University of Wisconsin Water Resources Institute
Annual Technical Report
FY 2001

Introduction

The University of Wisconsin - Water Resources Institute (WRI) is based at the University of Wisconsin-Madison as an academic unit of the Graduate School and works with the Universitys Office of Research and Sponsored Programs to ensure compliance with university, state, and federal guidelines. WRI is housed in the Aquatic Sciences Center (ACS) at UW-Madison, the administrative home of both WRI and the University of Wisconsin Sea Grant Institute. The staff at ACS provides support for administration, research and outreach activities of WRI. The Institute also supports a library, containing over 26,000 volumes covering all major water topics.

With nearly 75% of its current base budget targeted for research, the WRI is supporting 27 individual research projects that address a wide range of issues and problems. Research projects fall into the following four thematic areas: groundwater, surface water, groundwater/surface water interactions, and drinking water initiatives. Faculty, staff, and students at the University of Wisconsin System campuses at Madison, Milwaukee, Stevens Point, and Parkside, the University of Wisconsin-Extension, the Wisconsin State Laboratory of Hygiene, the U.S. Geological Survey, and individuals in private industry are participating in projects supported through the WRI.

In May 1984 a Comprehensive Groundwater Protection Bill for Wisconsin (1983 Act 410, Wisconsin Statutes) was signed into law. One of the provisions of the bill was to include 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 Chancellor of the University of Wisconsin-Madison. Because groundwater protection is deemed a priority issue by the WRI, the GRAC serves as an important advisory committee for the WRI. The GRAC, composed of a diversity of representatives with a great deal of scientific, political and administrative experience, 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 University of Wisconsin System. This Groundwater Research Program, administered by the Water Resources Institute, 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 which has effectively confronted a spectrum of societal concerns. Institute staff, University of Wisconsin System faculty, staff, and students, public officials, state administrators, industry, and the public have come to rely on the WRI for objective, timely scientific information. 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 a wide range of disciplines.

Research Program

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.

Hydrology and Biogeochemistry in the Wisconsin River Floodplain: Implications for Riverine Nitrogen Loads

Basic Information

Title:	Hydrology and Biogeochemistry in the Wisconsin River Floodplain: Implications for Riverine Nitrogen Loads
Project Number:	1999WI0016G
Start Date:	9/1/1999
End Date:	8/1/2001
Funding Source:	104G
Congressional District:	WI-2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Geochemical Processes, Surface Water, Nitrate Contamination
Descriptors:	Denitrification, Ecosystems, Groundwater hydrology, Land-water interactions, Nitrogen, Rivers, Wetlands
Principal Investigators:	, Randall Hunt, Emily H. Stanley

Publication

Hydrology and Biogeochemistry in the Wisconsin River Floodplain

Project Number: C-01
Start Date: 09/01/1999
End Date: 08/31/2001
Research Category: Water Quality
Focus Category #1: Groundwater
Focus Category #2: Hydrology
Focus Category #3: Nitrate Contamination
Lead Institution: Water Resources Institute

Principal Investigators:
Emily H. Stanley, Assistant Professor, University of Wisconsin
Randall J. Hunt, Professional Staff, US Geological Survey 02

Problem and Research Objectives:
Throughout the Midwest, surface and particularly groundwater concentrations of nitrate have been increasing over the past 50 years. This increase has been attributed to changing land uses, particularly intensification of agriculture. Accordingly, nonpoint source (NPS) inputs are generally viewed as a major cause of nutrient enrichment throughout much of the Midwest. There are two major consequences of this NPS pollution. First, a growing number of wells in Wisconsin have nitrate concentrations exceeding the U.S. Environmental Protection Agency's (EPA) 10 mg/liter maximum contaminant level, particularly in the southern part of the state where the combination of well-drained soils and high nitrate loading increases the risk of groundwater contamination. Second, nutrient-rich groundwater and/or the erosion of nutrient-rich particles eventually arrive in surface waters. As a result, many receiving fresh and salt water systems in the Mississippi drainage are becoming eutrophic. The best known example of this process is the expansion of the hypoxic zone in the Gulf of Mexico following the 1993 flood. It is clear that the ecological and economic ramifications of nonpoint nutrient loading are enormous and must be addressed. In response, agencies (including, EPA, U.S. Geological Survey and the U.S. Department of Agriculture) have sponsored initiatives to improve our understanding of NPS inputs and their controls. The proposed research is directly relevant to the numerous calls for basic and applied research aimed at understanding nutrient loading in the Mississippi River basin.

Methodology:
The proposed field site is a 570-ha floodplain area adjacent to the Wisconsin River between Wisconsin Dells and Portage. Piezometers and wells are already installed and information from well logs was collated. Additional wells were also installed for detailed information regarding changes in surface and groundwater interactions during and after inundation in low-lying sloughs adjacent to the channel. Groundwater samples were collected by pumping or bailing, and flood samples were collected by grab sampling. Temperature, oxygen, and conductivity of surface water samples were measured using handheld meters in the field and nutrient concentrations and isotopic composition (to trace the source of the water on the floodplain) of surface and groundwaters is being monitored from high-to low flow periods. Sediments from sloughs have been collected for determination of rates of denitrification, and to determine if these rates are limited by the availability of organic carbon or nitrate.

Principal Findings and Significance:

Water that inundates the floodplain of the Wisconsin River is dominated by channel-flow rather than groundwater. Thus, the water flowing onto the floodplain is relatively nitrate-rich in comparison with groundwater, which typically has nitrate-N concentrations >0.05 mg/L. Denitrification rates in sloughs are high during inundation, and if sloughs become hydrologically isolated from main channel flow, nitrate is rapidly lost from the slough. For unsaturated soils, denitrification rates are characterized by extreme spatial variability, but are highly correlated with soil moisture content. Frequent flood pulses maintain high potential for denitrification throughout the floodplain. Collectively, these results demonstrate the ability of floodplains to remove nitrate from surface waters, and emphasize the utility of these areas for reducing N loads given a regime of episodic flooding.

Descriptors:

Denitrification, Ecosystems, Groundwater hydrology, Land-water interactions, Nitrogen, Rivers, Wetlands

Publication Information:

This grant has provided partial support for two M.S. theses:

West, J. L. 2000. Denitrification of the Wisconsin River floodplain. M.S. Thesis. Denitrification in the Wisconsin River floodplain. Dept. of Zoology, University of Wisconsin-Madison.

Forshay, K.J. 2003. Nitrogen dynamics of floodplain water bodies following inundation on the Wisconsin River floodplain. Dept. of Zoology, University of Wisconsin-Madison

Other Publications:

West, J. L., and E. H. Stanley. 2000. Denitrification in soils of the Wisconsin River floodplain: patterns and potential controls. 48th Annual Meeting. North American Benthological Society, Keystone, Colorado.

West, J.L. and E.H. Stanley. 2001. Denitrification in soils of the Wisconsin river floodplain: observations on the role of floodplain inundation. 49th annual meeting, North American Benthological Society, LaCrosse, Wis.

Forshay, K.J. and E.H. Stanley. 2002. Nutrient dynamics of floodplain water bodies following inundation on the Wisconsin River floodplain. 50th annual meeting, North American Benthological Society, Pittsburgh, Pa.

Forshay, K.J. and E.H. Stanley. Rapid nitrogen loss in floodplain water bodies following spring floods in the Wisconsin River floodplain. In prep. (submission expected 4/03).

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, 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.

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

Phase 1 of METAALICUS involved pilot studies and baseline work in 2000 while Phase 2 is the full scale additions scheduled to begin in June 2001. The pilot studies are yielding fundamental new information about the cycling of mercury in terrestrial and aquatic ecosystems. For example, in 1999, we added 12.5 µg/m^2 of ^{202}HgII to a wetland plot, approximately doubling the annual mercury deposition rate of mercury at the ELA. The isotopic mercury was much more mobile than expected, penetrating into the 10-20 cm below the peat surface. In 1999, we also added 12.5 ug/m2 of ^{202}HgII to a 680m^2 upland catchment at the ELA. Over the first growing season, only about 8% of the ^{202}HgII was lost to the atmosphere, and only 0.3% of the ^{202}HgII was exported from the upland catchment. In 2000, we also added ^{200}HgII to the upland and wetland plots and to four 10-meter diameter lake enclosures. Preliminary results from the enclosures demonstrate loss of ^{200}HgII to the atmosphere, and rapid movement of ^{200}HgII to the periphyton on the sediment surface and walls of the enclosure, but minimal movement into sediments.

Our group also participated in characterization of Hg dynamics in Lake 658, the lake of the planned isotopic watershed/lake addition, to prepare for full-scale addition studies. Intense monitoring of the lake and the zone of the sediment-water interface were characterized in order to predict the response of added isotope within the lake. We observed trends in increasing dissolved organic carbon and total Hg in Lake 658 in response to rainfall runoff from both the upland and wetland. We also observed intense recycling of Hg and MeHg at the sediment-water interface in response to deposition of freshly-deposited material settled from the epilimnion.

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

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 nontoxic 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

During the first months of this project, we have been focusing on the development of a liquid electrode spectral emission chip (LEd-SpEC), which produces a microplasma between the anode and cathode. These are novel liquid anode and cathode electrodes, which attempt to avoid two problems facing the development of a micro-sized plasma device. Firstly, the liquid analyte is sputtered into the plasma from the cathode chamber elevating the need to develop a more complicated nebulizing system. Secondly, this liquid electrode system preserves the life of the electrode. It has taken a four mask process to produce this plasma chip. As shown in Figure 1, the device provides a reservoir and channels in a glass substrate, along with electrodes that bias the water sample. Liquid from the cathode chamber is sputtered into the discharge, for spectroscopic detection of impurities.

