University of Wisconsin Water Resources Institute

Annual Technical Report

FY 2000

Introduction

The University of Wisconsin Water Resources Institute (WRI), based at the University of Wisconsin-Madison, is an academic unit of the Graduate School and works with the University's Office of Research Administration, which ensures compliance with university, state, and federal guidelines. 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. 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 WRI's 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. 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. The following report summarizes our institute's achievements for fiscal year 2000. In addition to describing our projects supported through U.S. Geological Survey funds, we also describe our other projects that are an integral part of our programmatic objectives.

Research Program

Basic Information

Title:	Field Monitoring of Drainage and Nitrate Leaching from Managed and Unmanaged Ecosystems
Project Number:	B-01
Start Date:	3/1/2000
End Date:	2/28/2001
Research Category:	Water Quality
Focus Category:	Agriculture, Nitrate Contamination, Groundwater
Descriptors:	Agriculture, Groundwater contamination, Nitrate, Phosphorus, Water Quality
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	John Norman

Publication

1. Brye, K.R., T.W. Andraski, W.M. Jarrell, L.G. Bundy, and J.M. Norman. 2001. Phosphorus leaching under a restored tallgrass prairie and corn agroecosystems. J. Environ. Qual. Submitted
2. Brye, K.R., J.M. Norman, L.G. Bundy, and S.T. Gower. 2000. Nitrogen leaching losses from conventional- and no-tillage corn. Wisconsin Fertilizer, Aglime & Pest Management Conference Proceedings. p. 387-396.
3. Brye, K.R., J.M. Norman, L.G. Bundy, and S.T. Gower. 2000. Carbon leaching and its role in the carbon budgets of natural and managed ecosystems. AgronomyAbstracts. p. 199.
4. Brye, K.R. 2001. Soluble phosphorus leaching from corn systems. Wisconsin Fertilizer, Aglime & Pest Management Conference Proceedings. p. 70-82.
5. Brye, K.R., T.W. Andraski, W.M. Jarrell, L.G. Bundy, and J.M. Norman. 2001. Phosphorus leaching under a restored tallgrass prairie and corn agroecosystems. Agronomy Abstracts.

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

John M. Norman, Professor, University of Wisconsin
Kristofor R. Brye, Research Associate, University of Wisconsin

Problem and Research Objectives

Maintaining a balance between profitable agricultural production and environmental degradation is challenging because of the ease with which nitrate moves with water through soil. The fertilization of agricultural crops affects nitrate-leaching losses and groundwater quality. In Wisconsin 50 of 72 counties -- potentially impacting 1.5 million people -- have medium to high susceptibility for groundwater nitrate leaching from excess applications of nitrogen fertilizer. We evaluated the influence of two agricultural management and fertilization practices on nitrogen levels in corn. A continuous data set from direct field measurements of drainage and nitrate leaching was generated for fertilized and chisel plow and no-tillage corn and natural prairie ecosystems. These findings will advance the understanding of relationships between agricultural practices and nitrate leaching losses during the growing season and throughout frozen soil periods.

Methodology

Equilibrium-tension lysimeters (ETLs) were used to monitor drainage and solute transport from a restored tallgrass prairie and N-fertilized and N-unfertilized no-tillage (NT) and chisel-plowed (CP) corn agroecosystems. Replicate 0.2-µm-porous-stainless-steel ETLs (0.19 m^2) were installed at 1.4 m below the soil surface in the restored prairie and N-fertilized tillage treatments during Fall 1995. Replicate ETLs were installed at similar depths in the N-unfertilized tillage treatments during Fall 1999. Heat dissipation sensors were placed immediately above the porous plate of each ETL and in the surrounding bulk soil to continuously monitor the matric potential at the two locations. A portable, regulated vacuum system provided continuous suction to the porous plate of the ETLs. The regulated vacuum system was adjusted manually several times a week to provide suction that was slightly more negative (i.e., a few kilopascals) than the matric potential recorded in the surrounding bulk soil with the heat dissipation sensors.

The ETLs were sampled under vacuum every 2 weeks between Mar. and Dec. and once every 4 weeks during the rest of the year. Leachate was collected from the ETL's collection reservoir, which can contain 23 L (i.e., equivalent to 110 mm) of water, through a high-density polyethylene tube that was inserted into a stainless steel sampling tube that extends from the drain port of the lysimeter to the soil surface. The initial leachate (up to 1 L) was collected into a 1-L high-density polyethylene bottle and transported back to the laboratory where the leachate volume was measured. Any remaining leachate from the lysimeters (>1 L) was collected, volumes were recorded, and the leachate was discarded. Aliquots of the initial 1 L of leachate were filtered through glass fiber filter paper and stored in high-density polyethylene bottles at 4^oC for chemical analysis. Aliquots of unfiltered leachate were also stored at 4^oC for chemical analysis.

Leachate samples were analyzed for inorganic nitrate- and ammonium-N colorimetrically using a continuous-flow ion analyzer, total soluble and inorganic carbon

by high-temperature catalytic combustion, molybdate-reactive phosphorus (MRP) using the ascorbic acid color development method, and soluble cationic and anionic constituents (i.e., total phosphorus, potassium, calcium, magnesium, sulfur, zinc, boron, manganese, iron, copper, aluminum, and sodium) by inductively coupled plasma - optimal emission spectrometry.

Principal Findings and Significance

From January 2000 through January 2001, drainage below 1.4 was not significantly affected by ecosystem (i.e., prairie versus agriculture), tillage (i.e., no-tillage versus chisel-plow), or fertilizer-N rate (i.e., 0 versus 180 kg N ha^{-1} yr^{-1}) due to inherent spatial variability. Total precipitation was 1002 mm. However, mean drainage from the agricultural treatments (318 mm) was more than twice the mean drainage from the prairie (121 mm). Similarly, mean drainage from the N-fertilized corn agroecosystems (410 mm) was nearly twice the mean drainage from the N-unfertilized corn agroecosystems (226 mm). During this time period, mean flow-weighted nitrate-N concentrations and leaching losses were smaller from the prairie (0.01 mg L^{-1} and 0.03 kg ha^{-1}, respectively) than from the corn agroecosystems (6.9 mg L^{-1} and 22 kg ha^{-1}, respectively), while flow-weighted nitrate-N concentrations and leaching losses were significantly smaller for the N-unfertilized (1.2 mg L^{-1} and 3.8 kg ha^{-1}, respectively) than N-fertilized corn agroecosystems (13 mg L^{-1} and 41 kg ha^{-1}, respectively). Similar to drainage, soluble C concentrations and leaching losses did not differ significantly among ecosystems, tillage treatment, or fertilized-N rate, but mean concentrations and leaching losses of total soluble C were always higher for the N-fertilized corn agroecosystems (45 mg L^{-1} and 148 kg ha^{-1}, respectively) than the prairie (5.6 mg L^{-1} and 18 kg ha^{-1}, respectively) or N-unfertilized corn agroecosystems (40 mg L^{-1} and 129 kg ha^{-1}, respectively).

Mean volume-weighted total dissolved P (TDP) concentrations were similar within replicate samples, but significantly higher in N-fertilized corn (0.08 mg L^{-1}) than in the prairie (0.02 mg L^{-1}) or N-unfertilized corn (0.02 mg L^{-1}). Leachate-P concentrations from the natural and managed agroecosystems were environmentally significant (i.e., > 0.01 mg P L^{-1}) and leaching losses were significantly higher from N-fertilized corn (307 g ha^{-1}), regardless of tillage, than from the prairie (22 g ha^{-1}) or N-unfertilized corn systems (34 g ha^{-1}). Increased root growth from N fertilization could cause more macropore formation, preferential flow, and P-mineralization from decaying roots compared to N-unfertilized systems, which could contribute to an N-fertilization effect on P leaching. Since soil leachate solutions are hydrologically connected to sensitive groundwater and surface waters, these results indicate that environmentally significant P concentrations can leach below the root zone of corn grown with conventional N rates and that environmentally significant P concentrations can leach from the root zone of natural ecosystems even > 20-yr after being restored from a long history of cultivated agriculture.

Treatment	Drainage	Flow-weighted Nitrate-N Concentration	Nitrate-N Leaching Losses	Flow-weighted Total P Concentration
	mm	mg L^{-1}	kg ha^{-1}	mg L^{-1}
Prairie	121	0.01	0.03	0.02
NT	312	4.2	14	0.06
CP	325	9.5	31	0.04
N-unfertilized Ag	226	1.2	3.8	0.02
N-fertilized Ag	410	13	41	0.08

Basic Information

Title:	The Spatial Variability of Natural Groundwater Recharge
Project Number:	G-01
Start Date:	11/1/1999
End Date:	9/30/2001
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
Lead Institute:	University of Wisconsin - Madison
Principal Investigators:	Mary Anderson, Kenneth R Bradbury, Kenneth W. Potter

Publication

1. Dripps, W.R., Bradbury, K.R., Anderson, M.P., and Hankley, D.W., in prep. A Modified Thornthwaite Mather Soil Water Balance Model for Estimating the Spatial Distribution of Groundwater Recharge. 2002 Wisconsin Geological and Natural History Survey Circular.
2. Bradbury, K.R., Dripps, W.R., Hankley, D.W., Anderson, M.P. and Potter, K.W., 2000. Refinement of Two Methods for Estimation of Groundwater Recharge Rates. Final Project Report to the Wisconsin Department of Natural Resources, 84 p.
3. Bradbury, K.R., Hankley, D.W., Dripps, W.R., and Anderson, M.P., 2000. A GIS-Based Method for Estimating Groundwater Recharge Over Large Areas. American Water Resources Association Wisconsin Section, 24th Annual Meeting, Green Bay, WI, abstracts, p. 14.
4. Dripps, W.R., Anderson, M.P., Hunt, R.J., and Walker, J.F., 2000. A Comparison of Multiple Methods for Estimating Groundwater Recharge in the Trout Lake Basin, Northern Wisconsin. American Water Resources Association Wisconsin Section, 24th Annual Meeting, Green Bay, WI, abstracts, p. 5.
5. Dripps, W.R., Bradbury, K.R., Hankley, D.W., and Anderson, M.P., 2000. The Spatial Distribution of Groundwater Recharge: Its Estimation and Incorporation into Groundwater Flow Models. American Geophysical Union, 2000 Spring Meeting, Washington DC, Eos, Vol. 81.

The Spatial Variability of Natural Groundwater Recharge

Mary P. Anderson, Professor, Department of Geology and Geophysics
Kenneth R. Bradbury, Professor, Wisconsin Geological and Natural History Survey,
University of Wisconsin – Extension
Kenneth W. Potter, Professor, Department of Civil and Environmental Engineering

Problem and Research Objectives:
Understanding the spatial and temporal distribution of groundwater recharge is a basic prerequisite for effective groundwater management and modeling. Recharge, defined as the entry of water into the saturated zone, depends on a wide variety of variable factors (vegetation, soils, geology, topography, and climate), making it one of the most difficult and uncertain hydrologic parameters to quantify in the evaluation of groundwater resources. Although many researchers have proposed techniques for estimating groundwater recharge, only a few studies have considered its spatial and temporal variability, and there is still no standard method that is generally accepted for quantifying recharge for regional groundwater studies. Our main objective was to develop a practical method for estimating groundwater recharge distributions for humid areas at scales suitable for groundwater modeling and water resources planning at the scale of a watershed.

Methodology:
We developed a soil-water balance model to estimate the spatial and temporal distribution of groundwater recharge for watersheds in humid areas. The model is based on a modified Thornthwaite – Mather soil water balance approach and uses typically available soils, land cover, topographic, and climatic data. The model accounts for gains (precipitation), losses (runoff, evapotranspiration), and changes in storage for each grid cell and uses a rainfall-runoff algorithm and a digital elevation model to route runoff and allow for re-infiltration of water down slope. The model code is written in Visual Basic and requires Microsoft Excel 2000 to run. ArcView and ARCINFO are used to generate the input grids.

We tested the model by application to the Pheasant Branch Creek watershed, an urban/agricultural watershed in south-central Wisconsin. Output from the Pheasant Branch Creek model for the period 1993-1997 was compared to results from a field-intensive rainfall-runoff study that utilized the USGS PRMS model.

Principal Findings and Significance:

- The model generated recharge estimates for the Pheasant Branch Creek watershed that were comparable to those calculated by the PRMS model.

- Conceptually, the model is a marked improvement over existing water balance models as it allows for routing and down slope infiltration of surface runoff.

- The model calculates recharge on a cell-by-cell basis, and consequently can represent the spatial distribution of recharge, which few other models consider.

- The model is physically-based, uses readily available data, does not require extensive parameterization, can be applied in a relatively short time frame, and is easy to use.

- The model calculated three-fold inter-annual variations in recharge and large fluctuations in monthly rates. These fluctuations imply that water budgets also change monthly. There was also significant spatial variability in recharge, reflecting variability in land cover and soil.

Explicitly accounting for the temporal and spatial distributions of groundwater recharge across a watershed is a significant conceptual improvement over the more common practice of assuming that recharge is constant. Our model gives planners and policy makers a practical tool for estimating spatial and temporal variability in recharge for use in modeling studies in support of water resource planning.

