. 2001WI30O ("Groundwater-Lake Interaction: Response to Climate Change in Vilas County, Wisconsin") - Water Resources Research Institute Reports - Anderson, M. P. 2002. Groundwater-lake interaction: Response to climate change Vilas County, Wisconsin. Water Resources Institute, University of Wisconsin-Madison.
3. 2001WI35O ("Effect of Clean and Polluted Groundwater on Reproduction and Development of

Daphnia") - Water Resources Research Institute Reports - Dodson, S. 2002. Effect of clean and polluted groundwater on reproduction and development. Water Resources Institute, University of Wisconsin-Madison.

4. 2001WI101B ("Importance of Groundwater in Production and Transport of Methyl Mercury") - Water Resources Research Institute Reports - Stoor, R. W., D. E. Armstrong, K. Rolfhus, L. Cleckner and D. P. Krabbenhoft. 2002. Importance of groundwater in production and transport of methylmercury in Lake Superior tributaries. Water Resources Institute, University of Wisconsin-Madison.
5. 2001WI30O ("Groundwater-Lake Interaction: Response to Climate Change in Vilas County, Wisconsin") - Articles in Refereed Scientific Journals - Anderson, M.P., R.J. Hunt, J. Krohelski, and K. Chung, 2002. Using high hydraulic conductivity nodes to simulate seepage lakes. Ground Water 40: 117-122.
6. 2001WI101B ("Importance of Groundwater in Production and Transport of Methyl Mercury") - Dissertations - Stoor, R.W. 2002. Groundwater contributions of methylmercury to a Lake Superior Watershed. M.S. Thesis, Environmental Chemistry and Technology Program, University of Wisconsin-Madison.
7. 2001WI37O ("Field Evaluation of Rain Gardens as a Method for Enhancing Groundwater Recharge") - Dissertations - Dussaillant, A. 2002. Focused recharge in a rain garden: Numerical modeling and field experiments, Unpublished Ph.D. dissertation. Department of Civil & Environmental Engineering, University of Wisconsin-Madison. 139 pp.
8. 2001WI35O ("Effect of Clean and Polluted Groundwater on Reproduction and Development of Daphnia") - Dissertations - Kashian D.R. 2002. Reproduction and development in daphnia: The role of hormones, pesticides and detoxification. PhD dissertation. Department of Zoology, University of Wisconsin-Madison, 92 p.
9. 2000WI12O ("Admicelle-Catalyzed Reductive Dechlorination of Perchloroethylene (PCE)") - Book Chapters - Li, Z., C. Willms, P. Zhang, and R.S. Bowman. 2002. Rate and pathway changes in PCE dechlorination by zero valent iron in the presence of cationic surfactant. In A. R. Gavaskar and A. S. C. Chen (eds.) Remediation of Chlorinated and Recalcitrant Compounds, Battelle Press, p. 2C-35.
10. 2000WI6B ("Hydraulic Conductivity and Specific Storage of the Maquoketa Shale ") - Dissertations - Eaton, T.T. 2002. Fracture heterogeneity and hydrogeology of the Maquoketa aquitard, southeastern Wisconsin. Ph.D. dissertation. Department of Geology and Geophysics, University of Wisconsin-Madison. 211 p.