After developing the device, we used a small commercial spectrometer (Ocean Optics USB-2000) coupled to a fiber optic bundle located above the plasma to detect a Na analyte (concentrations < 10 ppm).

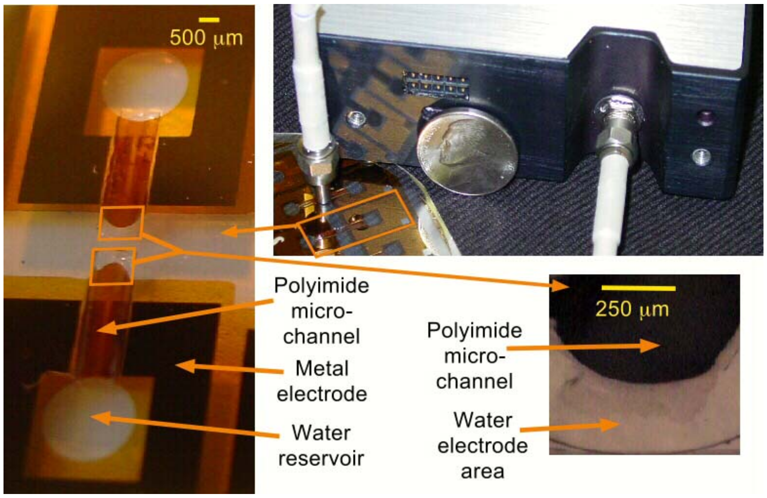

Fig. 1 Optical viewgraph of system and close-up view of the LEd-SpEC.

The optical spectrum from a sodium sample can be seen in Figure 2.

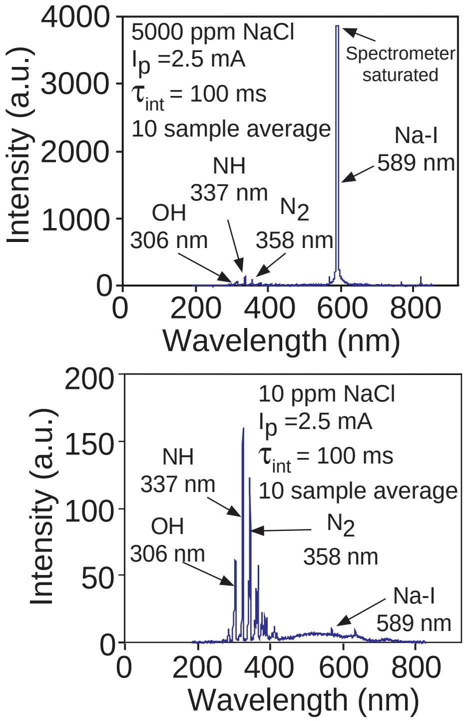

Fig. 2: Spectra for NaCl samples with concentrations of (a-upper) 5000 ppm, and (b-lower) 10 ppm.

We were able to develop a linear calibration curve for this system as shown in Figure 3. While these concentrations are not representative of very low ppb levels in real waters the results thus far are extremely promising. We are now in the process of further optimizing this system.

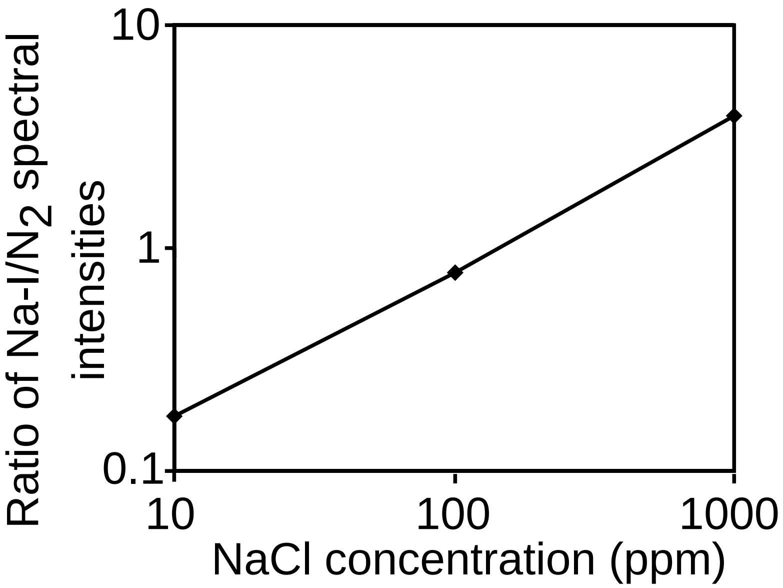

Fig. 3: Ratio of Na to N_2 spectral intensities as a function of NaCl concentration.

Optimization of system will include looking at the electrode configurations to determine proper spacing. Examining new wicking electrodes that will help in the further miniaturization of this system. We also need to increase sensitivities such that detection limits can be lowered. We also want to work with other metal species to determine if the device is also responding linearly with respect to concentration to other species. In addition, we would like to see if there are other contaminating species such as mixed electrolytes which would interfere with spectral interpretation. Lastly, we would like to move to the development of an on-board optical detector that would obviate the need to have a separate external fiber optic based detector.

We continued to be encouraged about our progress and believe that it will indeed be possible to develop a microscaled plasma detection system that will greatly reduce the costs associated with the field analysis of heavy metals. While we still have a long way to go in this pursuit our initial results are highly encouraging particularly with respect to the stability of the electrodes and the ability to sputter the sample from the cathode into the plasma without the need of a fancier nebulizer system. This would have complicated the structure of our final device.

Remediating Groundwater Using Reactive Walls Containing Waste Foundry Sands

Basic Information

Title:	Remediating Groundwater Using Reactive Walls Containing Waste Foundry Sands
Project Number:	2000WI13O
Start Date:	7/1/1999
End Date:	6/30/2001
Funding Source:	104B
Congressional District:	WI-2
Research Category:	Engineering
Focus Category:	Groundwater, Treatment, Water Quality
Descriptors:	Containment technology, Foundry sands, Groundwater, Reactive walls, Remediation technology, Water quality
Principal Investigators:	Craig H. Benson, Gerald R. Eykholt

Publication

Remediating Groundwater Using Reactive Walls Containing Waste Foundry Sands

Craig H. Benson, University of Wisconsin-Madison
Gerald R. Eykholt, University of Wisconsin-Madison

Problem and Research Objectives:

Reactive walls (RWs) are one of the most significant developments in groundwater restoration within the last decade. They are a containment technology that uses passive remediation to remove contaminants from groundwater. After construction, RWs require no energy or maintenance and can render effluent groundwater of drinking water quality. In addition, RWs can be used to treat the most difficult and pervasive groundwater contaminants.

One impediment to reactive wall technology is its large initial capital cost, much of which is due to the cost of the reactive media. As a result, RWs can be impractical for small sites in need of remediation. One method to make RWs more cost-effective is to use an industrial byproduct as the reactive media. One such medium is waste foundry sand, a reactive and sorptive medium that is currently being landfilled in large quantities throughout Wisconsin. Foundry sands can be obtained for virtually no cost for use at remediation projects local to gray iron foundries.

The objective of this study was to assess whether foundry sands can be beneficially reused in RWs and to identify transport parameters that can be used for selecting candidate sands and for conducting preliminary design calculations.

Methodology

The experimental program consisted of two distinct phases: (i) assessment of leaching characteristics of foundry sands and (ii) evaluation of reactivity and transport parameters for foundry sands.

The leaching study was conducted in the context of Wisconsin's NR 538 to determine if foundry sands could be placed below the ground water table without affecting ground water quality due to leaching of potentially toxic constituents in the foundry sands. This portion of the study consisted of water leach tests (to assess metals and anions of concern), soxlet extractions (for assess PAHs), and column tests. Tests were conducted on ten foundry sands, a typical iron medium currently used for reactive walls, and three coarse-grained materials characteristic of aquifer media.

The second phase of the study consisted of batch tests and column tests. Both tests were conducted to assess sorption and reactivity of the foundry sands for chlorinated compounds, with the column tests being more representative of field conditions. TCE and two herbicides were considered. Hydraulic conductivity tests were also conducted on the foundry sands.

Principal Findings and Significance

Results of leaching study showed that the foundry sands satisfied most of the criteria in NR 538 that must be met for placement below the water table. Exceedances of the criteria in NR 538 were no more common for the foundry sands than for the typical iron medium or the aquifer materials. Thus, using foundry sands in RWs will not impose any risk beyond that associated with a conventional RW or the existing aquifer medium.

Results of the batch and column tests that were conducted to assess reactivity and transport parameters showed that simple batch tests yield parameters that are representative of those obtained using more realistic column tests. These tests also showed that (i) the reactivity of iron in foundry sands is nearly identical to that of typical granular iron and (ii) partitioning of VOCs onto foundry sands can be estimated based on the organic carbon content of the sand.

The hydraulic conductivity tests showed that the hydraulic conductivity of some of the foundry sands is too low for use in permeable RWs, although they would be ideal for use in semi-permeable RWs used to isolate contaminant sources. Testing also showed that hydraulic conductivity of the foundry sands could be elevated sufficiently for use in permeable RWs by adding crushed glass from recycling operations.

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.