Basic Information

Title:	Compatibility of Containment Systems with Mine Waste Liquids
Project Number:	B-02
Start Date:	3/1/2000
End Date:	2/28/2001
Research Category:	Engineering
Focus Category:	Groundwater, Toxic Substances, Water Quantity
Descriptors:	Acid mine drainage, Groundwater, Landfill liners, Mining, Tailings, Water quality
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Tuncer B. Edil, Craig H. Benson

Publication

Compatibility of Containment Systems with Mine Waste Liquids

Tuncer B. Edil, University of Wisconsin-Madison
Craig H. Benson, University of Wisconsin-Madison

Problem and Research Objectives

Metallic mining at various locations in Wisconsin has become an issue of great interest. Concurrently, significant concern has developed regarding the potential for environmental impacts of mining, particularly the pollution of groundwater. Mining's greatest threat to Wisconsin groundwater is pollution from drainage of mine tailings. This aggressive liquid can pose a significant threat to groundwater due to its low pH,
and high concentrations of heavy metals.

One method to prevent groundwater contamination is to place the tailings in an engineered waste containment facility designed according to the principles used for modern municipal and industrial landfills. There is a need, however, to determine if containment systems proposed to contain mine wastes will effectively prevent groundwater contamination. Geosynthetic materials used in these containment systems must demonstrate resistance to chemical degradation while in contact with the aggressive chemicals throughout the life of the facility.

Therefore, the objective of this study is to assess the compatibility of landfill lining system materials and mine waste liquids to determine if the materials used for lining systems will function as intended in the presence of mine waste liquids. For this purpose, various geosynthetic materials (geomembrane, geotextile, and geonet) used in lining systems are exposed to synthetic acidic mine drainage solution under controlled environment.

Methodology

A modified version of EPA Method 9090 is being used for exposure and testing. Liner materials are immersed in a chemical environment for minimum period of 12 months at 20 ^{o}C, 40 ^{o}C and 60 ^{o}C. Three different chemical environments are being used; synthetic acidic mine drainage (low pH, high metals solution), control I (deinonized water), and control II (low pH, no metals solution). Samples are periodically taken from the immersion tanks, their physical properties are measured. A comparison is then made of the properties before and after exposure to assess the compatibility of the liner materials with the waste over time.

The following tests are performed on unexposed and exposed samples: determination of thickness, tear resistance, puncture resistance, tensile strength, elongation at break, modulus of elasticity, hydraulic properties, melt flow index and some specific techniques used in polymer testing (infrared spectroscopy analysis, and oxidation- induction time determination with differential scanning calorimetry).

Once the exposure period and associated testing is completed, the data will be used in an Arrhenius model to predict the lifetime of geosynthetic materials.

Principal Findings and Significance

The exposure testing is still ongoing, and definitive conclusions cannot yet be formulated. The exposure tests will be conducted through the end of the calendar year so that enough data are available to draw firm conclusions.

For the geosynthetics exposed to the simulated mine waste drainage, the data collected to data indicate that reductions in tensile strength and modulus have occurred. The tear and puncture resistance also are lower. Hydraulic properties of these geosynthetics remain unchanged. In contrast, no changes are apparent in the specimens exposed to the control liquids.

Chemical analyses are being conducted on the geosynthetic samples to determine the changes in the polymers that are occurring due to exposure. These analyses include melt flow index tests, infrared spectroscopy analysis, and oxidation- induction time determination with differential scanning calorimetry.

Basic Information

Title:	The Use of Subsurface Irrigation to Restore Degraded Groundwater-fed Wetlands
Project Number:	G-02
Start Date:	9/1/1998
End Date:	2/28/2001
Research Category:	Water Quality
Focus Category:	Groundwater, Surface Water, Wetlands
Descriptors:	Groundwater, Reed canarygrass, Restoration, Subsurface irrigation, Urbanization, Wetlands
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Kenneth Walter Potter, Jean Marie Bahr

Publication

1. Schwar, Michael T. 2001 (in prep). Hydrologic Restoration of a Groundwater-Fed Sedge Meadow Wetland in South-Central Wisconsin. Ph.D. Dissertation, Department of Civil and Environmental Engineering, University of Wisconsin, Madison WI.

The Use of Subsurface Irrigation to Restore Degraded Groundwater-fed Wetlands

Kenneth W. Potter, University of Wisconsin-Madison
Jean M. Bahr, University of Wisconsin-Madison

Problem and Research Objectives

Aquatic ecosystems can be significantly degraded by urban development. Increased impervious areas reduce recharge, thereby desiccating wetlands and springs. Groundwater extraction or drainage lowers water tables and stormwater runoff can increase flooding. Society is beginning to realize the value of wetland functions and in recent years wetland restoration is being undertaken more frequently. In an effort to develop a method for restoring groundwater-fed wetlands we are reintroducing water into a desiccated wetland via subsurface irrigation. In our test, highly treated effluent flows from the Madison Metropolitan Sewerage District (MMSD) pipeline are being introduced into a degraded sedge meadow via perforated pipes which allow flows to seep into the ground and thereby raise wetland water tables. Our results will indicate whether or not such irrigation is a viable means to restore wetlands and control reed canarygrass, an invasive wetland plant, and provide information on the importance of nutrients in wetlands restoration.

Methodology

Twenty-four 7.4 m^2 plots, four replicate groups of six treatments, were established within the reed canarygrass stand at a site in the Nine Springs Wetland in Madison, WI. For the initial phase of the experiment four of the six different treatments are controls and the other two treatments test the effects of changing hydrology. Experimental treatment consists of irrigation of hydrologically isolated plots by introducing the water through shallow irrigation during the growing season. Isolation was accomplished by driving interlocking panels of vinyl sheet piling into the wetland soil until the sheet piling extended from the soil surface well into the subsurface confining layer. Isolation of the wetland plot allows better control of water levels and is required to alleviate concerns regarding discharging effluent into a wetland. An additional advantage of isolation is that it disconnects the plots from the rhizomes of the surrounding reed canarygrass, through which the plant spreads vegetatively and may provide support to portions of the clone in otherwise disadvantageous conditions. The reed canarygrass mat was removed at the initiation of the project and a wetland seed source was introduced to the experimental plots in order to reduce the significant abilities of the reed canarygrass to exclude other wetland species.

Beginning with the first drought of the growing season and continuing through the first hard frost, supplemental water is supplied to each experimental cell when its water table falls below 20 cm beneath the surface. Two different sources provide supplemental water: groundwater from a nearby well and highly treated wastewater effluent. Flows are brought from either the well (groundwater) or a hydrant in the Madison Metropolitan

Sewerage District return flow line (effluent) and allowed to seep into the subsurface of the cells from hoses on the peat surface.

Water levels in monitoring wells located in the center of the isolated cells are measured using bubbler water level devices every half hour. At 6-hour intervals the water level in each experimental cell is evaluated, and if necessary valves are activated to allow flow to enter the cell from its water supply for 25 minutes. In addition to water levels, water supply flow rates and rainfall are measured on a continuous basis. Wetland restoration progress is measured by monthly plant surveys that evaluate species presence and percent cover in each experimental cell.

Principal Findings and Significance

Although reed canarygrass did return to the experimental plots, there is a clear relationship between the groundwater level maintained and the resilience of the reed canarygrass in the first year of experimental results. In areas with persistent high groundwater the reed canarygrass has not returned to high levels, allowing numerous other plant species to establish. In areas where the water level dropped somewhat reed canarygrass has returned to high levels, reducing the ability of other plant species to coexist. This has happened despite the fact that the reed canarygrass had to reestablish via seed and so did not have the advantages of an established clone.

Although one year of data is insufficient to establish the long-term trajectory of the wetland restoration, we anticipate that the relative advantage that native wetland species have over reed canarygrass is likely to persist, making for more diverse plant communities, in areas where groundwater levels remain close to the ground surface. In areas with lower groundwater the reed canarygrass appears ready to exclude most other plant species. It remains to be seen whether there will be a difference between the cells restored with groundwater and those restored with the treated effluent.

Basic Information

Title:	Macropore Flow: A Means for Enhancing Groundwater Recharge or a Potential Source of Groundwater Contamination
Project Number:	B-03
Start Date:	3/1/2000
End Date:	2/28/2001
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Non Point Pollution, Models
Descriptors:	Groundwater, Models, Runoff, Urbanization
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Kenneth Walter Potter, Peter J. Bosscher

Publication

1. DeMaster, D. W., E. B. Burmeister, and K. W. Potter. 2000. Increasing groundwater recharge by infiltrating runoff from impervious surfaces. p. 35. In: Water resources 2000 -- challenges for the new century. American Water Resources Association, Wisconsin Section Annual Meeting, Green Bay, Wisconsin. Water Resources Institute, University of Wisconsin-Madison.
2. Dussaillant, A., K. W. Potter, and C. Wu. 2001. Focused recharge in a theoretical raingarden (abst.). Spring Meeting, American Geophysical Union.
3. Potter, K. W. 2000. Stormwater infiltration: a vital component of low-impact development. Spring Technical Conference, March 23, 2000, American Society of Civil Engineers, Wisconsin Section, Madison, Wisconsin.
4. Potter, K. W. 2001. Mitigating the hydrologic impacts of development through stormwater infiltration (abst.). Spring Meeting, American Geophysical Union.

Macropore Flow: A Means for Enhancing Groundwater Recharge or a Potential Source

Kenneth W. Potter, University of Wisconsin-Madison
Peter J. Bosscher, University of Wisconsin-Madison

Problem and Research Objectives

As urban areas expand, groundwater levels and heads decrease as a result of the combined effects of groundwater pumping and loss of groundwater recharge. In some cases these decreases constrain the use of groundwater. More commonly, they result in reduced flows to springs, streams, lakes and wetlands. For example, it has been estimated that the mean annual flow through the Yahara Lakes in Dane County, Wisconsin, have been decreased by 20% as a result of groundwater pumping and diversion of the treated wastewater. This is due to the fact that the groundwater pumping rate in developed areas of Dane County is about twice the natural rate of groundwater recharge. Diffuse infiltration of stormwater has been proposed as a potential management strategy for mitigating groundwater depletion due to urban expansion. The idea is to carefully manage storm runoff from impervious surfaces so that as much runoff as possible sheetflows over, or ponds on, adjacent pervious surfaces that are managed to maximize infiltration capacity (focused infiltration). Throughout the United States innovative consulting firms are beginning to apply this strategy to urban and suburban land development. Much greater understanding of urban infiltration is required if this strategy is to be successful. Two questions stand out. Can focused infiltration significantly increase groundwater recharge? What threat does focused recharge pose to groundwater quality, particularly when macropores are present in the soil? This research considered these questions through the combined use of field measurements and modeling.

Methodology

This research had two principal components: infiltration testing of soils in urban/suburban greenspaces in Dane County, and modeling of infiltration of runoff from pervious surfaces. The infiltration testing had the following objectives: evaluation of the spatial variability of, and factors affecting, infiltration rates associated with urban greenspace in Dane County, Wisconsin; development of a protocol that could be used in practice to evaluate the infiltration capacity of urban greenspaces; and, collection of data for use in calibrating and verifying models of infiltration and groundwater recharge. The objective of the modeling component was to quantify the potential groundwater recharge rates achievable by coupling an impervious surface to a pervious one.

With respect to infiltration testing, our original intention was to measure infiltration rates using a standard double-ring infiltrometer and a disc permeameter/tension infiltrometer. Because of the small surface area associated with each of these methods and the destructive nature of the later method, we developed a flooding infiltrometer that can handle variable surface areas. This infiltrometer feeds water from either a point or line source of variable length and recovers it using a line sink attached to a vacuum pump.

At each site, testing was conducted over a 3-day period. On the first day, the test site was wetted for an hour to saturate the upper soil layer. After wetting, the site was covered with clear plastic. Infiltration measurements were made on days 2 and 3. Two application rates were used. The lower rate was chosen to correspond to a target rate of 4.3 inches /hour (11 cm/hr); the upper was chosen to correspond to a target rate of 8.7 inches /hour (22 cm/hr). As the unit area rate depends on the flow area (and hence the local topography), some adjustment was required during the initial stages of each test. The order of the flow rates was randomized.

A total of 63 tests were conducted at 31 sites. Of these, 27 were located on previous areas that receive runoff from rooftops, two were in swales that receive runoff from parking lots or residential areas, and one was on turf that receives no runoff from an impervious surface. Two tests were run at each site, except for one site where only one test was run and two sites where three tests were run.

Two approaches were used in the infiltration modeling. To model runoff from an impervious surface to a pervious one, we used an approach based on the "curve number" model developed by the Soil Conservation Service (SCS, 1986). The model was run using daily rainfall from the 50-year record at Madison, Wisconsin. (Only the "wet season" was modeled, assumed to extend from April 15 through October 15.) Roof runoff was modeled by increasing the rainfall on the connected lawn area by an amount equal to the rainfall on the impervious surface. Daily infiltration amounts were computed as the difference between the rainfall and the runoff. Daily groundwater recharge amounts were computed by subtracting from the infiltration amounts a constant daily evapotranspiration amount of 0.1 inches (25 mm), an amount equal to the average evapotranspiration for the region.

We also estimated rates of runoff, infiltration, and groundwater recharge associated with the use of a "raingarden," a garden located in a depression that receives runoff from an impervious surface. To do this we developed a physically-based water balance model that simulates ponding, infiltration, percolation, and evapotranspiration. Hourly wet-season rainfall data from Madison, Wisconsin (1992-1997) was used as input to the model. Inflow from the impervious surface was assumed to be proportional to the area of the surface. Infiltration into the soil was modeled using an explicit Green & Ampt model, where the total head included the ponding depth (where appropriate). Percolation in the soil followed a Darcy's equation approach. Evapotranspiration was modeled using the Priestly-Taylor method (Priestly and Taylor, 1972), and included evaporation from the ponded and soil water, as well as plant transpiration. Discharge from the raingarden was modeled by a weir equation, assuming a maximum ponding depth of 6 inches (15 cm) in the garden. The model was implemented in ModelMaker, an object oriented simulation software package.