Inorganic Carbon Dynamics in Allequash Creek: Ecological Implications of Subsurface-Surface Linkages

Basic Information

Title:	Inorganic Carbon Dynamics in Allequash Creek: Ecological Implications of Subsurface-Surface Linkages
Project Number:	2001WI31O
Start Date:	9/15/2000
End Date:	9/14/2001
Funding Source:	Other
Congressional District:	2nd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Groundwater, Wetlands, Models
Descriptors:	Inorganic carbon, groundwater hydrology, land-water interactions, wetlands, watershed budgets, watershed models
Principal Investigators:	Emily H. Stanley

Publication

Inorganic Carbon Dynamics in Allequash Creek: Ecological Implications of Subsurface-Surface Linkages

Project Number: R/OS-GSI-001
Start Date: September 15, 2000
End Date: September 14, 2001
Research Category: Water Quality
Focus Category #1: Groundwater (GW)
Focus Category #2: Wetlands (WL)
Focus Category #3: Models (ML)
Lead Institution: Water Resources Institute

Principal Investigator:

Emily H. Stanley, Assistant Professor, University of Wisconsin-Madison 01

Problem and Research Objectives:

Recent increases in atmospheric CO_2 have inspired considerable research on carbon cycling in terrestrial, marine, and freshwater ecosystems across several spatial scales. Nonetheless, we still have a poor understanding of belowground carbon dynamics and the role of drainage waters in carbon flux. Toward the overall goal of improving our understanding of carbon cycling, we will capitalize on the unusually detailed hydrologic and geochemical knowledge and data at the Wisconsin WEBB site to investigate inorganic carbon dynamics and losses from streams. We seek a mechanistic understanding of controls on inorganic carbon dynamics and losses from a north-temperate basin (Allequash Creek, Wisconsin), focusing on linkages between groundwater, near-stream, and channel environments. Specific objectives are to: (1) understand the spatial and temporal variation in streamwater inorganic carbon; (2) test a general model of soil respiration and watershed inorganic carbon dynamics; and (3) determine the effects of groundwater discharge on in-stream productivity in Allequash Creek

Methodology:

We are determining spatial and temporal patterns of dissolved inorganic carbon (DIC) in a central study reach in Allequash Creek through monthly measurements of groundwater and surface water chemistry, groundwater inputs into the study reach, in-stream metabolism, and gas exchange between the surface water and the atmosphere. These same data, along with supplemental information on cation concentration, precipitation, and streamflow will provide the input data needed to test the inorganic carbon model developed by J.B. Jones and P.J. Mulholland (published in Ecosystems [1998:1:183-196]). The influence of groundwater discharge is being studied through comparison studies of areas of high and low groundwater discharge, and by a set of supplemental experiments to identify possible mechanisms by which groundwater discharge may enhance rates of benthic metabolism. This work includes experiments identifying the element that limits primary production, comparisons of groundwater chemistry in flowpaths that pass through near-stream wetlands to those that enter the stream without passing through such zones, and surveys of inorganic carbon and nutrient content along flowpaths to document the changes in carbon dioxide, methane, nitrogen, and phosphorus content of water as it moves from the hillslope to the channel.

Principal Findings and Significance

In-stream rates of primary production are relatively low, and metabolism and DIC concentration show a strong seasonal pattern in Allequash Creek. Concentrations of DIC in groundwater are extremely heterogeneous within and between different hillslope-to-channel transects. Notably, methane and carbon dioxide are often extremely high in near-stream wetland areas, and it appears that these trace gases can be transported into the stream channel. Similarly, groundwater collected from these wetland areas has high inorganic phosphorus concentrations (ca. 50 ug/L, compared to hillslope groundwater concentrations of 1-2 ug/L, and streamwater concentrations of 2-5 ug/L). Low in-stream concentrations and elevated riparian groundwater concentrations have led us to hypothesize that in-stream metabolism is limited by P availability, and that groundwater discharge through wetland areas provides the stream with this limiting nutrient. Similarly, the major inorganic carbon signature of groundwater is a result of flow through riparian areas. While groundwater flow through riparian areas has been shown to be an essential determinant of quantity and quality of nitrogen delivered to the stream, this study emphasizes the critical role of riparian wetland areas to streamwater inorganic carbon and phosphorus dynamics.

Descriptors:

Inorganic carbon, groundwater hydrology, land-water interactions, wetlands, watershed budgets, watershed models.

Publication Information:

Stanley, E.H., J.C. Finlay, and P.C. Hanson. 2002. Dynamics of dissolved oxygen, carbon dioxide, and ecosystem metabolism in a groundwater dominated stream. 50th annual meeting, North American Benthological Society, Pittsburgh, Pa.

Manuscript preparation is ongoing and submission is expected in mid-2003.

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.

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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, Geology 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

The stream temperature model (Gaffield 2000) that we are using in this study is currently unpublished. Through this project, we have further tested and refined the model and have submitted it for publication:

> Gaffield, S.J., K.W. Potter and L.Wang, (submitted to *Jour Amer Water Res Assoc*). Predicting the Summer Temperature of Small Streams.

We are currently applying this model to six new watersheds in the other three Wisconsin ecoregions. During the summer of 2001, we collected field data on water temperature, stream discharge, channel geometry, land use, and fish community composition from each stream. We have obtained additional data for one of the streams – Rowan Creek in Columbia County – from the 2002 University of Wisconsin Water Resources Management workshop.

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 linking three models for groundwater recharge, groundwater flow and stream temperature. 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:
Our baseline studies on Lake 658 during the open water period of 2000 allowed for determination of the best methods for characterizing both native and isotopic Hg partitioning and transport during full scale isotope addition for 2001. Key sampling techniques in 2000 (continued during 2001) included:

1. Detailed water column sampling- At numerous depths in the Deep (West) Basin we collected profiles of unfiltered and filtered Hg and MeHg and ancillary chemistries. We also sampled the East Basin with less frequency and depth detail.

2. Estimation of downward flux of particulates- 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 installed a Close Interval Sampler (CIS) device in the West 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 conditions that would affect a sampling boat and thus stability of fixed depth sampling from above.

4. Ultrafiltration- Characterization of colloidal phases was achieved by processing filtered water through a tangential flow ultrafiltration system. Samples were collected from outflows from upland test plots and from Lake 658.

During spring 2001, our group continued to analyze samples and determine best approaches for the upcoming full-scale addition. We determined that for 2001, it was necessary to conduct detailed research at both the West and the East Basin of Lake 658. The basins have contrasting depths (13.5 m vs. 10 m) and are physically separated by a 6m sill. It was apparent that the basins differed in rates of oxygen depletion and sulfide build-up. This may potentially be important for recycling of hypolimnetic Hg and MeHg.

The West Basin is also in closer contact to the wetland on Lake 658 which may mean differences in behavior of specific isotopes added. Therefore, we constructed additional sediment traps and installed a second CIS in the East Basin for 2001.

Prior to isotope addition, a large group of METAAILICUS investigators felt that some experiments comparing ligands for lake isotope additions were necessary. Dave Krabbenhoft, Cindy Gilmour, Rob Mason, Mark Amyot worked together with Hurley and Babiarz to conduct a series of experiments on lake 658 water and contrasting ligand types (DOC, chloride, etc.) to determine if our lake addition of isotope would be similar to rain water addition. Samples were split among the group for various speciation and partitioning. Babiarz employed ultrafiltration techniques on sample splits. Results of this work were included in a manuscript that was submitted to Science of the Total Environment (See Minamata details below) entitled "Application of ultrafiltration and stable isotopic amendments to field studies of mercury partitioning to filterable carbon in lake water and overland runoff". The manuscript is presently in review.

The first isotopic spike to the eplilimnion of Lake 658 was added during the evening hours of June 19, 2001. Since this was the only opportunity to track new, original isotope in the lake, we developed a plan to follow the initial isotope through the water column and toward the surface sediments. Our group performed detailed sampling of both the water column and sediment trap material at days 2, 4, 6 and 14 after the initial spike. We observed isotopic spike in the lower sediment traps within 6 days of the initial spike. This indicated rapid partitioning of spike to particles in the epilimnion followed by rapid settling. Methyl Hg from the spike was observed in sediment trap material between 2 and 4 weeks of the initial spike.

During the summer of 2001, Shawn Chadwick began graduate studies at UW-ECT. He helped perform general field and laboratory techniques in Madison and at ELA during the summer of 2001. During his first full year of graduate studies, he helped analyze samples for METAALICUS and began to develop a thesis project. Upon analysis of isotope and ancillary measurements, Chadwick has developed a graduate research project that will focus mainly on processes occurring at the sediment-water interface in Lake 658. He will focus on the dynamics of iron and manganese and their effects on Hg and MeHg cycling. He will additionally study the quality of organic carbon in both the dissolved and particulate forms to better determine binding constants.

In October 2001, Hurley and Babiarz attended the Sixth International Conference on Mercury as a Global Pollutant in Minamata, Japan. Babiarz presented his METAALICUS data on colloidal partitioning of Hg and MeHg at contrasting sites at ELA including the experimental plots and Lake 658. The manuscript mentioned above (STOTEN) was a result of this presentation. At the meeting, the Madison group (led by Hurley and David Krabbenhoft, USGS) presented a plan to the conference steering committee to host the Eighth International Conference on Mercury as a Global Pollutant. The steering committee approved the request and at the closing ceremony, Hurley presented an overview of the planned meeting for Madison, WI for August 2006. We plan to use the venue to highlight the results of the METAALICUS project, which we assume would be prominent at the meeting.

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

Field Monitoring of Drainage and Nitrate Leaching from Managed and Unmanaged Ecosystems

Basic Information

Title:	Field Monitoring of Drainage and Nitrate Leaching from Managed and Unmanaged Ecosystems
Project Number:	2001WI36O
Start Date:	7/1/1999
End Date:	6/30/2001
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Agriculture, Nitrate Contamination, Groundwater
Descriptors:	Agriculture, Groundwater contamination, Nitrate, Phophorus, Water Quality
Principal Investigators:	John Norman

Publication

PROJECT SUMMARY

Title: Field monitoring of drainage and nitrate leaching from managed and unmanaged ecosystems

Project I.D.: R/UW-BMP-001S

Investigators: Dr. John M. Norman, Professor of Soil Science, University of Wisconsin
Dr. Kristofor R. Brye, Assistant Professor of Applied Soil Physics, University of Arkansas

Period of Contract: July 1, 1999 to June 30, 2001

Background/Need: The appropriate balance between profitable agricultural production and environmental degradation is challenging to maintain because of the relative ease with which potentially environmentally harmful solutes, like nitrate-nitrogen (N), move with water through soil. Overfertilization of agricultural crops with N affects nitrate-N leaching and impacts groundwater quality. In Wisconsin alone, a significant number of counties, potentially affecting more than one million people, have areas of medium to high susceptibility for groundwater nitrate-N leaching from excess applications of N fertilizers. This is a problem that plagues the majority of the states in the upper Midwest.

Objectives: The main objective of this study was to continuously monitor drainage and nitrate-N leaching from managed and unmanaged ecosystems. Specific objectives accomplished during this study were the following: 1) continuous year-around monitoring of drainage and nitrate-N leaching from pre-existing, optimally N-fertilized, no-tillage and chisel plow corn plots; 2) installation of 4 new equilibrium-tension lysimeters in pre-existing no-tillage and chisel plow corn plots that monitored drainage and nitrate leaching at a reduced level of N fertilization; 3) cation and heavy metal leaching associated with nitrate leaching were monitored; and 4) a solute transport computer model was developed and validated with field measurements.

Methods: The objectives of this study were achieved through continuous year-round field monitoring of drainage and solute leaching from undisturbed soil columns using equilibrium tension lysimeters installed in fertilized (i.e., installed Fall 1995) and unfertilized (i.e., installed Fall 1999) chisel-plowed and no-tillage corn agroecosystems and a restored prairie (i.e., installed Fall 1995). Chemical analyses for nitrate-N and ammonium-N were determined colorimetrically using a continuous-flow ion analyzer. Soluble organic carbon was determined by high-temperature catalytic combustion. Soluble potassium, calcium, magnesium, zinc, manganese, copper, iron, sodium, and aluminum were performed by inductively coupled plasma - optimal emission spectrometry. All chemical analyses were conducted on instruments operated by the State Soil and Plant Analysis Lab. The solute transport computer model subroutine was developed in Fortran language and validated against drainage and nitrate-N leaching losses measured in the fertilized no-tillage and chisel-plowed corn agroecosystems as part of a doctoral dissertation.

Results and Discussion: Drainage generally occurred between January and June with, at times, high variability among replicate lysimeters. Between January 2000 and early January 2001, cumulative mean drainage was highest for the fertilized chisel-plowed corn agroecosystem, similar for the fertilized and unfertilized no-tillage corn agroecosystems, and lowest for the restored prairie and unfertilized chisel-plowed corn agroecosystems. Nitrate-N leaching losses were < 0.03, 3.5, 4.2, 23, and 58 kg ha^{-1} yr^{-1} in the prairie, unfertilized no-tillage, unfertilized chisel-plowed, fertilized no-tillage, and fertilized chisel-plowed corn agroecosystems, respectively. Significant cationic nutrient leaching (i.e., Ca, Mg, and Na) occurred along with nitrate-N leaching to preserve neutrality of the soil solution.

Conclusions/Implications/Recommendations: Corn crops fertilized with N at the optimum recommended rate to maximize profits from yields result in flow-weighted NO_3^--N concentrations at the bottom of corn root zones of 8.9 mgN L^{-1} and 11.7 mgN L^{-1} for chisel-plowed and no-till treatments. Significant drainage and leaching losses typically begin in January when, depending on the amount of residue cover on the soil surface, a portion of the upper soil profile is frozen. In addition, to maintain charge balance and neutrality of the soil leachate solution, an equivalent amount of positive charge must leach with each negatively charged NO_3^--N ion. Therefore, the long-term loss of soil fertility and cation exchange capacity may be a threat when nitrate-N leaching continues to occur due to N fertilization above and beyond what is required by a crop to produce a sufficient yield.

Based on the results of this study and on the information gathered in previous years prior to this study, we would recommend against Fall applications of inorganic N fertilizer or N-rich manure due to the potential for significant leaching to occur over the winter through frozen soil and in the spring of the year when the soil thaws. Because NO_3^--N concentrations are near the 10 mgN L^{-1} drinking-water standard for optimal fertilizer applications, our results suggest that excessively high groundwater concentrations may be caused by excessive fertilization so that strong incentives for farmers to apply fertilizers at optimal rates (or less) should be imposed.

Related Publications:

Brye, K.R., J.M. Norman, L.G. Bundy, and S.T. Gower. 2001. Nitrogen and carbon leaching in agroecosystems and their role in denitrification potential. *J. Environ. Qual.* 30:58-70.

Key Words: drainage, leaching, nitrogen, nitrate, prairie, corn, no-tillage, and chisel-plowed

Funding: State of Wisconsin Groundwater Research Program through the University of Wisconsin Water Resources Institute (WRI)

Field Evaluation of Rain Gardens as a Method for Enhancing Groundwater Recharge

Basic Information

Title:	Field Evaluation of Rain Gardens as a Method for Enhancing Groundwater Recharge
Project Number:	2001WI37O
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:	Treatment, Groundwater, Water Quality
Descriptors:	raingardens, urban hydrology, recharge
Principal Investigators:	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 purpose of the proposed project is to undertake this testing at one or more experimental raingardens. At each 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 essentially a lysimeter, in that it 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 run off 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 have evidence that the discrepancy is due to leakage through the openings that provide access to the TDR probes. We have developed a plan for eliminating this leakage, and will implement it in the spring of 2003.

Compatibility of Containment Systems with Mine Waste Liquids

Basic Information

Title:	Compatibility of Containment Systems with Mine Waste Liquids
Project Number:	2001WI38O
Start Date:	7/1/1999
End Date:	6/30/2001
Funding Source:	Other
Congressional District:	2nd
Research Category:	Engineering
Focus Category:	Groundwater, Toxic Substances, Water Quantity
Descriptors:	Acid mine drainage, Groundwater, Landfill liners, Mining, Tailings, Water quality
Principal Investigators:	Tuncer B. Edil, Craig H. Benson

Publication

1. PROJECT SUMMARY

Title: Compatibility of Containment Systems with Mine Waste Liquids
Project I.D.: R/UW-CTP-001S
Investigators: Principal Investigators Tuncer B. Edil and Craig H. Benson
Department of Civil and Environmental Engineering,
University of Wisconsin-Madison
Research Assistant S. Basak Gulec
Department of Civil and Environmental Engineering,
University of Wisconsin-Madison
Period of Contract: July 1999 - June 2001

Background/Need:
Great interest has arisen in metallic mining at various locations in Wisconsin. Significant concern has developed regarding the potential for environmental impacts of mining, particularly the pollution of groundwater. This concern has arisen due to the poor environmental track record of most mining companies.

Mining's greatest threat to groundwater is pollution from drainage of mine tailings. Tailings are the residue remaining after benefication of the ore. Drainage from tailings may consist of process water present at the time of disposal or acidic water caused by percolate passing through tailings undergoing oxidation. Acidic mine drainage pollution is characterized by a low pH and elevated concentrations of heavy metals affecting both surface and groundwaters.

One method to prevent groundwater contamination is to place tailings in an engineered waste containment facility designed using the principles employed for modern municipal and industrial landfills. Design of an engineered containment system consists of reducing the leakage to a negligible amount so that the only important contaminant transport mechanism is molecular diffusion. Recent studies sponsored by USEPA have shown that modern landfill liners do perform as intended and have very low leakage rates typically less than 30 L/ha-d (1 mm/yr). However, mine tailings are very different than municipal waste and stabilized hazardous waste placed in industrial landfills. Thus the lining systems used for municipal and industrial waste may perform differently when they are exposed to mine drainage. In fact, an extensive review of literature has revealed no case studies regarding the environmental performance of engineered containment facilities for tailings. Therefore, efficiency of the lining systems used for mine waste containment must be assessed in order to make responsible decisions regarding mine waste management.

Objectives:
The main objective of this study is to assess the compatibility of lining system materials and mine waste liquids, with the intent of determining if materials used for lining systems will function as intended when they are exposed to mine waste liquids. The second objective is to predict the lifetime of lining system materials by extrapolating the experimental behavior to site-specific conditions.

Methods:

A variety of lining system materials (geomembrane, geotextile, and geocomposite) are exposed to synthetic acidic mine drainage solution and two control solutions. A modified version of EPA Method 9090 is used for exposure.

Geosynthetic materials are immersed in the chemical environment for a period of 15 months at 20 °C, 40 °C and 60 °C. Three different chemical environments are used for the exposures: Control I (Deionized water), Control II (low pH, no metals solution), and synthetic acidic mine drainage (low pH, high metals solution).

During exposure, samples are periodically taken from the immersion tanks, and physical and engineering properties of geosynthetics are tested to confirm whether the liquids have an adverse effect on engineering properties. The following tests are performed on unexposed and exposed samples: thickness, mass, tear resistance, puncture resistance, tensile strength, elongation at break, modulus of elasticity, melt flow index test, transmissivity test and infrared spectroscopy analysis, which is a special test used for the detection of degradation in polymer science.

Results and Discussion:

Comparison of exposed and unexposed geomembrane samples of acidic mine drainage set over a period of six months suggests that the HDPE geomembrane was slightly deteriorating due to exposure. This deterioration was not easily detectable with puncture and tear test results due to the high standard deviations recorded in these tests. Puncture and tear strength values recorded during the exposure were fluctuating within the high standard deviations of unexposed samples. Melt flow index (MFI) results also suggest a certain amount of degradation of the geomembrane. Test results have still fluctuations mostly within the standard deviation of unexposed samples for geotextiles. This made it difficult to detect any degradation over this short period of exposure. Significant reduction in transmissivity values were observed in geotextile in acidic mine drainage exposure at 60 °C.