Principal Findings and Significance

The infiltration rates obtained from the 63 infiltration tests ranged from 0.6 to 12.7 inches /hour (0.15 to 32.3 cm/hr); the average was 2.46 inches /hour (6.25 cm/hr). The few high

values were clearly due to macropores in the upper soil layers. However, because the macropores were shallow, they did not appear to pose a threat to groundwater quality.

The volumetric infiltration rate per unit flow length for the 63 tests was controlled more by the unit-area infiltration rate than by the flow width (Figure 1). In fact, 83% of the variance in the volumetric infiltration rate per unit flow length was due to the variance in unit-area infiltration rate. This largely explains why infiltration results did not vary significantly with the supply rate.

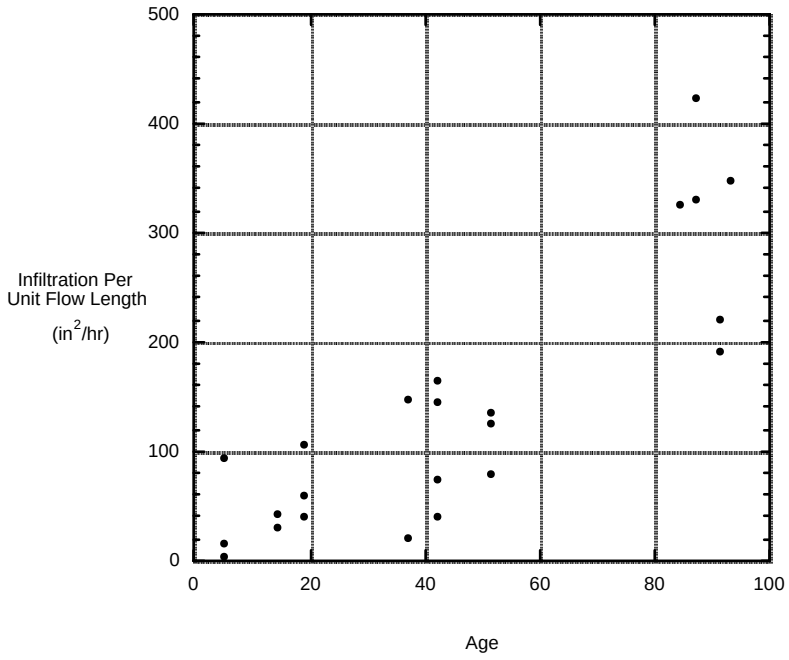

Figure 1. Volumetric infiltration rate as a function of the unit-area infiltration rate.

As shown in Figure 2, the unit-area infiltration rate is strongly related to the age of the developed area. This is undoubtedly due to the fact that the soil is usually highly disturbed at the time of development, and the impact diminishes over time.

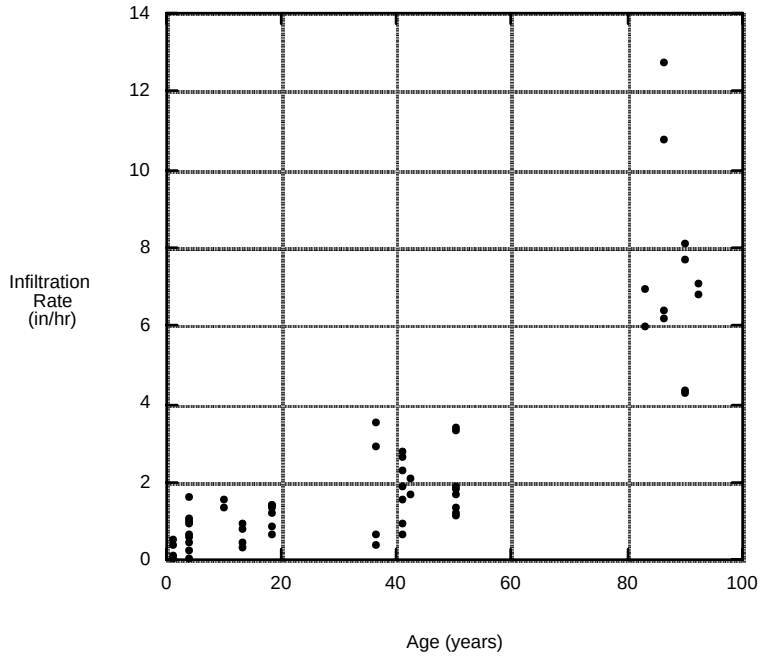

Figure 2. Unit-area infiltration rate vs. age of developed area.

Figure 3 summarizes the results of the curve number modeling. The figure shows the estimated wet-season groundwater recharge as a function of the curve number of the pervious surface and the ratio of the area of the impervious surface to that of the pervious surface. (Note that the curve number is a parameter reflecting the infiltration capacity of the soil. An impervious surface would have a curve number just less than 100, while an uncompacted sandy soil could have a curve number as low as 40.). There are two remarkable features of Figure 3. First, the wet-season groundwater recharge peaks at a pervious-to-impervious surface area of about 0.1, and decreases for larger ratios. The decrease is due to the fact that evapotranspiration increases as the runoff from the impervious area is spread over larger and larger pervious areas. (As the ratio approaches infinity, the recharge approaches the recharge rate for the pervious surface.) Second, the maximum achievable groundwater recharge is remarkably high. For example, for a curve number of 60, which would apply to a well-managed, uncompacted silt loam soil, the wet-season recharge would be about 8 inches (20 cm). (Note that this amount is the recharge volume divided by the combined area of the impervious and pervious surfaces.) For a pervious surface only receiving precipitation, the annual recharge rate for this climate would be about 8 inches (20 cm), but almost all of this would occur outside of the wet-season. Hence in this case the focusing of runoff from an impervious surface would about double annual groundwater recharge.

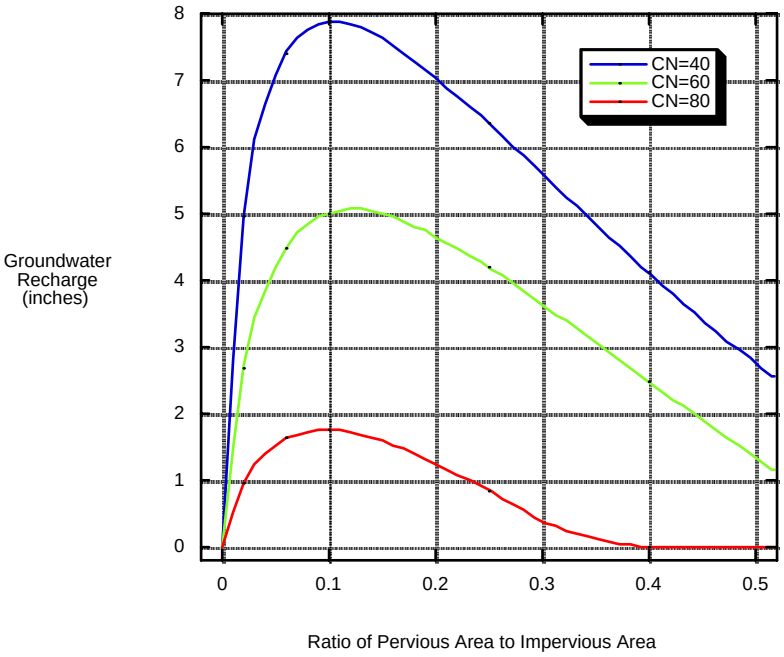

Figure 3. Results of the model of an impervious surface draining onto a pervious surface.

The raingarden modeling results are similar. Figure 4 shows the the results of a case where the raingarden is depressed 6 inches (15 cm) below the surface and has a steady-state infiltration rate of 4 inches per hour 10 cm/hr). As in the case of the non-depressional case, groundwater recharge peaks at a pervious-to-impervious surface area of about 0.1. However, because of the depressional storage, the estimated groundwater recharge rate for the wet season is much higher, equaling about 18 inches (46 cm).

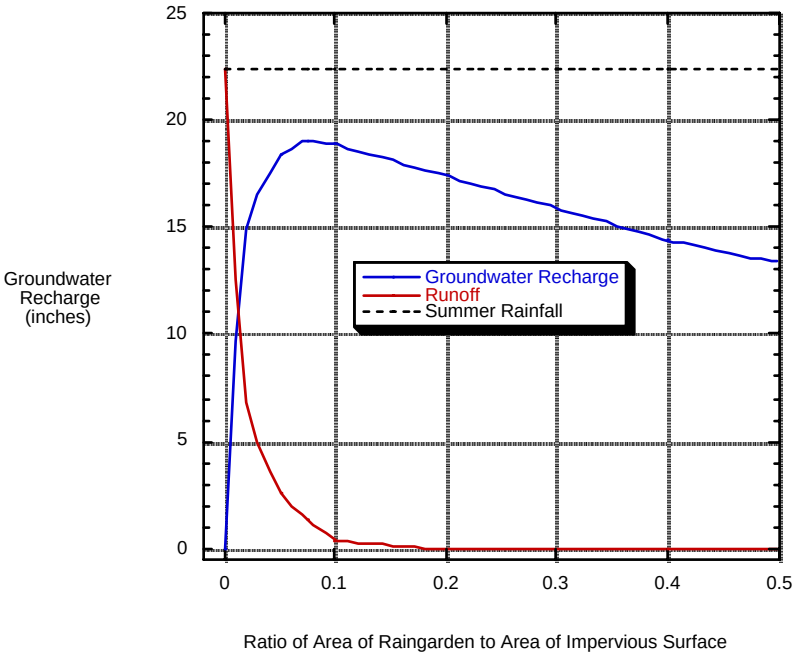

Figure 4 Results of the model of an impervious surface draining into a raingarden.

Main Findings

1. Based on 63 flooding infiltration tests at 31 sites in urbanized Dane Co., Wisconsin, there is little evidence that the spreading of runoff from impervious surfaces onto existing pervious surfaces would threaten groundwater quality as a result of macropore flow.

2. Infiltration rates associated with urban greenspaces vary by over an order of magnitude; time since development explains a large part of the variability.

3. Spreading runoff from impervious surfaces onto lawns or other pervious surfaces could increase groundwater recharge rates by as much as 8 inches per year (20 cm/yr) in southern Wisconsin.

4. Directing runoff from impervious surfaces to depressional gardens ("raingardens") could increase groundwater recharge rates by as much as 18 inches per year (46 cm/yr) in southern Wisconsin.

5. In southern Wisconsin, to maximize groundwater recharge, the area of the infiltrating surface should be about 10% of the area of the impervious surface contributing runoff.

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Basic Information

Title:	Hydraulic Conductivity and Specific Storage of the Maquoketa Shale
Project Number:	B-04
Start Date:	3/1/2000
End Date:	2/28/2001
Research Category:	Water Quality
Focus Category:	Groundwater, Water Quality, Water Quality
Descriptors:	Aquifers, Groundwater, Hydrogeologic parameters
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Lizhu Wang, Kenneth R Bradbury, Randall Hunt, Timothy T. Eaton

Publication

1. Eaton T.T. and K.R. Bradbury, 1998, Evaluation of the confining properties of the Maquoketa Formation in the SEWRPC region of southeastern Wisconsin, Final report prepared for the Wisconsin Department of Natural Resources, Wisconsin Geological and Natural History Survey Open-File Report 98-11, 32pp
2. Eaton, T.T., M.P. Anderson, K.R. Bradbury & H.F. Wang, 2000a, Evaluation of the hydraulic properties of a sparsely fractured confining unit: importance of fracture connectivity, GSA Abstracts with Programs 32(7), presented at Geological Society of America Annual Meeting, Reno, NV, November 12-16, 2000.
3. Eaton, T.T., M.P. Anderson, K.R. Bradbury & H.F. Wang, 2000b, Anatomy of a fracture network: hydraulic properties of a confining unit and adjacent aquifer, abstract submitted to Fractured Rock 2001, Conference on Groundwater Flow, Solute Transport, Multiphase Flow and Remediation in Fractured Rock, Toronto, Ontario, Canada, March 26-28, 2001
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Hydraulic Conductivity and Specific Storage of the Maquoketa Shale

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Timothy T. Eaton, University of Wisconsin-Extension

Problem and Research Objectives

The Maquoketa Formation, a dolomitic shale, is an important regional confining unit between the Silurian dolomite aquifer and the deep Cambrian-Ordovician aquifer system in southeastern Wisconsin. Rapidly growing communities in the region rely on pumping municipal water supplies primarily from the deep aquifer system, which has caused the formerly upward vertical gradient across the Maquoketa Formation to be reversed. In addition, significant quantities of water are pumped from the Silurian dolomite aquifer, which is the upper bedrock formation. Hence, the role that the Maquoketa confining unit plays in the regional multi-aquifer hydrogeologic system needs to be better understood for the purpose of long-term groundwater management and protection. At present, the only estimates of hydraulic conductivity of this regional confining unit have been made from flow-net analysis or computer modeling. The objective of this research is to determine the hydrogeologic properties of the Maquoketa Formation in Waukesha County using laboratory and field data, and use poroelastic modeling to predict reverse well fluctuations.

Methodology

Due to the generally low conductivity of this confining unit, which is a lithologically diverse dolomitic shale, hydrogeologic testing is considerably more difficult than for a conventional aquifer. We therefore employed two complementary approaches in our research. One is based on laboratory rock core tests and modeling, and subsequent field verification, using Biot=s (1941) theory of poroelasticity, which accounts for coupled deformation of the rock mass with fluid pressure changes.