Conclusions/Implications/Recommendations:

Even though exposure and experiments are continuing, the following conclusions can be drawn for the first six months of the study: HDPE geomembrane has slightly deteriorated due to acidic mine drainage exposure as it was concluded from wide width test and melt flow index results. This deterioration was not easily detectable with puncture and tear test results due to the high standard deviations recorded in these tests; for geotextile specimens, significant changes, physical and engineering properties were not detected due to high variability in the test results of unexposed samples. However, reductions in the transmissivity results were detected for geocomposite (i.e., geonet) specimen.

These results and conclusions will be updated with continuing testing.

Kew Words:
acid mine drainage, groundwater, landfill liners, mining, tailings, chemical compatibility, geosynthetics

Funding: UWS Groundwater Research Program

Groundwater Modeling: Semi-Analytical Approaches for Heterogeneity and Reaction Networks

Basic Information

Title:	Groundwater Modeling: Semi-Analytical Approaches for Heterogeneity and Reaction Networks
Project Number:	2001WI39O
Start Date:	7/1/2000
End Date:	6/30/2001
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Treatment, Toxic Substances, Geochemical Processes
Descriptors:	Heterogeneity, multiple species reactive transport, groundwater, response function, residence time distribution
Principal Investigators:	Craig H. Benson

Publication

PROJECT SUMMARY

Title: Groundwater Modeling: Semi-Analytical Approaches for Heterogeneity and Reaction Networks

Project I.D.: R/UW-CTP-002

Investigator(s): Dr. Gerald R. Eykholt, formerly Assistant Professor, Department of Civil and Environmental Engineering; Dr. Craig H. Benson, Professor, Department of Civil and Environmental Engineering; Lin Li, Graduate Research Assistant, Department of Civil and Environmental Engineering, University of Wisconsin-Madison.

Period of Contract: July 1, 2000 - June 30, 2001

Background/Need: Reactive transport modeling for heterogeneous aquifers is challenging and computationally intensive. While numerical packages allow simulation of multiple species transport with aquifer heterogeneity, run times on high speed PCs and workstations make many jobs impractical. Stream tube approaches, such as that used in this study, are computationally efficient numerical methods, and offer significant advantages in run time over more numerical methods.

Objectives: The objectives of this study include testing the performance of linear operator methods for simulation of first-order decay reactions in heterogeneous aquifers, and how to extend the solutions to assess how irregular sources and mixed-order kinetics processes affect the contaminant transport. Accuracy of the proposed numerical approach solutions and run times is compared with predictions made with RT3D and analytical solutions.

Methods: A new stream tube model was developed for multiple species reactive transport in a heterogeneous aquifer. The model is based on the primary hypothesis that reactive transport in heterogeneous aquifers can be approximated with linear transforms, where reactivity and flow distributions are not coupled. For many cases, the method provides good accuracy and significant computational advantages, especially for complex reaction networks and more heterogeneous aquifers.

Realistic heterogeneous synthetic aquifers were created using a stochastic turning bands procedure. MODFLOW was used to solve the head solutions and provide steady state flow for reactive transport. Path3D or MT3D were modified to generate residence time distributions from a tracer source. Distributed and multiple point sources were considered, and residence time distributions were found through superposition. The kinetic response function for each species in the reaction network was analytically expressed. Convolution and other linear operator methods were used to generate responses from irregular source loading and to determine transient concentrations over the aquifer domain.

Results and Discussion: Comparisons between the new modeling approach, other analytical models and numerical models showed that the hypothesis is correct. Reasonable agreement was obtained for all of the cases that were tested. Significant computational time was saved using the method. For a 2D-aquifer simulation, the new approach was found to be 1,500 times faster than RT3D, a popular numerical application. Parameter sensitivity analysis includes mean of log-normal hydraulic conductivity, standard deviation of log-normal hydraulic conductivity, correlation length, retardation coefficients and first order reaction rate constants.

Conclusions/Implications: A new stream tube modeling approach was developed for multiple species reactive transport in heterogeneous aquifers. The method can handle complex flow and reaction networks. The approach has been extensively tested and compared with a full numerical model. For heterogeneous hydraulic conductivity and homogeneous reaction rate, the results indicate that reactive transport can be de-coupled into flow and reaction processes. This decoupling significantly decreases the simulation time and ensures an acceptable level of accuracy.

Related Publications: None to date.

Key Words: Reactive transport, multispecies, heterogeneous aquifer, stream tube approach, retardation coefficients, numerical model

Funding: University of Wisconsin System

Development of Neural Network Models for Predicting Nitrate Concentration in Well Water in the Tomorrow-Waupaca Watershed

Basic Information

Title:	Development of Neural Network Models for Predicting Nitrate Concentration in Well Water in the Tomorrow-Waupaca Watershed
Project Number:	2001WI40O
Start Date:	7/1/1999
End Date:	6/30/2001
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Nitrate Contamination, Groundwater, Non Point Pollution
Descriptors:	Geographic Information Systems, Groundwater, Model studies, Nitrate contamination, Nonpoint source pollution, Water quality
Principal Investigators:	Hangsheng Lin

Publication

Title: Development of Neural Network Models for Predicting Nitrate Concentration in Surface and Well Waters in the Tomorrow-Waupaca Watershed

Project I.D.: R/UW-HDG-003

Investigators: Hangsheng Lin, Assistant Professor of Hydropedology/Soil Hydrology, Dept. of Crop and Soil Sciences, 116 ASI Building, The Pennsylvania State University, University Park, PA 16802; Byron Shaw, Professor Emeritus of Soil & Water, College of Natural Resources, University of Wisconsin, Stevens Point, WI 54481.

Period of Contract: July 1, 1999 – June 30, 2001

Background/Need: Assessment of water susceptibility to contamination under conditions of uncertainty continues to be an important issue. The prediction of nonpoint pollution at the watershed scale has two important characteristics. First, surface/subsurface processes require enormous amounts of spatially related data as inputs, because many environmental factors have an obvious spatial dimension. Second, complex relationships between data sets are highly heuristic and are characterized by a great deal of uncertainty. The complex relationships among the parameters involved do not lend themselves well to traditional computational methods. These two characteristics make it imperative to use the integrated technologies of Geographic Information Systems (GIS) and artificial intelligence (AI) in watershed water quality assessment. We addressed this issue through integrated use of artificial neural network (ANN) with a GIS and a bootstrap method for modeling nitrate concentration in surface and well waters using a large water quality database developed for the Tomorrow-Waupaca Watershed in central Wisconsin.

Objective: To develop optimal neural network models for modeling nitrate concentration in surface and well waters in the watershed.

Methods: We used a combined neural network-bootstrap method to develop optimal ANN models. A modified TRAINLM routine of the neural network toolbox of MatLab® (MathWorks, Inc., Natick, Mass.) was used for the analysis. We used a feedforward-backpropagation ANN modeling approach. Three-layer backpropagation neural networks consist of an input, a hidden, and an output layer all containing "nodes." The number of nodes in input and output layers corresponds to the number of input and output variables of the model. Several user definable parameters for developing optimal ANN models include training algorithm, epochs, learning rate, and number of hidden nodes. The bootstrap method is essential to obtain independent calibration and validation sets and to calculate confidence intervals of the ANN predictions. After the training phase, a validation ("testing") phase serves to validate the ANN models on independent input and output data by keeping weight matrices constant. Evaluation criteria used in this study for the goodness-of-fit of the predicted and measured data included R^2, R^2_{adj} and average absolute percent error.

Results and Discussion: The optimal ANN model for predicting monthly averaged baseflow nitrate concentrations in the watershed was a four-input-variable model with the inputs of the percentages of agricultural land and grassland, stream order, and the average slope of ground water-flow path. These four variables are generally easily obtainable from GIS maps (such as land use map, hydrology map and groundwater contour map). Additional variables introduced to the ANN did not significantly improve the prediction; rather, they required longer time to train the network, increased the uncertainty in model prediction, and would cost more for model application. Optimal groundwater ANN model was insufficient to obtain in this study because of the following two main reasons: 1) all well locations were only approximated by quarter-quarter sections, which blurred the spatial accuracy; and 2) groundwater delineations were different from surface subwatershed delineations, and the available surface environmental data were too coarse.

In all the data sets modeled, ANN was superior to linear regression (LIN) and quadratic response surface model (RSM) in terms of both the nitrate concentration variation explained (internal R^2_{adj}) and prediction consistency (external R^2_{adj}). For example, the internal R^2_{adj} values for the optimal four-variable surface water ANN model were, on average, 42% higher than RSM and 126% higher than LIN; the external R^2_{adj} for the same four-variable model ranged from 0.13 to 0.47 for LIN (with an average of 0.32) and from 0.37 to 0.67 for RSM (average 0.53), whereas that of ANN ranged from 0.59 to 0.92 (with an average of 0.77).

Conclusions/Implementations/Recommendations: ANN was apparently superior to LIN and RSM in terms of both the nitrate concentration variance it could explain and external prediction consistency. ANN also permitted flexible model development that is difficult to achieve using a predefined model. This study indicated that the percentages of agricultural land and grassland, stream order, and the average slope of groundwater flow path were among the key variables impacting the stream baseflow nitrate concentrations in the watershed

Although the groundwater contamination is highly convolved with the surface water, more work needs to be done to improve the model prediction. Future improvements needed include sub-basin delineation of the groundwater watershed and collection of more precise location data for well locations and relevant environmental maps.

Related Publications:

- Lin, H.S., R.C. Cook, and B. Shaw. 2001. Nitrate relationships between stream baseflow, well water, and land use in the Tomorrow-Waupaca Watershed. *The Scientific World Journal.* 1(S2):187-193.
- Lin, H.S., and S. Wang. 2001. Artificial neural network for nonpoint source pollution assessment in the Tomorrow-Waupaca Watershed. In Proc. of the 5th International Conference on Diffuse/Nonpoint Pollution and Watershed Management. Milwaukee, WI.
- Lin, H.S., and S. Wang. 2001. Coupling ANN with GIS for predicting water quality in the Tomorrow-Waupaca Watershed. ASA-CSSA-SSSA annual meeting, Oct. 21-25, 2001, Charlotte, N.C. Agronomy Abstract.
- Lin, H.S., C. Jaskolski, and S. Wang. 2000. Development of neural network models for predicting nitrate concentration in well water in the Tomorrow-Waupaca Watershed. ASA-CSSA-SSSA annual meeting, Nov. 5-9, 2000, Minneapolis, Minn. Agronomy Abstract.
- Cook, R. 2000. Relationships between Private Well Water, Stream Baseflow Water, and Land Use in the Tomorrow-Waupaca River Watershed. M.S. Thesis, University of Wisconsin, Stevens Point, Wis.

Key Words: Neural network modeling, nonpoint source pollution, stream water, groundwater, nitrate, land use, bootstrap method, uncertainty

Funding Agency: UWS Groundwater Research Program

The Spatial and Temporal Variability of Groundwater Recharge

Basic Information

Title:	The Spatial and Temporal Variability of Groundwater Recharge
Project Number:	2001WI41O
Start Date:	7/1/2000
End Date:	6/30/2001
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Hydrology, Management and Planning, Water Quality
Descriptors:	Groundwater recharge, recharge estimation, groundwater hydrology, groundwater management, groundwater modeling, geographic information systems, water resource management
Principal Investigators:	Mary Anderson, KENNETH W POTTER

Publication

Project Summary

Title: The Spatial and Temporal Variability of Groundwater Recharge

Project ID: R/UW-HDG-004

Investigators: Dr. Mary P. Anderson, Professor, Geology and Geophysics; Dr. Kenneth W. Potter, Professor, Civil and Environmental Engineering; Weston Dripps, Research Assistant, Geology and Geophysics.

Period of Contract: July 2000 – June 2001

Background / Need: Understanding the spatial and temporal distribution of groundwater recharge is a prerequisite for effective groundwater management and modeling. Recharge, defined as the entry of water into the saturated zone, is influenced by a wide variety of factors including the vegetation, topography, climate, geology, and soils. Despite its dependence on these spatially variable parameters, recharge is typically assumed to be constant and uniform within a watershed. The recharge estimate is usually empirically derived, is a fitted parameter determined by calibration, or is calculated using baseflow of streams as a surrogate.

Since the distribution, rate, and timing of recharge are dictated by the interaction of these variable parameters, recharge should vary temporally and spatially at the watershed scale and the use of a constant value for an entire watershed may be inappropriate. Using a combination of fieldwork and integrated modeling, we developed a suite of techniques for estimating recharge and tested our methods by quantifying the spatial and temporal distribution of recharge at the watershed scale and a daily time step for the Trout Lake basin, a small forested watershed in northern Wisconsin.

Objective: Our main objective was to develop a methodology for estimating the spatial and temporal distribution of groundwater recharge. The methodology was tested by application to the Trout Lake basin for the period 1996 – 2000.

Methods: We estimated the spatial and temporal distribution of recharge using: (1) a daily soil water balance (SWB) model, (2) an integrated terrestrial biosphere model (IBIS, (3) a two-dimensional analytic element groundwater flow model (GFLOW) linked to a parameter estimation code (UCODE) and (4) field techniques (water level fluctuations and time domain reflectometry).

Results and Discussion: The three models (SWB, IBIS, and GFLOW/UCODE) gave comparable recharge estimates, which also agreed well with estimates calculated from water-level fluctuations measured in wells. The SWB and IBIS models calculated an average annual recharge rate for the Trout Lake basin that varied more than two-fold, as well as large monthly variations. Spatial variations were not as significant although heterogeneity attributed to variability in soil and vegetation type was evident.

Conclusions / Implications / Recommendations:

- There is significant annual variation in recharge rate to the Trout Lake basin but spatial variability is less pronounced.

- Water level fluctuations and reflectometers are useful in estimating recharge amounts and the timing of recharge events.
- The IBIS model, originally designed as a global dynamic ecosystem model, can be successfully applied at a watershed scale.
- Assuming a linear correlation between precipitation and recharge is inappropriate since soil moisture conditions and the timing of precipitation events are more important in controlling recharge rates than the actual amount of precipitation that falls.
- Collectively the models used in this research, particularly the less rigorous soil water balance model, give modelers, planners, and policy makers practical water resource management tools for estimating spatially and temporally distributed recharge for modeling and water resource planning purposes.
- Training in the use of these models and methods would be a useful follow up to this project.

Related Publications:

Dripps, W. R. Expected May 2002. The Spatial and Temporal Variability of Natural Groundwater Recharge. PhD thesis, University of Wisconsin – Madison, Department of Geology and Geophysics.

Dripps, W.R., C.J. Kucharik, J.D. Lenters, M.P. Anderson, and J.A. Foley. 2001. Modeling the Spatial and Temporal Distribution of Groundwater Recharge Across a Forested Watershed in northern Wisconsin. Abstract. American Geophysical Union, 2001 Spring Meeting, Boston, Mass., Eos, Vol. 82.

Dripps, W.R., M.P. Anderson, and R.J. Hunt. 2001. The Use of Temperature Profiles through Unsaturated Soils to Estimate Short-term Rates of Natural Groundwater Recharge. Abstract. American Geophysical Union, 2001 Spring Meeting, Boston, Mass., Eos, Vol. 82.

Dripps, W.R, M.P. Anderson, and R.J. Hunt. 2001. Use of a Coupled Heat and Water Transport Model (VS2DH) for Estimating Rates of Natural Groundwater Recharge. Abstract. American Water Resources Association – Wisconsin Section, 25th Annual Meeting, Green Lake, Wis., abstracts, p. 27.

Dripps, W.R., M.P. Anderson, and R.J. Hunt. 2000. Incorporating Recharge Variability into Groundwater Flow Models. Abstract. Geological Society of America, 2000 Fall Meeting, Reno, Nev., Abstracts with Programs, Vol. 33, p. 335.

Awards given to Wes Dripps for work on this project: Horton Grant, Hydrology Section of the American Geophysical Union, Bailey Distinguished Graduate Fellowship, UW-Madison, Outstanding student paper award, AGU Spring 2001 meeting.

Key Words: Groundwater recharge, recharge estimation, groundwater hydrology, groundwater management, groundwater modeling, water resource management, IBIS, GFLOW, analytic element modeling, UCODE, parameter estimation

Funding: UWS Groundwater Research Program

Causes of Historical Changes in Groundwater Recharge Rates in Southeastern Wisconsin

Basic Information

Title:	Causes of Historical Changes in Groundwater Recharge Rates in Southeastern Wisconsin
Project Number:	2001WI42O
Start Date:	7/1/1999
End Date:	6/30/2001
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Models, Management and Planning
Descriptors:	Climate change, Drinking water, Groundwater, Recharge, Water resources, Watersheds
Principal Investigators:	Douglas S. Cherkauer

Publication

Causes of Historical Changes in Groundwater Recharge Rates in Southeastern Wisconsin

Project Number R/UW-HDG-005

Douglas S. Cherkauer, Professor, Department of Geosciences, University of Wisconsin-Milwaukee and Craig J. LaCosse, Research Assistant, Department of Geosciences, University of Wisconsin-Milwaukee

Contract: July 1, 1999 to June 30, 2001
Funding: University of Wisconsin System (UWS)
Focus Area: HDG
Key Words: Recharge, groundwater resources.

BACKGROUND/NEED

Recharge is the process by which rain, snowmelt and surface waters infiltrate to and replenish groundwater. As such, it is the ultimate source of all of our groundwater resources. Yet it is also very difficult to measure, because of its diffuseness. Information on the rates of recharge is usually sparse. To date there has been very little examination of how recharge rates vary through time in response to climatic or land-use changes, making long-term planning difficult for groundwater-dependent communities.

The spatial distribution of recharge in SE Wisconsin was examined during a previous Groundwater Research Program project, showing that it can be quantitatively linked to a number of topographic, hydrogeologic and land-use properties. That work has successfully provided recharge influxes for regional ground-water flow models of southeastern Wisconsin and Fond du Lac County. It has assumed, however, that the recharge rates are static, which they clearly are not. As areas undergo droughts or extended wet periods, recharge undoubtedly varies. As regional or global climate changes, so too will recharge. The question is, how much?

OBJECTIVES

The purpose of this work was to define how recharge rates change through time in response to precipitation changes, to ascertain what factors control that response, and then to develop a mechanism for predicting future recharge changes.

METHODS

Stream baseflow was used as a surrogate measure for recharge. Baseflow is groundwater discharge, so it is equivalent to surface infiltration less evapotranspiration, or net recharge. The use of baseflow opens up the entire USGS streamflow monitoring database as a source of recharge information. There are hundreds of gaging sites in Wisconsin alone, and many have an extensive historical record. Net recharge was obtained for 14 study watersheds in SE Wisconsin using stream baseflow separation (with the USGS HYSEP program).

For each of the watersheds, precipitation and temperature were obtained using Thiessen polygon weighing of daily values from nearby NOAA weather sites. A 34-year time period (1963 through 1997) was selected for analysis. In addition, measures of topography (surface slope, watershed area and shape, among others), hydrogeology (depths to water table and rock, water table gradient, composite subsurface transmissivities and porosities), and land cover (natural, developed, and agricultural) were obtained using GIS databases.

The procedure used was to determine what factors control the baseflow/recharge response to precipitation change in southeastern Wisconsin, which has relatively uniform geologic conditions. Then these relations were tested on another 14 watersheds distributed throughout Wisconsin to ascertain whether they are universal. These test watersheds were selected to include very different bedrock and surficial geology from that in southeast Wisconsin.