The other approach is more conventional, relying on field hydraulic testing using multiple wells. With a multiple-well configuration, a much larger and potentially more representative rock volume can be tested than with single-well methods, and scaling effects can be evaluated. The major goal of the conventional approach was to conduct a pumping test in the underlying Sinnipee Group dolomite, and analyze resulting head change at multiple observation points in the Maquoketa Formation using the Aleaky aquifer@ method of Hantush (1956) and Neuman and Witherspoon (1972) to estimate vertical hydraulic conductivity in the confining unit. The pumping was anticipated to provide the stress needed to induce the reverse water level fluctuations predicted by poroelastic theory.

Principal Findings and Significance

Preliminary poroelastic modeling of the Maquoketa Formation indicated that a maximum reverse well fluctuation of 0.2 to 0.3 ft should occur 65 to 165 ft from the pumping well. Laboratory pulse-decay testing of rock core has established that hydraulic conductivity ranges between 6.2×10^{-14} and 4.3×10^{-12} ft/s, and specific storage ranges between 3.7×10^{-9} and 8.5×10^{-7} ft^{-1}, which we consider representative of unfractured rock

matrix at small scales. Some of our field head data may reflect a coupled poroelastic response to pumping, but results were inconclusive.

However, prior field hydrogeologic testing (Eaton & Bradbury, 1998) resulted in considerably higher hydraulic conductivity values ranging between $1x10^{-9}$ ft/s and $1x10^{-4}$ ft/s. Multiple-well geophysical logging and hydraulic testing reported here indicate that significant bedding plane fractures occur in the upper 100 ft of the Maquoketa Formation, and that these conductive fractures are well connected vertically to the overlying Silurian dolomite aquifer. "Leaky aquifer" testing by pumping the adjacent formations failed to provide bulk hydraulic conductivity values for the Maquoketa Formation, in part because of the fractures but also because the underlying Sinnipee Group dolomite has a very low hydraulic conductivity of $2x10^{-9}$ ft/s at this site.

We suggest a new conceptual model of the hydrogeology of this important regional confining unit, consisting of a relatively high transmissivity, interconnected, but sparse fracture network embedded in a low conductivity rock matrix. Bulk hydraulic conductivity of the rock mass is therefore a complex function of matrix conductivity, fracture density and transmissivity, and fracture network interconnectedness. Areas of relatively low fracture density and interconnectedness, such as the shale-rich base of the formation, do not readily transmit head changes, and may account for the regional confining properties of the Maquoketa Formation. In contrast, the upper fractured 100 ft of the Maquoketa Formation have a good hydraulic connection to the overlying Silurian aquifer via this fracture network.

These results have significant implications for the role of the Maquoketa confining unit in the regional groundwater flow system. Although at large scales, the shale-rich base of the formation provides an effective confining unit, the upper part is hydraulically coupled to the overlying Silurian aquifer. This suggests that it is not a good assumption that the top of the Maquoketa Formation is an effectively "impermeable" or no-flow boundary to the Silurian aquifer

Basic Information

Title:	Development of Translators for Filterable Metals Based upon Watershed Characteristics
Project Number:	G-03
Start Date:	9/1/1999
End Date:	8/31/2001
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Toxic Substances, Models
Descriptors:	Trace Elements, Metals, Mathematical Models, Watershed Management, Rivers, GIS, Translators, Particle-Partitioning, Suspended Sediment, Toxic Substances, Water Quality, Geochemistry, Contaminant Transport, Organic Carbon
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	David E. Armstrong, James P. Hurley, Martin M. Shafer, William C. Sonzogni

Publication

1. 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, WI
2. 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, WI.

Development of Translators for Filterable Metals Based upon Watershed Characteristics

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

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 (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 field work 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 sub-classes; (2) Surficial Deposits - Texture (5 sub-classes); (3) Bedrock Geology (6 sub-classes); (4) Depth to Bedrock (4 sub-classes); and 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 on 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 sub-sets 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, Surfical 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 representiveness 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 it's 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 re-sampled 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.

Basic Information

Title:	Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study
Project Number:	G-04
Start Date:	9/1/2000
End Date:	8/31/2003
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Toxic Substances, Non Point Pollution
Descriptors:	mercury, hydrology, dissolved organic carbon, transport, wetlands, lakes
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	James P. Hurley, Kristofer R Rolfhus, David P. Krabbenhoft

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.

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 $\mu g/m^2$ 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 $680 m^2$ 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.

Basic Information

Title:	Hydrology and Biogeochemistry in the Wisconsin River Floodplain
Project Number:	G-05
Start Date:	9/1/1999
End Date:	8/31/2001
Research Category:	Water Quality
Focus Category:	Groundwater, Hydrology, Nitrate Contamination
Descriptors:	Denitrification, Ecosystems, Groundwater hydrology, Land-water interactions, Nitrogen, Rivers, Wetlands
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Emily H. Stanley, Randall Hunt

Publication

1. West, J. L. 2000. Denitrification of the Wisconsin River floodplain. M.S. Thesis. Detrification in the Wisconsin River floodplain. Dept. of Zoology, University of Wisconsin-Madison.
2. 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.
3. 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, WI.

Hydrology and Biogeochemistry in the Wisconsin River Floodplain

Emily H. Stanley, University of Wisconsin-Madison
Randall J. Hunt, US Geological Survey-Middleton

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 hand-held 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.

Basic Information

Title:	Inorganic Carbon Dynamics in Allequash Creek: Ecological Implications of Subsurface-Surface Linkages
Project Number:	S-01
Start Date:	9/15/2000
End Date:	9/14/2001
Research Category:	Not Applicable
Focus Category:	Groundwater, Wetlands, Models
Descriptors:	Inorganic carbon, groundwater hydrology, land-water interactions, wetlands, watershed budgets, watershed models
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Emily H. Stanley

Publication

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

Emily H. Stanley, University of Wisconsin-Madison

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 below-ground 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 ground- and surface water chemistry, groundwater inputs into the study reach, instream 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 hillslop-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 instream 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.

Basic Information

Title:	Development of Neural Network for Predicting Nitrate Concentration in Well Water in the Tomorrow-Waupaca Watershed
Project Number:	N-01
Start Date:	7/1/1999
End Date:	6/30/2001
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
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Hangsheng Lin, Byron Shaw

Publication

1. Cook, R. C. 2000. Relationship between private well water, stream base flow, and land use in the Tomorrow-Waupaca River watershed. M.S. Thesis. College of Natural Resources, University of Wisconsin-Stevens Point.
2. Lin, H.S., and S. Wang. 2001. Artificial neural network for nonpoint source pollution assessment in watersheds. In the Proceedings of the 5th International Conference on Diffuse/Nonpoint Pollution and Watershed Management. June 10-15, 2001, Milwaukee, WI.
3. Lin, H. S., C. Jaskolski, R. C. Cook, and B. Shaw. 2000. Development of neural network models for predicting nitrate concentration in well water in the Tomorrow-Waupaca Watershed. Agronomy Abstract. 2000 Annual Meeting of the Soil Science Society of America, Minneapolis, Minnesota.

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

Hangsheng (Henry) Lin, University of Wisconsin-Stevens Point
Byron Shaw, University of Wisconsin-Stevens Point

Problem and Research Objectives:
Assessment of groundwater susceptibility to contamination under conditions of uncertainty is an important issue facing the state and the nation. Because of its ubiquitous nature and potential chronic health effects, nonpoint source pollution of groundwater has become a focal point for the public. We are addressing this issue by developing a new approach to predict nitrate concentration in well water from nonpoint sources in a watershed. Artificial neural network (ANN) models will be developed using a large groundwater quality database in combination with a Geographic Information System (GIS). This approach will be tested for a priority watershed in central Wisconsin and should provide insights on the factors governing groundwater quality in a watershed and on implementing best management practices (BMPs).

Methodology:
We use feedforward artificial neural network (ANN) technology to model nitrate concentrations in both surface and well waters in the Tomorrow-Waupaca watershed. We then compare the accuracy and predictive power of the ANN model to standard linear regression (REG) and surface response methodology (RSREG). We wish to demonstrate the superiority of ANN modeling over standard regression techniques. Although other work has been done showing that ANN modeling yields results similar to nonlinear modeling, our approach explores important differences between the methods ignored in other studies. Specifically, other studies have focused on how well a given model can fit the data used to generate the model (e.g., the R^2 value normally reported with regressions). We are shifting the focus to how well the models can actually predict when given data not used in model creation. Another technique we are using to generate a better picture of the model's predictive power is the bootstrap method, which allows us to test models against multiple realizations of the input data, hence providing some insights regarding the underlying uncertainties.

Principal Findings and Significance:
Our results showed that ANN was apparently superior to multivariate linear regression and nonlinear quadratic response surface model in terms of both the nitrate variance it could explain and external prediction consistency. ANN also permitted flexible model development that is difficult to achieve using a pre-defined model. This is to the advantage of nonpoint source water quality assessment since we often look for a function that relate input data (e.g., land use) to output data (e.g., well water nitrate concentration) that is difficult to use a pre-defined model to describe. This study indicated that the percentages of agricultural land and grassland within a sub-basin, stream order and the average slope of groundwater flow path were among the key variables impacting the stream baseflow nitrate concentrations in the watershed. Stream baseflow nitrate concentrations were found to have strong positive correlations with groundwater nitrate concentrations when the sub-basins were second order or higher, suggesting that stream baseflow may be used to represent mean groundwater quality in the watershed for sub-basins greater than first order. It was apparent from this study that as the amount of agricultural land

increased in a sub-basin, average nitrate concentration in stream and groundwaters in the sub-basin also increased.

Basic Information

Title:	Admicelle-Catalyzed Reductive Dechlorination of Perchloroethylene (PCE)
Project Number:	N-02
Start Date:	7/1/1999
End Date:	6/30/2001
Research Category:	Water Quality
Focus Category:	Groundwater, Methods, Toxic Substances
Descriptors:	Chlorinated solvents, Groundwater contamination, Permeable membranes, Remediation technology, Zero valent iron
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Zhaohui Li

Publication

1. Li, Z., H. K. Jones, R. S. Bowman, and R. Helferich. 1999. Enhanced reduction of chromate and PCE by pelletized surfactant-modified zeolite/zero valent iron. Environ. Sci. Technol. 33:4326-4330.
2. Alessi, D. S. and Z. Li. 2001. Synergistic effect of cationic surfactants on perchloroethylene degradation by zero valent iron. Environ. Sci. Technol. in second review.
3. Alessi, D.S. and Z.L. 2000. Reductive Dechlorination of PCE and TCE Using Surfactant Modified Zero Valent Iron. Geological Society of America, Reno, NV. November.

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

Zhaohui Li, Assistant Professor, The University of Wisconsin-Parkside

Problem and Research Objectives:
Chlorinated solvents are a major groundwater contaminant at industrial sites, U.S. Department of Energy facilities, and military installations. When these toxic compounds enter the subsurface they are quite mobile and degradation or transformation by natural processes is very slow. Subsurface permeable membranes are showing promise as an efficient, cost-effective means of addressing long-term, low-concentration groundwater contamination. The membrane serves as a giant filter that allows contaminated groundwater to pass through while retaining the toxic compounds by sorption or destroy the contaminants on the barrier by reaction. Recently, the use of zero valent iron (ZVI) as degradation barriers to remediate groundwater contaminated by chlorinated solvents has attracted attention. In addition to its low materials cost and rapid degradation rate for chlorinated solvents, it has been observed that coating ZVI surfaces with a surfactant enhances degradation. We are researching this novel observation using laboratory experiments followed by model studies. This research could have far-reaching impacts on the implementation of permeable barrier technology at sites contaminated with chlorinated solvents throughout the United States.

Methodology:
Laboratory batch sorption will be performed to determine the sorption maxima from different types of surfactants and from the same type of surfactant with different hydrophobic chain lengths. The zero valent iron (ZVI) surfaces will be modified to surfactant sorption maxima with cationic surfactatn having 8, 12, and 16 carbons in the tail group. The modified ZVI will be subjected to batch perchloroethylene (PCE) reduction kinetic study to determine the PCE degradation rate constant. The generation of trichloroethylene (TCE) due to the degration of PCE will be monitored with time. The aqueous chloride concentration due to degradation of chlorinated compounds will also be quantified. The PCE degradation kinetics will be studied under different initial pH and ionic strength conditions. Column study will be performed to verify the enhancement of PCE reduction catalyzed by admicelles of cationic surfactant on ZVI surfaces. The results will be simulated with current solute transport and degradation models.

Principal Findings and Significance:
During laboratory batch study we found that the sorption of cationic surfactant on ZVI surfaces is a function of the hydrophobicity of the surfactant. The longer the surfactant tail group, the more hydrophobic the surfactant is. Thus, the sorption maximum of hexadecyltrimethylammonium (HDTMA) (C16) on ZVI is higher than that of dodecyltrimethylammonium (DDTMA) (C12), which is higher than that of octadecyltrimethylammonium (OTA) (C8). Compared to unmodified ZVI, The rate constants of PCE reductive dechlorination increased by 15 to 20 times when ZVI was modified by HDTMA. A six to nine fold increase in rate constant was found for ZVI modified with DDTMA, while a five to seven time increase was found for ZVI modified with OTMA. The half-life of PCE in the presence of unmodified ZVI was about 10 days. But under the catalysis of HDTMA, the PCE half-life is reduced to 0.4 day. Rate of TCE degradation by admicelle catalyzed ZVI degradation

increased by an order of magnitude compared to unmodified counterpart. Solutions with an ionic strength of 0.001, 0.01, and 0.1 M of NaCl had no effect on PCE reduction rate. PCE reduction rate was not affected by initial solution pH at 3, 5, and 7. When initial solution pH was 11, significant slowdown of PCE reduction was observed, possibly due to the inhibition of iron corrosion. From the preliminary study it can be seen that the increase in dechlorination rate would greatly enhance the performance of the ZVI barrier if surfactant could be added. On one hand, to achieve the same reduction effect in a given period of time, only fractional ZVI will be needed if catalyzed by surfactant admicelle. On the other hand, if the same amount of ZVI used, under the catalysis of surfactant admicelle, the time required for reducing PCE to a limited final concentration will be dramatically reduced. The finding from the batch study was used as the support document for a proposal to the U.S. Environmental Protection Agency. However, the application for further funding was not successful. The finding from the batch study was summarized into a manuscript that was sent to Environmental Science and Technology for publication. Currently, it is under second review.

To verify the batch results we initiated the column study. First, we modified ZVI with HDTMA at a larger scale (1-2 kg) to high and low surface coverage. After surfactant modification, the surfactant loading was 2-3 mmol/kg and 7-8 mmol/kg for the low and high surface coverage, respectively. We packed 2 columns with HDTMA modified to high surface coverage and 2 columns with unmodified fisher ZVI. The dimension of the columns was 30 cm long and 2.5 cm in diameter. The columns were fed with DI water at a flow rate of 0.25 mL/min for 2 days before 20 mg/L PCE solution was introduced via a syringe pump that has 4 10-mL gastight syringes attached. The flow rate corresponds to 2-3 hours per pore volume. The both the influent and effluent concentrations were measured every 2-3 hours using an HPLC method. After flushing the columns with 24 hours, steady state was reached. However, the column experiments continued for another 72 hours. The steady state effluent PCE concentrations for unmodified column were 1.52 ± 0.76 and 0.43 ± 0.32 mg/L, respectively. For modified columns, the steady state effluent concentrations were 0.11 ± 0.09 and 0.10 ± 0.07, respectively. Compared to the unmodified ZVI, modified ZVI reduced the effluent PCE concentration by a factor of 4 to 14, similar to the batch results.

We will continue our column experiments with different flow rate and with the iron modified to low HDTMA surface coverage. If time permit, we will try the anionic surfactant SDS and nonionic surfactant Triton X-100.

Basic Information

Title:	Remediating Groundwater Using Reactive Walls Containing Waste Foundry Sands
Project Number:	N-07
Start Date:	7/1/1999
End Date:	6/30/2001
Research Category:	Engineering
Focus Category:	Groundwater, Treatment, Water Quality
Descriptors:	Containment technology, Foundry sands, Groundwater, Reactive walls, Remediation technology, Water quality
Lead Institute:	University of Wisconsin Water Resources Institute
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.

Basic Information

Title:	Causes of Historical Changes in Groundwater Recharge Rates in Southeastern Wisconsin
Project Number:	N-08
Start Date:	7/1/1999
End Date:	6/30/2001
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Models, Management and Planning
Descriptors:	Climate change, Drinking water, Groundwater, Recharge, Water resources, Watersheds
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Douglas S. Cherkauer

Publication

1. LaCosse, C. 2000. Causes of Historical Changes in Groundwater Recharge Rates in Southeastern Wisconsin. Annual meeting of National Association of Professional Geologists (this paper was awarded honorable mention among student posters)
2. LaCosse, C. and D. Cherkauer, 2000. Causes of Historical Changes in Groundwater Recharge Rates in Southeastern Wisconsin. Wisconsin chapter of the American Water Resources Association. Green Bay, WI. March

Causes of Historical Changes in Groundwater Recharge Rates in Southeastern Wisconsin

Principal Investigators:
Douglas S. Cherkauer, University of Wisconsin-Milwaukee

Problem and Research Objectives:
Large suburban and rural populations in southeastern Wisconsin depend on recharge-fed groundwater as their sole source of drinking water. Proper management of the groundwater resource requires the fullest possible understanding of how recharge varies spatially and through time and how it might change in climatic change scenarios. Such information is also absolutely essential input to regional and local scale groundwater models developed for resources management. The objective of the study has been to define the temporal variation of ground-water recharge and the climatic and hydrogeologic controls on those changes.

Methodology:
Baseflow in streams has been used as a surrogate measure for ground-water recharge. Watersheds have been selected for study in which the primary ground-water inflow is precipitation and the primary outflow is discharge to streams (baseflow). Selected watersheds must also have a USGS gaging station with 30 years of continuous record and sufficient nearby NOAA climatic stations to define the precipitation. Baseflow has been separated from total streamflow at a gaging station using the USGS program HYSEP.

Thirteen watersheds in southeastern Wisconsin were examined as the primary data set. They all have relatively similar underlying geology. The variation of baseflow quantity through the period 1965 to 1998 was compared to the variation in annual precipitation, temperature and various measures of the timing and intensity of precipitation. The rate of recharge (baseflow) change to climatic change through time was then established for each watershed. Similar responses were then grouped together and topographic, hydrogeologic and land cover conditions were examined as causes for the differences.

After the cause was identified, it was tested for applicability in other watersheds with different geology throughout Wisconsin. Another 15 watersheds were used to test the observed relations.

Principal Findings and Significance:
The primary factor controlling the variation of ground-water recharge through time is annual precipitation. Recharge did not show any significant relation to either precipitation intensity or seasonality or to air temperature. The ratio of recharge response to precipitation change ranged in the study watersheds from essentially 0 to nearly 1.0. The response in areas of thick glacial sediments over a predominantly dolomitic bedrock (southeastern Wisconsin) is controlled by 2 topographic factors, average topographic slope and average length of overland flow. Land cover, aquifer conductivity, watershed size and shape, all factors anticipated to be important, were not.

The same relation between these 2 parameters and the temporal variation of recharge in response to precipitation changes persists at all the other glaciated watersheds tested in Wisconsin. As the product of hillslope and length of overland flow increases, the ratio of recharge change to precipitation change increases. This relation is valid whether the underlying rock is carbonate or clastic sedimentary or igneous. It is valid whether the glacial sediments are clay-dominated till or coarse-grained outwash. There is not enough information to establish a relationship for non-glaciated watersheds (southwestern Wisconsin).

The study has shown that ground-water recharge is controlled predominantly by precipitation. Is precipitation decreases through time, recharge in watersheds which have relatively steep slopes or sparsely developed drainage systems will drop at the same rate. The effect of precipitation change will be muted in watersheds with gentler slopes or denser drainage networks. This allows determination of what parts of the state will experience the greatest impact on ground-water resources in the future if climatic change occurs and results in precipitation changes.

Basic Information

Title:	Watershed Influences on Transport, Fate and Bioavailability of Mercury in Lake Superior
Project Number:	N-09
Start Date:	10/1/1999
End Date:	9/30/2002
Research Category:	Water Quality
Focus Category:	Toxic Substances, Surface Water, Geomorphological Processes
Descriptors:	Contaminant transport, Geochemistry, Mathematical models, Metals, Suspended sediment, Trace elements, Toxic substances, Water quality
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	James P. Hurley, David E. Armstrong, Martin M. Shafer

Publication

1. Stoor, R.W, D.E. Armstrong, J.P. Hurley, D.P. Krabbenhoft, K.R. Rolfhus, L.B. Cleckner. 2001. Groundwater Contributions of methylmercury to a small stream in the Lake Superior Watershed Poster Presentation at the American Water Resources Association - Wisconsin Section Meeting, March.
2. Stoor, R.W, D.E. Armstrong, J.P. Hurley, D.P. Krabbenhoft, K.R. Rolfhus, L.B. Cleckner. 2001. The Role of Groundwater in Contributing Methylmercury to a Small Michigan Stream. Oral Presentation at International Association of Great Lakes Research Conference, June.
3. Babiarz, C.L., S.R. Hoffmann, M.M. Shafer, J.P. Hurley, A.W. Andren, D.E. Armstrong. 2000. A critical evaluation of tangental-flow ultrafiltration for trace metal investigations in fresh water systems: Part II Total and Methylmercury. Environmental Science and Technology 34: 3428-3434.
4. Hurley, J.P., L.B. Cleckner, and M.M. Shafer. 2000. Watershed influences on mercury transport to Lake Superior. Verhundlungen Internationale Vereinigung Limnologie (In Press).
5. Cleckner, L.B., J.P. Hurley, K.R. Rolfhus, R.C. Back, C.L. Babiarz, and D.E. Armstrong. 2000. Watershed influences on transport, fate, and bioavailability of mercury in Lake Superior. American Society of Limnology and Oceanography, Copenhagen, Denmark. June.
6. Hurley, J.P., C.L. Babiarz, L.B. Cleckner, K.R. Rolfhus and M.M. Shafer and R.C. Back. 2000. Partitioning and transport of total and methyl mercury in Lake Superior tributaries. International Association for Great Lake Research, Cornwall, ONT, Canada. May.
7. Hurley, J.P., K.R. Rolfhus, L.B. Cleckner, M.M. Shafer, C.L. Babiarz, D.E. Armstrong, R.C. Back and R. Harris. 2000. Watershed Influences on Fate and Transport of Total and Methyl Mercury in the Lake Superior Basin. Air and Waste Management Association, Annual Meeting. Banff, AB Canada. April.
8. Rolfhus, K.R., J.P. Hurley, B. Hall, D.P. Krabbenhoft, and D. Bodaly. 2001. The "Reservoir Effect": Synthesis and Biological Uptake of Methylmercury in Seasonally Inundated Systems. 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.

9. Rolfhus, K.R., J.P. Hurley, L.B. Cleckner, R.C. Back, R. Stoor, P.R. Gorski, H. Sakamoto, C.L. Babiarz, and R. Moore. 2001. The speciation and bioavailability of mercury in Lake Superior and its tributary mixing zones. International Association of Great Lakes Research. Green Bay, WI. June.
10. Hurley, J.P., R.C. Back, K.R. Rolfhus, R.C. Harris, D.E. Armstrong, R. Harris, C.L. Babiarz, M.M. Shafer. Watershed Influences on Transport, Fate, and Bioavailability of Mercury in Lake Superior. 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.

Watershed Influences on Transport, Fate and Bioavailability of Mercury in Lake Superior

Principal Investigators:
James P. Hurley, David E. Armstrong, Martin M. Shafer, University of Wisconsin
Richard C. Back, Lake Superior State University
David P. Krabbenhoft, US Geological Survey

Problem and Research Objectives:
Loading of trace metals from point and nonpoint sources (NPS) 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 is a trend which can be traced to watershed disturbances and both point and nonpoint 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. To address this issue, metal speciation will be quantified as a function of watershed environmental characteristics and readily determined geochemical variables. In addition, model development will provide the basis for assessment and prediction of metal speciation across divergent watersheds.

Methodology:
Our approach combines field and laboratory studies with modeling to assess the importance of watershed processes in controlling Hg fate and transport in Lake Superior (Figure C1). Each phase (field studies, laboratory studies, modeling efforts) is strongly linked to provide feedback for the remaining phases. Frequent interaction among project participants (group meetings, conference calls) will allow for adjustments to better assess important processes for success of objectives. Our approach builds on research conducted by our group on Lake Superior tributaries from 1995-1998 and develops new research objectives in fate and transport of Hg, including factors regulating bioavailability. Techniques developed and adapted by our group during previous projects (i.e., "clean" ultrafiltration, resin techniques, biota processing) will be supplemented by new techniques (i.e., stable isotope Hg analysis by ICP-MS; phytoplankton and zooplankton uptake experiments, "bio-reporter" work by Canadian colleagues). Modeling efforts combine efforts of ongoing GIS-based watershed yield modeling with the Dynamic Mercury Cycling Model (D-MCM) model development at Tetra Tech, Inc.
Principal Findings and Significance

The field aspects of the project began with the onset of spring melt on three study tributaries. Our group participated in a spring cruise to the open waters of Lake Superior aboard the USEPA's R/V Lake Guardian. A total of 19 sites were sampled in the lake, with six sites considered master stations for detailed phytoplankton, watercolumn and sediment sampling. Preliminary analyses suggest that offshore regions of the lake have Hg levels in the range of 0.2 to 0.4 ng/L, while sites located near urban areas can exceed 1 ng/L. A second cruise is scheduled for August 2000 and we will continue with detailed mixing zone and watershed studies.

Principal Findings and Significance

Our research efforts during the first year of the project were focused on: 1) Investigating differences between processes influencing offshore and nearshore bioaccumulation of Hg in Lake Superior, particularly with regards to the spatial/temporal distribution of Hg in near-shore and offshore environments; 2) Investigating watershed processes that enhance production and transport of methyl Hg to tributaries; and, 3) Developing laboratory techniques for "trace-metal clean" plankton culturing/uptake studies.

Two cruises on Lake Superior aboard the EPA research vessel *R/V Lake Guardian* were conducted during 2000 (April, August). Nineteen open water stations on Lake Superior were visited in order to determine the spatial/temporal distribution and speciation of Hg. Our results indicate that, as expected, Hg species concentrations are quite low in Lake Superior, similar to Lake Michigan and oceanic waters. Total Hg averaged 0.49 ± 0.22 ng L^{-1} (mean, sd) for all stations, depths, and cruises, with little difference found between surface and deep samples; 74% was 0.7 μm filter passing. Surface water total Hg samples were elevated along the Minnesota north shore in April, 2000, indicative of river inputs during this high-flow period. During August 2000, methyl Hg (MeHg) averaged 6.4 ± 3.8 pg L^{-1} (with no discernable spatial trends), dissolved gaseous Hg was 20 ± 10 pg L^{-1}, and reactive Hg averaged 45 ± 33 pg L^{-1}. For the August 2000 cruise, aqueous samples averaged 1.5% MeHg, 3.5% Hg^o, 10% reactive Hg(II), and 85% unreactive organic Hg(II) complexes. Initial comparisons of phytoplankton revealed about a two to threefold enrichment of MeHg in riverine mixing zones versus offshore regions of the lake. Analyses of the plankton and sediments (solid phase and pore waters) are ongoing.