RESULTS/DISCUSSION

Time series data (precipitation, temperature, baseflow) were plotted as cumulative departures from average conditions. During the study period, most of Wisconsin experienced drier than normal conditions from 1963 to 1971. The period 1971 to 1993 was wetter than average, and from 1993 to 1997, precipitation dropped below normal again. Baseflow in some watersheds in southeastern Wisconsin follows the precipitation trend almost identically; precipitation 20% below normal produces baseflow/recharge 20% below normal. In other watersheds, the baseflow response is smaller than the precipitation change, and in a few urbanized watersheds, baseflow and precipitation appear almost unrelated.

The rate of baseflow/recharge change with respect to precipitation change (dQ/dP) was compared to all the independent controlling factors for the study watersheds. It was found that dQ/dP is directly related to the product of land surface slope and length of overland flow (S*L), which explains 74% of the observed variation. No other factor or combination thereof (including temperature) showed any significant relation to dQ/dP. When the observed relationship was used to calculate dQ/dP for the 14 test watersheds, it explained 75% of the variance in all areas except the unglaciated southwest.

CONCLUSIONS/IMPLICATIONS/RECOMMENDATIONS

The temporal variation of recharge in Wisconsin is controlled directly by the temporal variation of precipitation. In areas of steep slopes, or where water must travel a long distance before it enters a main channel (often regions with less-developed drainage networks or very permeable soils), the response is essentially 1:1. In areas where slopes are gentle and/or main channels are more closely spaced, recharge changes at only a fraction of the rate of change of precipitation.

The relation uncovered is valid for all of Wisconsin except the Driftless Area. We do not have an explanation for its failure there. However, in glaciated areas, the relation can be coupled with climate change projections to give communities a handle on how much their groundwater supply is likely to change in the foreseeable future.

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 will examine and monitor 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 construction of homes will likely begin in 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 snow melt 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. 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. This shows that frequent sampling is essential in order to differentiate the effects of subdivision construction from preexisting conditions. A summary of the 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]	55	< 0.1	36.4	6.9	7.4
Chloride[2]	55	0.3	279.5	29.2	48.0
Atrazine[3]	11	< 0.1	0.8	0.3	0.3
Conductivity[4]	55	531	1839	903	247
			Bedrock wells		
Nitrate[1]	8	< 0.1	13.6	5.1	5.3
Chloride[2]	8	1.5	56.8	15.5	18.5
Atrazine[3]	5	< 0.1	0.3	0.2	0.1
Conductivity[4]	8	608	921	780	94
			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.

By the end of the current project, we expect to have a good understanding of the site geology and hydrogeology, the current distribution of contaminants from past agricultural land use, temporal variations in groundwater conditions, and the level of monitoring necessary to detect any impacts of the subdivision on water levels or groundwater quality.

Admicelle-Catalyzed Reductive Dechlorination of PCE by Zero Valent Iron

Basic Information

Title:	Admicelle-Catalyzed Reductive Dechlorination of PCE by Zero Valent Iron
Project Number:	2001WI44O
Start Date:	7/1/1999
End Date:	6/30/2001
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Groundwater, Methods, Toxic Substances
Descriptors:	Chlorinated solvents, Groundwater contamination, Permeable membranes, Remediation technology, Zero valent iron
Principal Investigators:	Zhaohui Li

Publication

Project Summary

Title: Admicelle-Catalyzed Reductive Dechlorination of Perchloroethylene (PCE) by Zero Valent Iron

Project ID: R/UW-REM-002

Investigator: Dr. Zhaohui Li, Assistant Professor of Geology and Assistant Professor of Chemistry, Geology Department and Chemistry Department, University of Wisconsin – Parkside

Period of Contract: 07/01/1999 – 06/30/2001

Background/Need: Chlorinated solvents are a major groundwater contaminant at industrial sites, U.S. Department of Energy facilities, and military installations. Recent discovery of using zero valent iron (ZVI) as permeable barriers to degrade chlorinated solvents dissolved in groundwater has attracted great attention. Numerous researches on using ZVI for groundwater remediation have been focused on increasing the degradation rate constant of chlorinated solvents. However, most of them involve in coating the metals with noble metals such as Pt or Pd. Thus a search for an inexpensive, yet effective material, to enhance the rate of degradation of chlorinated solvents becomes more imminent.

Objectives: The objectives of this research are to further study a novel observation made by the PI on enhanced perchloroethylene degradation by ZVI under the catalysis of a cationic surfactant hexadecyltrimethylammonium (HDTMA). The influence of surfactant chain length of several quaternary ammonium surfactants, the surfactant coverage and the surfactant surface configuration on ZVI, the initial PCE concentrations, and initial solution pH and ionic strength on PCE reduction kinetics will be studied in batch scale. Column experiments will be conducted as a function of initial PCE concentrations and contaminant injection rates to verify the batch results and to provide further justification for future pilot scale and/or field tests.

Methods: Laboratory batch sorption was performed to determine the sorption maxima of surfactants with different hydrophobic chain lengths (8, 12, and 16 carbons in the tail group, respectively). Batch reduction kinetic study was performed to determine the rate constants of PCE degradation and trichloroethylene (TCE) generation due to the degradation of PCE. For column studies, both modified and unmodified ZVIs were packed in duplicates to glass columns of 30 cm long and 2.5 cm in diameter. Contaminant solutions were made in 12-L collapsible Teflon bags and were delivered by a precision syringe pump with four 10-mL gas-tight syringes attached at different flow rates and different initial PCE and TCE concentrations to verify the enhancement of PCE reduction catalyzed by HDTMA on ZVI surfaces.

Results and Discussion:

Batch results indicate that the longer the surfactant tail group, the more hydrophobic the surfactant is, thus the higher the surfactant sorption. Compared to unmodified ZVI, the rate constants of PCE dechlorination increased by 15 to 20 folds when ZVI was modified by HDTMA. A six-to-nine-fold increase in rate constants was found for ZVI modified with dodecyltrimethylammonium, while a five-to-seven-fold increase was found for ZVI modified with octyltrymethylammonium. The half-life of PCE in the presence of unmodified ZVI was about 10 days, but reduced to 0.4 day when HDTMA-ZVI was used. Solutions with ionic strengths of 0.001, 0.01, and 0.1 M of NaCl, and with initial pHs at 3, 5, and 7 had little effect on PCE reduction rates. Significant slowdown of PCE reduction was found at an initial pH of 11, maybe due to the inhibition of iron corrosion.

Column results show that a 10-fold reduction in effluent PCE concentrations was achieved when HDTMA-ZVI was used compared to unmodified ZVI. With an initial PCE concentration of 20 mg/L and a flow rate of 0.25 mL/min, the effluent PCE concentrations were 0.08-0.1 mg/L and 1.1-2.4 mg/L for modified and unmodified columns, respectively. As the flow rate increased to 2 mL/min, the effluent PCE concentrations increased to 1.5-1.7 mg/L and 13-14 mg/L for modified and unmodified columns, respectively. As the input concentration reduced to 6 mg/L, at a flow rate of 2 mL/min, the effluent PCE concentrations was 0.1-0.2 mg/L and 3.0-3.3 mg/L for modified and unmodified columns, respectively.

Conclusions/ Implications/ Recommendations:

The research shows that the sorbed cationic surfactant, particularly HDTMA, drastically increase the PCE degradation rate. In addition, the pathway of PCE degradation could be predominant by reductively dechlorination when surfactant was present compared to β-elimination when surfactant was absent. Due to the superior enhancement of PCE reduction under the influence of surfactant, it is recommended for a pilot scale test, which will be proposed to US DOE.

Related Publications:

Alessi, D. S. and Z. Li, (2001) Synergistic Effect of Cationic Surfactants on Perchloroethylene Degradation by Zero Valent Iron, *Environ. Sci. Technol.*, in press.

Key Words: Perchloroethylene, Reductive Dechlorination, Trichloroethylene, Surfactant, Zero Valent Iron

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

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.

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.

Removal of Arsenic in Groundwater Using Novel Mesoporous Sorbent

Basic Information

Title:	Removal of Arsenic in Groundwater Using Novel Mesoporous Sorbent
Project Number:	2001WI48O
Start Date:	7/1/2001
End Date:	6/30/2002
Funding Source:	Other
Congressional District:	2nd
Research Category:	Engineering
Focus Category:	Treatment, Toxic Substances, Water Quality
Descriptors:	arsenic, treatment, sorbents
Principal Investigators:	JAE K PARK

Publication

Progress Report of WRI

Title: Removal of Arsenic in Groundwater Using Novel Mesoporous Sorbent

The highly ordered mesoporous silica media, SBA-15, were synthesized and incorporated with iron, zinc, aluminum, and lanthanum oxides using an incipient wetness impregnation technique. Adsorption capacities and kinetics of aluminum impregnated mesoporous media and activated alumina were evaluated. Media impregnated with 10% of aluminum by weight had 1.9 ~ 2.7 times greater arsenate adsorption capacities and 15 times greater initial sorption rate than activated alumina. Surface complexation modeling was conducted to investigate the relationship between the oxidation status of solids and adsorption behaviors such as isotherms and kinetics by employing the one- and two-site models. The oxidation status of aluminum 10% (w/w) into SBA-15 was found to be lower than activated alumina, which is consistent with XPS results, suggesting that the different ratio between monodentate and bidentate hydroxyls can cause the different speciation of surface complexes and kinetic behaviors.

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. Based on the HRTEM analysis, the mean pore sizes of both La_{10}SBA-15 and La_{20}SBA-15 were estimated to be 5.67 nm and 5.15 nm, respectively; however, the data distribution of La_{20}SBA-15 was more skewed to have smaller pore sizes than La_{10}SBA-15, suggesting heterogeneous incorporation.