The role of watershed composition on MeHg transport is being examined in two focused studies: 1) homogeneous watershed subunits have been identified for the south shore of Lake Superior (based upon GIS surficial geology and land use data), whose tributaries have been sampled for Hg speciation in surface waters, and 2) the role of groundwater in producing/transporting MeHg within a forest-wetland dominated watershed. An extensive set of monitoring wells has been placed in the East Creek watershed in the Tahquamenon River; groundwater, stream water and porewater samples are also being taken to detect areas of enhanced MeHg production and transport. Initial results from 2000 sampling indicate that groundwater and stream porewater are significant sources of MeHg, with wetland-dominated sites exhibiting the highest MeHg concentrations, at times exceeding 12 ng/L.

We have also initiated laboratory studies directed at predicting bioavailability of Hg and MeHg in algal and zooplankton cultures, through a cooperative effort with the Wisconsin State Lab of Hygiene Biomonitoring Laboratory, implementing trace-metal clean culturing techniques and constructing laboratory areas for Hg-clean research. We have begun testing various algal growth media (Fraquil, Nutrient Enhanced Fraquil, and Bold's Basal Media) to assess both algal growth and background Hg levels, and are evaluating Hg speciation using MINEQL.

Basic Information

Title:	The Spatial and Temporal Variability of Groundwater Recharge
Project Number:	N-05
Start Date:	8/5/1999
End Date:	8/4/2000
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Water Quantity, Climatological Processes
Descriptors:	groundwater recharge, recharge estimation, groundwater hydrology, groundwater management, groundwater modeling, water resource management, temperature profiling, IBIS, VS2DH, GFLOW, analytic element modeling, UCODE, inverse parameter estimation
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Mary Anderson, Kenneth Walter Potter

Publication

1. Dripps, W.R., Kucharik, C.J., Lenters, J.D., Anderson, M.P. and Foley, J.A., 2001. Modeling the Spatial and Temporal Distribution of Groundwater Recharge Across a Forested Watershed in northern Wisconsin. American Geophysical Union, 2001 Spring Meeting, Boston, MA, Eos, Vol. 82
2. Dripps, W.R, Anderson, M.P., and Hunt, R.J., 2001. Use of a Coupled Heat and Water Transport Model (VS2DH) for Estimating Rates of Natural Groundwater Recharge. American Water Resources Association ? Wisconsin Section, 25th Annual Meeting, Green Lake, WI, abstracts, p. 27.
3. Dripps, W.R., Anderson, M.P., and Hunt, R.J., 2000. Incorporating Recharge Variability into Groundwater Flow Models. Geological Society of America, 2000 Fall Meeting, Reno, NV, Abstracts with Programs, Vol. 33, p. 335.
4. Dripps, W.R., Bradbury, K.R., Anderson, M.P., and Hankley, D.W., in prep. A Modified Thornthwaite ? Mather Soil Water Balance Model for Estimating the Spatial Distribution of Groundwater Recharge. 2002 Wisconsin Geological and Natural History Survey Circular.

The Temporal and Spatial Variability of Groundwater Recharge

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Kenneth W. Potter, Professor, Department of Civil and Environmental Engineering, The University of Wisconsin - Madison

Problem and Research Objectives:
Understanding the spatial and temporal distribution of groundwater recharge is a basic prerequisite for effective groundwater management and modeling. Recharge rate, defined as the entry of water into the saturated zone, is determined by a variety of factors including vegetation, topography, climate, geology, and soils. Typically, however, a constant annual average value of recharge is assumed to occur over an entire watershed. Average annual recharge is usually estimated empirically as a percent of precipitation, determined by calibration of a groundwater model, or equated to stream baseflow. Since the distribution, rate, and timing of recharge are dictated by the interaction of parameters that vary spatially and temporarily, it is expected that recharge should also vary. We have investigated the daily fluctuation and spatial variation of recharge at the watershed scale in the Trout Lake Basin, a forested watershed in northern Wisconsin, using a combination of field investigations and integrated modeling.

We used three modeling approaches to estimate the spatial and temporal variation of recharge in the Trout Lake Basin. These were: (1) a soil water balance model, which we developed in a previous study; (2) an integrated terrestrial biosphere model (IBIS); (3) a two-dimensional analytic element groundwater flow model (GFLOW) linked to a parameter estimation (inverse) code (UCODE). We also applied a series of field techniques (temperature profile modeling, water-level fluctuations, and time domain reflectometry) to calculate site-specific recharge estimates and the timing of groundwater recharge events for 1999 - 2000, and compared the field estimated recharge rates with the simulated values generated by the three models.

Methodology:
Regional Recharge Modeling
We applied three different models (a soil water balance model, IBIS, and GFLOW) to estimate the spatial and temporal distribution of groundwater recharge across the study watershed.

The soil-water balance model is based on a modified Thornthwaite – Mather soil water balance approach that uses typically available soil, land cover, topographic, and climatic data within a GIS framework to estimate fluctuations and spatial variability in recharge rate.

IBIS (Integrated BIosphere Simulator) is a comprehensive, modular terrestrial biosphere model that explicitly links land surface and hydrologic processes, terrestrial biogeochemical cycles, and vegetation dynamics within a single, physically consistent framework. We used IBIS to calculate distributed recharge rates in the Trout Lake Basin. In this application, we utilized the atmosphere, land surface, and vegetation phenology modules to calculate at the basin water balance. Hourly climate data were used to drive the land surface module, which simulates energy, water, carbon, and momentum balances of the soil – vegetation – atmosphere system.

The land surface module simulates two vegetation layers (an upper and lower canopy), a six layer soil scheme, and a three layer thermodynamic snow melt system. Inputs to the module included many vegetation variables (land cover physiology), soil variables (type and hydrologic characteristics), and meteorological variables including precipitation, temperature, relative humidity, solar radiation, and wind speed. The vegetation and soil parameters for the Trout Lake Basin were taken from previous work and regional studies in the area. The required meteorological inputs were obtained from a weather station within the watershed. The model was run at an hourly time step for 1989 – 2000 at a grid cell spacing of roughly 120 meters. IBIS was designed as a global scale model, but model equations are independent of scale such that model application at the watershed scale is possible, but had not been attempted prior to this study. Besides providing a check on output from the soil water balance model, the application of IBIS to the Trout Lake Basin provided an evaluation of the performance of this model at the watershed scale.

Lastly, a two-dimensional analytic element (AE) code (GFLOW) was coupled to a nonlinear parameter estimation code (UCODE) to estimate annual recharge rates for 1996 – 2000 for the basin by optimizing the AE model to estimates of baseflow in five streams. Baseflow recession techniques produced a single estimate of recharge for the contributing area around each stream gage. Consequently, these techniques are incapable of assessing spatial recharge variability within a contributing area, but they can be used to assess annual temporal variability as well as provide an independent measure of recharge for the entire basin. The analytic element method solves regional groundwater flow problems by superposing analytic solutions within a mathematically infinite aquifer domain. Hydrologic features such as a well, stream, or lake are represented by an analytic function or a string of analytic functions. AE models are appealing as they require no grid discretization or *a priori* specification of boundary conditions such that regional and local flow systems can be modeled within the same model. AE models, however, cannot easily simulate complex three-dimensional systems or transient systems, and subsequently are most commonly used as screening models to help assign boundary conditions for more complex three-dimensional finite difference models.

UCODE, a recently developed computer code for universal inverse modeling, performs parameter estimation using nonlinear regression. The nonlinear regression problem is solved by minimizing a weighted least squares objective function with respect to the parameter values using a modified Gauss-Newton method. UCODE can be linked to any application model and will optimize the application model, determining parameter values that provide a quantified best fit between the simulated values and the observed calibration targets. For this study we coupled UCODE to the USGS Trout Lake basin analytic element model. The BFI method, a computer automated, deterministic approach developed by the British Institute of Hydrology, was used to estimate annual baseflows from the daily discharge data for the stream gages in the basin for 1996 – 2000. UCODE was then used to optimize a regional recharge estimate for the AE model to best fit the baseflow estimates for these gages.

Field Study

Field measurements of recharge were made at eight well-instrumented field sites during the period 1999-2001. The field sites covered a range of different vegetation, soil, geologic, and topographic features. At each site we recorded hourly water levels in wells, hourly soil moisture

at three depths (10", 3 feet, and 7 feet), and hourly temperature profiles at depths of 0.05, 0.2, 0.5, 1, 3, and 5 meters. In addition, we recorded hourly measurements of precipitation and collected monthly throughfall data at each of the eight sites.

The temperature data were analyzed using a two-dimensional, numerical, variably saturated, coupled heat and water flow model, VS2DH. UCODE was linked to VS2DH to optimize the temperature profile fitting procedure. Thermal and physical parameters required for the model were extensive and came from previous field studies and the literature. Grain size and bulk density analyses of vibracores, infiltrometer tests at multiple depths using a Guelph permeameter, slug tests in water table wells, hourly soil moisture measurements at multiple depths, and soil characteristic curve analyses of soil cores provided the majority of the requisite model input parameters.

Hourly water level data from numerous wells within the basin were analyzed to provide an additional measure of annual groundwater recharge rates within the basin. Water-level fluctuations over the course of the year were converted to recharge rates by multiplying the magnitude of the fluctuations by estimates of the aquifer's specific yield. Constraints for the estimated specific yield were based on a combination of field measurements of porosity and grain size and published values in the literature.

Reflectometer data at each site provided a record of the timing of recharge events, denoted by sharp rises in the soil moisture content as pulses of infiltrating recharge moved through the unsaturated zone en route to the water table.

Collectively, the temperature, water level, and reflectometer data provided field estimates of the timing and rate of recharge, which were compared to recharge estimates produced by the three models.

Principal Findings and Significance:
The following key points summarize our findings and their significance:

- The three models produced recharge estimates comparable to those derived from field-based estimates using water-level fluctuations and time domain reflectometry.

- The soil water balance model yielded recharge estimates and distributions similar to those calculated by the more complex and data intensive IBIS and GFLOW models. In contrast to these two models, the soil water balance model does not require extensive parameterization, uses readily available input data and is easy to use.

- In our application to the Trout Lake Basin, IBIS, which was originally designed as a global dynamic ecosystem model, worked well at a watershed scale.

- Methods for explicitly accounting for the temporal and spatial distributions of groundwater recharge are a significant conceptual improvement over assuming that recharge is constant. In the Trout Lake Basin, there were three-fold inter-annual variations in recharge and large monthly fluctuations in recharge. Spatial variability is controlled by differences in land cover type.

Hence, land cover changes could have a significant effect on the basin's water budget and on nutrient and contaminant transport processes within the watershed. Collectively these models, particularly our soil water balance model, present modelers, planners, and policy makers with practical water resource management tools for calculating spatially and temporally distributed recharge estimates for modeling and water resources planning purposes.

- Although there is typically a general correlation between precipitation and annual average recharge, a constant linear correlation between the two is a bad assumption as soil moisture conditions and the timing of precipitation events can be more important than the actual amount of precipitation in determining recharge rate.

- Temperature within the upper one meter of the soil profile potentially can be used to track recharge events. Temperature measurements collected at several sites in the Trout Lake Basin exhibited responses that appeared to correlate with recharge events. Simulations using a flow and heat transport model (VS2DH) indicated that the size and shape of the temperature response is most sensitive to the temperature and rate of the infiltrating precipitation, the initial moisture content, and the saturated hydraulic conductivity of the system. Our attempts, however, to use temperature profiles measured in the Trout Lake Basin in a joint inversion of temperature and moisture content/pressure head data (using VS2DH with UCODE) were unsuccessful in estimating recharge rates. We suspect that heterogeneity in the unsaturated zone caused macropore flow and two-dimensional flow effects that were not included in our model.

Basic Information

Title:	A Basin-scale Denitrification Budget for a Nitrate-contaminated Wisconsin Aquifer: A Study at the Groundwater/Surface Water Interface
Project Number:	N-06
Start Date:	7/1/2000
End Date:	6/30/2001
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Surface Water, Nitrate Contamination
Descriptors:	nitrate, nitrous oxide, aquifer, denitrification, groundwater/surface water interface, basin scale
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	, George Kraft

Publication

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

Bryant A. Browne and George Kraft, College of Natural Resources, University of Wisconsin – Stevens Point
David Saad, U.S. Geological Survey, Middleton, Wisconsin

Problem and Research Objectives:

Nitrate is the most pervasive groundwater contaminant in the US. In Wisconsin, 10% of wells exceed the nitrate drinking water standard on a statewide basis, but the exceedance rate averages about 20% in predominantly agricultural area. Denitrification reactions in ground water can potentially transform nitrate to dissolved gases (most notably dinitrogen and nitrous oxide). Dinitrogen gas is an innocuous form and its production has a beneficial effect on ground water quality. Nitrous oxide gas is both a greenhouse gas and a regulator of atmospheric ozone. The relative contribution of ground water discharge to the increasing atmospheric burden of nitrous oxide is not well established. There is a need to achieve a better understanding of denitrification as a basin-scale control of nitrate concentration and export in Wisconsin aquifers. Our objective is to quantify nitrate losses by denitrification in the Little Plover River Basin, a nitrate contaminated basin typical of many in the state.