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, 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. Other techniques such as XRD, XPS, and N_2 gas *isotherm* analysis should be performed to get valuable information on physicochemical properties of media. Through conducting a series of arsenate adsorption *kinetic* and *isotherm* tests under various conditions, the relationships between physicochemical properties and arsenic adsorption behaviors will be found.

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, E., 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, and J.K. Park. Mechanisms of Arsenic 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.

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 twenty, 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 minimizes 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.

Although the investigation continues to explore the limitations to the removal of arsenic through iron treatment, 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

Information Transfer Program

Information Transfer (IT) Plan

Basic Information

Title:	Information Transfer (IT) Plan
Project Number:	2001WI51B
Start Date:	3/1/2001
End Date:	2/28/2002
Funding Source:	104B
Congressional District:	Wisconsin 2nd
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	Information Technology
Principal Investigators:	, James P. Hurley, JoAnn M. Savoy

Publication

12. Title University of Wisconsin-Water Resources Institute - Information Transfer

13. Statement of critical regional or State water problem 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 WRI 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 WRI's information transfer program includes:

- Promoting and coordinating water resources research;
- Enhancing educational capability through training and public service;
- Providing information to government agencies, the scientific community, the private sector, and the general public.

In 2002, the Wisconsin Academy of Sciences, Arts and Letters coordinated a statewide initiative to examine how best to use and conserve Wisconsin's endangered water resources. As a result of this initiative, then-Governor Scott McCallum declared 2003 the Year of Water (YOW). WRI has assumed a leadership role in YOW planning and activities.

WRI's YOW activities will be in addition to its traditional information transfer responsibilities. WRI will continue to assist researchers and the public with their information needs by maintaining a Web site to disseminate water information and increase awareness of 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

- Year of Water activities - continuous
- Web site update – continuous, weekly at minimum.
- Web site upgrade to include adding a searchable database of Wisconsin groundwater research and another of publications resulting from WRI-funded research – February 2004.
- Final Reports resulting from WRI projects – edited and published as received.
- UW Aquatic Sciences Center report describing and highlighting the impacts of the Water Resources and Sea Grant programs - June 2003
- *Library Recent Acquisitions and Web Sites of Interest* – monthly
- Library reference services and assistance – continuous
- Library book acquisition and circulation - continuous
- AWRA Wisconsin Section 2004 Annual Meeting Preparation
    - First announcement and call for abstracts – September 2003
    - Second announcement and call for abstracts – December 2003
    - Abstracts sent to printer – Mid-February 2004
    - Meeting – late February 2004

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

WRI Web Site:

Web site development and upkeep are essential for water resources information dissemination. Researchers, state agency staff, legislators and the public increasingly turn to the Web for their information needs. To better meet those needs, staff will upgrade the WRI Web site in the coming year and, more specifically, add two new research-related databases.

Currently the WRI home page (*wri.wisc.edu*) contains links to eight major subsections.

1. Projects: Summaries of projects currently and previously 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 are provided, including the base program and the national competition as well as links to other water-related funding opportunities (U.S. EPA, NSF, etc.).

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. Links to announcements for other regional, national and international water-related conferences are also provided.

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” (wri.wisc.edu/library/finding_jobsall.html) and a “Guide to Finding Water Related Information” (wri.wisc.edu/library/subject.html).

6. Water Links: Listing of important Wisconsin water-related Web sites, 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 1966-2002.

8. Expert Directory: Database of more than 800 water experts, which can be searched by area of expertise, research interest or name.

In the coming year, staff will place the groundwater research summaries and the publications (numbers 2 and 7 above) into online databases Users will be able to search these databases by keywords or project investigators, or browse the contents by broad subject areas. Users should find the information more accessible in a searchable database rather than in its current list format.

Publications

In addition to “virtual” Web publications, WRI staff will produce several hard-copy publications. Staff will publish the final reports resulting from WRI-funded research, 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 major UW Aquatic Sciences Center report describing and highlighting the impacts of the Water Resources and Sea Grant programs.

Water Resources Library

The WRL is a unique collection of more than 24,000 titles covering all major water topics. It is particularly strong in Wisconsin and Great Lakes water resources issues, groundwater protection, wetlands issues, and the impacts of agricultural chemicals. The library 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 *madcat.library.wisc.edu/*. Anyone may check out materials. The WRL is located on the UW-Madison campus and has access to that major research collection.

The WRI Library will provide the following services:

- *Recent Acquisitions and Web Sites of Interest* will be written and circulated monthly by mail and email to more than 300 users as well as being posted on the Web. Anyone can request materials.
- WRL Web site (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 provided.
- Reference service to assist users in finding water-related information will continue.
- 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 will continue.
- Distribution of WRI research reports and other publications will be enhanced.
- Document procurement through interlibrary loan, request from sources, or purchase will continue.

Conferences

The WRI continues to 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. WRI will design and distribute the program announcements, provide a Web site, and edit and print the meeting abstracts.

17. Related research NA.

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

19. Investigator's qualifications See attached resume.

JoAnn Savoy

Title: Special Librarian

Education:

Degree:	Universitv	Date Awarded
B.A.	College of St. Teresa Winona, Minnesota History and Social Sciences	1967
M.A.	University of Wisconsin-Madison Library Science	1977

Professional:

1967-1970	Reference Librarian - Kansas City Public Library Kansas City, Missouri
1970	Bookmobile Librarian -Boston Public Library Boston, Massachusetts
1970	Research Specialist – Encyclopaedia Britannica Chicago, Illinois
1972-1973	Reference Librarian-Thomas Crane Public Library Quincy, Massachusetts
1975-1978	Library Assistant-Business and Science Division Madison Public Library, Madison, Wisconsin
1978-1982	Librarian, Wisconsin Department of Administration Library, Madison, Wisconsin
1982-1987	Research Analyst - State of Wisconsin Institutional Conservation Program, Madison, Wisconsin
1987-1991	Program and Planning Analyst - State of Wisconsin Coastal Management Program, Madison, Wisconsin
1991-present	Special Librarian - UW Water Resources Reference Services, Madison, Wisconsin

Memberships:

Wisconsin Interlibrary Loan Service	1995-present
Special Campus Libraries Group	1991-present
South Central Library System	1991-present
UW Science Library Cluster Group	1991-present
Wisconsin Library Association	1975-1982, 1993-present
Council of Wisconsin Libraries	1995-1997

OCLC	1995-present
Special Library Association	1996-present

Publications:

Madison Public Library Municipal Reference Service. *A Bibliography of Government Publications by and about Dane County, Wisconsin, Madison, Wisconsin, and Other Cities and Towns in Dane County.* 1977. 2nd ed. Madison, Wisconsin.

Olle, M., J. Howlett (now Savoy), and L. Schapp. *Energy Management in Wisconsin Public and Commercial Buildings: Results of the Institutional Conservation Program*. 1984. Madison, Wis.: Wisconsin Division of State Energy & Coastal Management.

Olle, M. and J. Howlett. *Energy Management in Wisconsin Schools and Hospitals: 1985 ICP Performance Review.* 1986. Madison, Wis.: Wisconsin Division of State Energy and Coastal Management.

Howlett, J. *Energy Management in Wisconsin Schools and Hospitals: 1985 ICP Performance Review: Appendices.* 1986. Madison, Wis.: Wisconsin Division of State Energy & Coastal Management.

Howlett, J., editor. *Wood Fuel Use in Wisconsin Schools and Hospitals: Site Visit Reports.* 1986. Madison, Wis.: Wisconsin Division of State Energy & Coastal Management.

Wisconsin's Coastal Management Program for the Great Lakes. 1989. Madison, Wis.: Wisconsin Division of Energy and Intergovernmental Relations.

Wetlands Needs Assessment. 1991. Chapter contained in *Wisconsin Coastal Management Program Needs Assessment for the Great Lakes.* Madison, Wis.: Wisconsin Division of Energy and Intergovernmental Relations.

Savoy, J. A. *Guide to Finding Water-Related Information.* 2000. wri.wisc.edu/library/subject.html

Savoy, J. A. *Finding a Water-Related Job.* 2000. wri.wisc.edu/library/finding_jobsall.html

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	5	6	0	5	16
Masters	2	2	0	4	8
Ph.D.	1	2	0	4	7
Post-Doc.	0	1	0	1	2
Total	8	11	0	14	33

Notable Awards and Achievements

Publications from Prior Projects

1. Gorski, P.R. L.B. Cleckner, J.P. Hurley, M.E. Sierszen and D.E. Armstrong. 2002. Factors Affecting Enhanced Mercury Bioaccumulation in Inland Lakes of Isle Royale National Park, USA. Science of the Total Environment. In Press.
2. Cleckner L.B., R.C. Back, P.R. Gorski, J.P. Hurley and S. Byler. 2003. Seasonal and size-specific distribution of methylmercury in seston and zooplankton of two contrasting Great Lakes embayments. Journal of Great Lakes Research. In Press.
3. Krabbenhoft, D.P., J.P. Hurley, G. Aiken, C.C. Gilmour, M. Marvin-DiPasquale, W.H. Orem and R. Harris. 2000. Mercury cycling in Florida Everglades: A mechanistic field Study. Verhundlungen Internationale Vereinigung Limnologie, 27:1657-1660.
4. Allran, J.W. and W.H. Karasov, 2001. Effects of atrazine on embryos, larvae, and adults of anuran amphibians. Environ. Toxicol. Chem. 20: 769-775.
5. Kraft, G.J., W. Stites, and D. J. Mechenich. 1999. Impacts of irrigated vegetable agriculture on a humid north-central U.S. sand plain aquifer. Ground Water 37(4): 572-580.