Methodology:

We will gather data on denitrification in 1) regional groundwater flowpaths that discharge to stream segments with deep hydaulic penetration, 2) shallow groundwater flowpaths through riparian soil, and 3) hyporheic sediments associated with losing stretches of the stream. We will draw upon 1) an extensive sampling infrastructure and database for the groundwater/surface water interface in the LPRB; 2) new quantitative approaches for using the groundwater/surface water interface to study basin scale hydrology and water quality relationships; 3) techniques that provide direct qualitative (e.g., stable isotopes of N and O) and quantitative (excess nitrogen gas, and nitrous oxide) measures of denitrified N; and 4) recently established groundwater discharge and nitrate export budgets that have been linked to basin-wide groundwater flow paths and historical land use patterns.

Principal Findings and Significance:

Our findings will 1) contribute to understanding the hydrogeological and historical controls on the distribution of nitrate contamination, 2) provide insight into evolving trends in groundwater and surface water quality throughout the state, and 3) illustrate the potential to apply the groundwater/surface water interface to study groundwater quality at the basin scale.

Basic Information

Title:	An Investigation of Processes Influencing Elevated Fish Mercury Levels in Isle Royale National Park
Project Number:	N-11
Start Date:	7/1/1999
End Date:	2/28/2001
Research Category:	Biological Sciences
Focus Category:	Sediments, Geochemical Processes, None
Descriptors:	Mercury, biota, sediments, lakes
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	David E. Armstrong, James P. Hurley

Publication

1. Gorski, P. R., L. B. Cleckner and J. P. Hurley. 2000. An investigation in the Food Web of Inland Lakes of Isle Royale National Park. American Water Resources Association (AWRA) - Wisconsin Section. Green Bay, WI. March.
2. Gorski, P. R., L. B. Cleckner, J. P. Hurley and J. Oelfke. 2000. An investigation of Mercury Levels in the Inland Lakes of Isle Royale National Park. Lake Superior National Parks Research Conference and Chequamegon Bay Natural Resources Conference. Ashland, WI. March.

An Investigation of Mercury Levels in the Food Web of Isle Royale National Park, Michigan

James P. Hurley, University of Wisconsin Water Resources Institute

Problem and Research Objectives:

The goal of this project is to determine why six lakes in Isle Royale National Park have fish with Hg levels high enough to trigger health consumption advisories while fish in other lakes remain low in Hg concentration. A dual approach (Table 2) will be used on a subset of lakes (presently Sargent Lake and Richie Lake) with high and low fish Hg concentrations: Are fish Hg levels elevated due to (A) existing trophic level processes within lakes? or (B) different watershed processes and Hg inputs into the lakes? In order to determine if lakes containing fish with high Hg levels have unique trophic characteristics, the first step will be to use the heuristic capabilities of the Regional Mercury Cycling Model in lakes with existing data. Second, methyl Hg levels in biota will be measured to supplement data that is deterministic in the model. Finally, stable isotopes will be measured on biota to determine trophic length and trophic relationships within the lakes. To assess watershed processes that influence Hg accumulation in fish, Geographical Information System (GIS) data will be analyzed to determine physical characteristics of lakes and their watersheds. Factors that have been shown to be associated with elevated levels of Hg in water and fish (e.g, percent wetland influence in watershed, elevation and amount of drainage basin relative to lake volume) will be examined. Next, methyl Hg levels in the lakes including epilimnion and hypolimnetic waters, as well as feeder streams and wetlands will be measured. Finally, input of Hg from localized precipitation will be measured and compared to in-lake and watershed processes.

Methodology

Water will be collected for Hg analysis employing ultra-clean techniques as outlined in Hurley et al. (1996) and United States Environmental Protection Agency (USEPA) Method 1669. Water samples from lakes and possible wetland inputs will be collected at least twice a year. Water will be analyzed for total mercury (HgT) and methyl mercury (MeHg). Water samples will be further analyzed for MeHg associated with particles and the mass of suspended particulate matter (SPM) as well as pigment composition. Biota will monitored for Hg from the selected lakes at least twice a year. Small aquatic insects will be collected using ultra-clean techniques as outlined in Cleckner et al. (1998) while zooplankton will be sampled as in Herrin et al. (1998). Samples will be collected using non-metallic nets and sieves. Small fish will be collected using minnow traps. Collected biota will be placed into Teflon vials with site water, double-bagged, and frozen until analysis. Aquatic insects targeted for collection include those from the following orders: Ephemeroptera, Odonata, Trichoptera and Hemiptera. Zooplankton groups targeted for collection are cladocerans and copepods. Small fish collected will be cyprinids or perch (Perca flavescens). At least 12 organisms of each type will be collected at each site and date with the exception of zooplankton, where hundreds will be collected. The whole body of all biota will be homogenized. Analysis of Hg will be done on either individuals (e.g., Odonata, Hemiptera, fishes) or on composites of several individuals (e.g., Ephemeroptera, Trichoptera, zooplankton). Subsamples of biota will be dried and weighed so final concentrations can be expressed as ng×g-1 dry weight.

Principal Findings and Significance

In 1998 and 1999, using Hg-clean techniques, we collected water, sediment, zooplankton, macroinvertebrates, and fishes from one advisory lake, Sargent Lake, for total (Hg_T) and methyl mercury (MeHg) analysis. Similar samples were also collected from a non-advisory lake, Lake Richie. Both lakes have similar physical and watershed characteristics and both lakes develop anoxic hypolimnia during the summer with associated increases in MeHg (from below detection to 0.3 ng/L). Counter to expectations, Lake Richie had slightly higher average Hg (both Hg_T and MeHg) in open water samples and much higher MeHg bound to suspended particles in the water. Streams flowing into both lakes were relatively higher in dissolved organic carbon and MeHg. Sargent Lake had higher average concentrations of Hg_T and MeHg in zooplankton than Lake Richie, while Hg concentrations in macroinvertebrate taxa were similar between the lakes. Age-1 yellow perch contained slightly higher Hg_T levels in Sargent Lake (22.0 ng/g wet weight) relative to Lake Richie (19.0 ng/g wet weight). Concentrations of Hg_T in adult yellow perch and northern pike increased similarly with length between lakes, but Sargent fishes were higher on average. The largest pike in Sargent had above-advisory Hg concentrations. Preliminary analysis of stable isotopes ($\delta^{13}C$ and $\delta^{15}N$) from biota did not show food web differences between lakes. Sediment cores exhibited recent increases in Hg_T for both lakes with concentrations increasing from about 120 ng/g dry weight (background) to 320 ng/g dry weight (present). Sargent Lake had higher MeHg (26 ng/g dry weight) than Richie (17 ng/g dry weight) at 1 cm. A diatom community analysis of the core suggests an increasing total phosphorous concentration of about 2 μg/L over time in Lake Richie, whereas phosphorous in Sargent Lake has remained constant. This suggests a higher degree of recent eutrophication in Richie, possibly affecting Hg levels in phytoplankton.

Both lakes have Hg concentrations similar to other lakes studied in the Upper Midwest and do not reach Hg levels found in lakes affected by industrial contamination. The sediment core history suggests atmospheric inputs are the main external source of Hg to both lakes. Relatively higher MeHg concentrations in particles in Lake Richie may result in less MeHg reaching zooplankton and the food chain as particles settle out of the water column and become buried in sediments. On the other hand, Sargent Lake has higher Hg concentrations in zooplankton and higher BAFs and BMFs than Lake Richie suggesting that MeHg may be more available to Sargent Lake's zooplankton. Differences in Hg between the two lakes become most pronounced at the large pike level, perhaps suggesting unique processes occurring at the pike trophic level, which we were not able to measure in this study.

Basic Information

Title:	Importance of Groundwater in Productions and Transport of Methyl Mercury in Lake Superior Tributaries
Project Number:	N-12
Start Date:	7/1/2000
End Date:	6/30/2001
Research Category:	Ground-water Flow and Transport
Focus Category:	Hydrogeochemistry, Toxic Substances, Hydrology
Descriptors:	Methylmercury, groundwater
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	David E. Armstrong, Kristofer R Rolfhus, David P. Krabbenhoft

Publication

1. Stoor, R.W, D.E. Armstrong, J.P. Hurley, D.P. Krabbenhoft, K.R. Rolfhus, L.B. Cleckner. 2001. The Role of Groundwater in Contributing Methylmercury to a Small Michigan Stream. Oral Presentation at International Association of Great Lakes Research Conference, June.
2. Stoor, R.W, D.E. Armstrong, J.P. Hurley, D.P. Krabbenhoft, K.R. Rolfhus, L.B. Cleckner. 2001. Groundwater Contributions of methylmercury to a small stream in the Lake Superior Watershed Poster Presentation at the American Water Resources Association - Wisconsin Section Meeting, March.

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

David Armstrong, Kristofer Rolfhus, and Lisa Cleckner, Environmental Science and Technology Program, University of Wisconsin-Madison; David Krabbenhoft U.S. Geological Survey, Middleton, Wisconsin
Research Assistant, Richard Stoor

Problem and Research Objectives:
Much has been learned about the cycling of Mercury (Hg) species in surficial waters in recent years, and evidence from prior studies suggests that factors such as land use and surficial geology likely control the speciation, bioavailability, and transport of Hg species in watersheds. Very little is known about the subsurface behavior of Hg; few studies have examined groundwater systems to determine its significance as a source of Hg species to surface waters, the rates at which methyl mercury (MeHg) may be synthesized in the subsurface environment, or the environmental factors that govern its fate and transport. The principal goal of this study is to determine the importance of groundwater systems as a source of MeHg to temperate streams. Specific objectives include: 1) documenting the subsurface locations and biogeochemical conditions under which MeHg is produced, 2) quantifying MeHg fluxes from subsurface zones via groundwater, and 3) characterizing the relationships between land use/coverage characteristics and MeHg fluxes from the subsurface environment.

Methodology:
A site at East Creek, a small catchment located in the Tahquamenon River watershed of Lake Superior in the Upper Peninsula of Michigan was chosen for intensive study of processes regulating production and transport of MeHg. The site contains zones with two contrasting land cover types, forest and wetland. Numerous groundwater wells have been placed near the creek in order to characterize possible zones of MeHg formation and transport. Sampling of these wells, as well as surficial and pore waters, is aimed at recognizing zones and/or biogeochemical conditions favorable for Hg transformation and transport.

Principal Findings and Significance:
Initial results indicate the importance of the oxic/anoxic interfaces in the hyporheic zone and wetland areas as zones of increased methyl mercury concentration. Water level monitors have also been placed to determine direction and gradient of groundwater-streamwater interaction, and the importance of these conditions on the production and transport of methyl mercury at these interfaces.

Basic Information

Title:	Effect of Clean and Polluted Groundwater on Reproduction and Development of Daphnia
Project Number:	N-13
Start Date:	7/1/2001
End Date:	6/30/2002
Research Category:	Biological Sciences
Focus Category:	Toxic Substances, None, None
Descriptors:	groundwater, Daphnia, pesticide, bioassay, biomonitoring, malathion, dimilin, methoprene, ecdysone, hormones, P-450
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Stanley Ivan Dodson

Publication

1. Peterson, J.K., Kashian, D.R., and Dodson, S.I. 2001. Methoprene and 20-OH-Ecdysone affect male production in Daphnia pulex. Environmental Toxicology and Chemistry 20(3) 582-588.
2. Kashian, D. R. and Dodson, S. I. 2000. The effects of Xenobiotics on sex determination and reproduction in Daphnia. Presented at The Society of Environmental Toxicology & Chemistry annual meeting in Nashville TN
3. Kashian, D.R. and S. I. Dodson. 2000. Ecologically-relevant effects of pesticides on Daphnia magna. To be presented at The Ecological Society of America Annual Meeting in Madison, WI Aug. 2001.

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

Stanley I. Dodson, University of Wisconsin -- Madison, WI

Problem and Research Objectives: To identify ecologically important (adverse) effects of polluted groundwater in a sensitive, efficient, cost-effective invertebrate whole animal assay.

1) Does the source (chemistry) of Wisconsin groundwater affect reproduction and development in *Daphnia*?
2) Do *Daphnia* reproductive and developmental responses (endpoints) allow us to detect water of known contamination?

Methodology:

Laboratory biological assays, using the water flea *Daphnia magna*. Endpoints include sex ratio, morphological development, survivorship, and fecundity. We have developed two assays: a short-term assay of 6 days to test for effects on developing embryos, and a long-term assay to gather life table data concerning long-term fecundity and survivorship.

Principal Findings and Significance:

Several common ground water contaminants have been shown (in the laboratory) to modify *Daphnia* sexual development, including **toxaphene**, **methoprene**, and **malathion**. At a concentration of 100 µg/L, toxaphene increased male production two-fold relative to the controls. Toxaphene significantly decreased the average clutch size from 17 to 13 individuals and adult size by 5% ($p=0.01$). *Daphnia* exposed to methoprene concentrations at 10 and 100 µg/L produced fewer male broods and more female broods relative to the controls. Long-term assays of 0.1 µg/L malathion exposed *Daphnia* showed significantly decreased growth and survivorship, male skewed sex ratio, and decreased total fecundity. Short-term assay concentrations ranging from 0.1 to 0.0001 µg/L also showed appropriately decreasing exposure-response relationship at lower concentrations. At 0.1 to 0.001 µg/L, exposed *Daphnia* showed decreased fecundity, skewed sex ratios, increased neonate deformity, and adult mortality.

Ground water collected from a predominantly sandstone aquifer (high hardness) in Waukesha Co. WI significantly increased male production in *Daphnia*. Increases in **nitrate** levels (50 mg/l) and elevated **conductivity** had no apparent effects on *Daphnia* growth and reproduction. Long-term assays of 0.1 ppb malathion exposed *Daphnia* showed significantly decreased growth and survivorship, male skewed sex ratio, and decreased total fecundity. Short-term assay concentrations ranging from 0.1 to 0.0001 ppb also showed appropriately decreasing exposure-response relationship at lower concentrations. At 0.1 to 0.001 ppb, exposed *Daphnia* showed decreased fecundity, skewed sex ratios, increased neonate deformity, and adult mortality.

Basic Information

Title:	Groundwater Modeling: Semi-analytical Approaches for Heterogeneity and Reaction Networks
Project Number:	N-4
Start Date:	7/1/2000
End Date:	6/30/2001
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.
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Gerald R. Eykholt

Publication

1. Eykholt, G.R., and Lin Li (2000), "Fate and transport of species in a linear reaction network with different retardation coefficients," J. Contam. Hydrol. 46: 163-185.
2. Lin LI, Gerald R. Eykholt, and Craig H.Benson, (2001), Reactive Transport from Path3D: A Stream Tube Approach for Heterogeneous Aquifers. American Geophysical Union Spring Meeting, Boston, May 29-June 2, 2001.

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

Dr. Gerald Eykholt, Department of Civil and Environmental Engineering, University of Wisconsin-Madison

Problem and Research Objectives

Modeling contaminant transport and fate in heterogeneous aquifers is currently feasible, but generally time consuming. Available numerical packages take long computer run time. In order to fasten the multiple reactive species transport simulation, a new modeling approach needed to be developed in this study.

There are three main objectives to the study: 1) Test and demonstrate the performance of linear operator methods for simulations of first-order decay reactions in heterogeneous aquifers. Compare solutions and run times with MT3D and analytical approximations. 2) Test and demonstrate irregular sources, reversible reactions, and mixed-order kinetics processes. 3) Explore inverse modeling exercises to determine whether linear response factor methods can provide acceptable estimates of contaminant fate parameters, such as those that might be estimated in a monitored natural attenuation study.

Methodology

This approach makes use of properties of a linear system, working with decoupled reaction and sorption processes and mixing processes described by residence time distributions (RTDs). RTDs are abstracted from Path3D particle-tracking results and additional temporal and spatial dispersion (not caused by aquifer heterogeneity) is ignored. Reactions, including first order reactions and linear, reversible sorption, are applied through analytical transfer functions (called kinetic response functions). Convolution can then be applied to determine contaminant concentrations at monitoring points, using the RTDs determined from Path3D, kinetic transfer functions (expressed analytically), and expected trends of the source concentration.

Principal Findings and Significance

This modeling approach has been extensively tested in linear reaction system at heterogeneous aquifer. Various heterogeneity in hydraulic conductivity and reaction rates among multiple component reactions were used. Compared to other analytical models at homogeneous aquifer, the semi-approach model is identically matched. The model achieves thousands times faster than the numerical package, RT3D in heterogeneous aquifer. The results of comparison between this modeling approach and RT3D are very well, except the numerical dispersion of RT3D at large Peclet number. This study developed a computationally efficient model for multiple species reactive transport in heterogeneous aquifer. It is valid for linear reaction systems, i.e., linear sorption isotherm and first order reactions rates among components. The work is expected to be applicable to problems of monitored natural attenuation, reactive barriers, and other systems, dealing with complex reactions and heterogeneous aquifers.

Basic Information

Title:	Removal of As(III) and As(V) in Contaminated Ground Water with Thin-Film Microporous Oxide Adsorbents
Project Number:	N-03
Start Date:	1/1/2000
End Date:	1/1/2000
Research Category:	Water Quality
Focus Category:	Treatment, Toxic Substances, Water Quality
Descriptors:	Adsorbents; arsenic treatment; arsenic removal; oxides; nanoparticles
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Marc A Anderson

Publication

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

Prof. Marc A. Anderson, University of Wisconsin - Madison

Problem and Research Objectives:

Problem Statement: There is an epidemiological problem caused by elevated concentrations of arsenic in ground waters used for irrigation, human consumption, and industrial activity. Generally, both acute and chronic toxicity are caused by inorganic arsenic species that can be ingested, inhaled, or absorbed through the skin and subsequently incorporated into body organs. The present maximum contaminant level for arsenic in drinking water in the U.S. is 0.05 mg/L. Canada has lowered its level to 0.025 mg/L because of suspected cancer risks. A recent national drinking water survey indicated that particulate arsenic was more abundant than reported in earlier studies. As a result, the Environmental Protection Agency is reevaluating its arsenic regulations. Problems also exist in Wisconsin. Wells monitored by the Department of Natural Resources show arsenic exceeding the enforcement standard in 50 samples and the preventative action limit in 204 cases. Studies of well waters in northeastern Wisconsin have found arsenic concentrations up to 15 times the drinking water standard! If this standard is lowered, many municipal treatment facilities and individual homes could become non-compliant.

Research Objectives: Our primary objective is to develop high surface area microporous oxides as adsorbents for removing both As(III) and As(V) from water supply systems. These materials would be applied as thin-film coatings on inert supports for use in stand-alone column treatment or would be added directly to sand filters to enhance arsenic removal.

Methodology:

Stable suspensions of nanoparticulate boehmite (AlOOH) were synthesized using procedures developed in our laboratories. To investigate the maximum arsenic adsorption capacity of this material, a series of batch adsorption tests were conducted with these particles at several pH values using 0.02 M KNO_3 as the background electrolyte and an initial concentration of arsenic of 20 mg/L. The adsorption data were analyzed by Langmuir isotherm over a range of adsorbent from 0.04 g/L to 1 g/L. The pH was adjusted by adding appropriate amounts of HNO_3 and NaOH. After 24 hours, the boehmite particles were separated from the supernatant using a Millipore Centriocon® Plus-20 centrifugal filter. The molecular weight cut off for this device was 15,000 nominal molecular weight limit(NMWL). Particle size and surface charges were measured by a Malvern 3000 Zetasizer, which employs photon correlation spectroscopy(PCS) methods for these analyses. The arsenic concentration was measured by ICP-AES. The detection limit of this device is 20 ppb for arsenic.

Principal Findings and Significance:

The primary arsenic species of concern are arsenate (+5 oxidation state) and arsenite (+3 oxidation state). Because arsenate has a higher oxidation state than arsenite, arsenate displays more covalent behavior (Ebbing, 1993)[1], which makes arsenite harder to control by adsorption. Arsenate is present in the environment as negatively charged oxyanions ($pK_1 = 2.20$), whereas arsenite only forms negatively charged oxyanions at pH values of ca. 9 ($pK_1 = 9.22$). Adsorption

[1] D. Ebbing, General Chemistry 4th Edition, Houghton Mifflin, Boston MA (1993).

of these arsenic species would be favored on oxide surfaces that remain positively charged at pH values as high as possible. Of the available materials, boehmite (AlOOH) was chosen because its isoelectric point (iep – the pH at which the surface charge of the particles is zero) was reported to be higher than for the other candidates. The measured iep of our boehmite particles was 9.7. Below this value, the boehmite particles will be positively charged.

When the batch adsorption study was performed, maximum adsorption was observed at 1.17 mmol/g for arsenate at pH 4.5 and 0.09 mmol/g for arsenite at pH 9.3. The highest arsenate adsorption is expected at a low pH because of the electrostatic attraction between arsenate oxyanions and the positive boehmite surface. This adsorption then decreases as the pH increases. On the other hand, arsenite adsorption gradually increases as the pH increases to 9.3 because significant numbers of negative arsenite oxyanions only form when the pH approaches 9.22, the first pK for arsenite. At pH 9.3, both arsenite and arsenate show almost the same adsorption efficiency. Adsorption of both anions decreases at pH values above the iep for boehmite, pH 9.7, because the negative surface charge of boehmite repels negatively charged arsenic ions. For boehmite, the most effective pH range for removing both arsenite and arsenate appears to be ~8.5-9.5, which is higher than the typical pH of source waters (~6-8). These results show tjhat adsorption may not be very effective at removing both arsenite and arsenate at the typical pH of a source water.

Since removing both arsenate and arsenite by adsorption on boehmite is limited, we are developing a multi-component coating material consisting of boehmite mixed with titanium dioxide (TiO_2) particles. Titanium dioxide is a strong photocatalyst when illuminated with UV light, so we expect to oxidize arsenite to arsenate on the titanium dioxide particles and then adsorb the arsenate on the boehmite particles. If this test is successful, we will conduct column tests with this newly developed material.

Basic Information

Title:	Remediation of Soil and Groundwater Using Effectively and Ineffectively Nodulated Alfalfa
Project Number:	N-10
Start Date:	7/1/2000
End Date:	6/30/2002
Research Category:	Water Quality
Focus Category:	Agriculture, Nitrate Contamination, Water Quality
Descriptors:	phytoremediation, groundwater contamination, soil nutrients, alfalfa cultivars
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Nancy Turyk, Byron Shaw

Publication

Remediation of Soil and Groundwater Using Effectively and Ineffectively Nodulated Alfalfa

Nancy Turyk and Byron Shaw, College of Natural Resources, University of Wisconsin-Stevens Point and Michael Russelle, USDA Agricultural Research Service, St. Paul, Minnesota

Problem and Research Objectives:

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 will show whether normal, N2-fixing (effectively nodulated) alfalfa or special non-N2-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. The primary objective of this study is 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. The project is a cooperative venture between University of Wisconsin-Stevens Point, USDA's Agricultural Research Service, Portage and Waupaca County Land Conservation Districts, the Tomorrow/Waupaca River Priority Watershed Project, and the Dopp family farm.

Methodology:

Sample Plot Design: Location of alfalfa research plots were established parallel to the direction of groundwater flow. A randomized complete block design structure was employed. The block consists of four 30 x 61 m plots. Plots consist of Agate and Saranac (standard fixing alfalfa), and Ineffective Agate and Saranac (cultivars selected to inhibit nitrogen fixation). Both cultivars are selected for enhanced rooting depth and winter hardiness.

Groundwater Monitoring: We have installed a series of monitoring well nests both up and down gradient of the study plots. Sampling frequency is monthly through the growing season, from March through October, plus a January sampling, totaling nine sample dates per year. Samples are obtained from wells using a peristaltic pump and polypropelene tubing. Water table depth in each well is recorded during the sampling sessions. Samples are field-filtered in-line using .45 u membrane filters; bottles are unpreserved as well as preserved with H2SO4 and transported on ice to the laboratory. Analyses include NO2+NO3-N and Cl- on all sample dates plus two samples per year for total reactive P, K and NH4-N. Groundwater analysis is being conducted by UWSP's state certified Environmental Task Force Lab.

Herbage Yield: Eight samples will be obtained per plot from $1m^2$ areas located in areas of contrasting soil fertility at each of 3 or 4 normal alfalfa harvest times per year (depending on growing season conditions). Alfalfa and weeds (when present) are separated, oven dried, ground, and analyzed for total N and total P concentration. Nutrient content (yield) will be determined by multiplying concentration by dry matter yield in each sampling site.

Topsoil samples (0-15 cm) taken in the same microplots at each harvest will be used to relate soil fertility to herbage nutrient yield. We will determine total N and Bray-extractable P in each soil sample, and then extrapolate the results from the sampling sites to the entire plot area using mapped soil fertility characteristics. In this way, we can produce large-scale estimates of N and

P uptake over this highly (and typically) heterogeneous site. Soil samples are being analyzed at the USDA-ARS laboratory located in St. Paul, Minnesota.

Principal Findings and Significance:

We are anticipating seeing differences in nutrient uptake between Effective and Ineffective alfalfa. We hope the alfalfa uptake will be great enough to significantly reduce infiltration of contaminants to groundwater and possible removal from groundwater. If we obtain positive results these alfalfa cultivars should be utilized at other similarly contaminated sites to see if results are reproducible. In addition, this study site can be used as a demonstration site for farmers and agricultural agents working with medium and coarse textured soils. Results will be disseminated in peer-reviewed journals.

Information Transfer Program

Basic Information

Title:	Information Transfer Program
Start Date:	3/1/2000
End Date:	2/28/2001
Descriptors:	Information transfer, library, web, reports
Lead Institute:	University of Wisconsin Water Resources Institute
Principal Investigators:	Anders W. Andren, James P. Hurley

Publication

1. University of Wisconsin Water Resources Institute. 2000. Water Resources 2000: Challenges For The New Century. American Water Resources Association. Wisconsin Section 24th Annual Meeting. Green Bay, WI.

Information Transfer Program

JoAnn M. Savoy, Anders W. Andren, James P. Hurley
University of Wisconsin Water Resources Institute

Library Collection and Facilities

The Water Resources Institute Library (WRIL) maintains a specialized collection of over 21,000 water-related publications and more than 35 journals and 135 newsletters. The collection covers all major topics in water resources, including the water cycle, water conservation, water management, water quality and quantity, point and nonpoint water pollution sources, water law, and aquatic life. The collection is particularly strong in Wisconsin and Great Lakes water resources issues, groundwater protection, wetlands issues, and the impacts of agricultural chemicals. Access to additional water-related indices, databases, full-text journals and eBooks is gained through the University of Wisconsin Electronic Library, Dialog, and the Internet. The Library also maintains a Web Site (*http://wri.wisc.edu/library*) which serves both as a portal to water-related information on the Web and a guide to the library.

The Library's primary clientele is Wisconsin citizens – particularly University of Wisconsin faculty, staff, and students, state government employees, and business and industry. The Library lends documents to non-Wisconsin residents, but only provides other services as time and resources permit. The Library is staffed and open to the public 9 a.m. to 4:30 p.m., Monday through Friday. The entire collection is included in Madcat, the University of Wisconsin online catalog. Anyone with access to the Web can easily search the collection by author, title, or subject at http://madcat.library.wisc.edu/ . The collection is also available online in the Committee on Institutional Cooperation (CIC) Virtual Catalog and the Online Computer Library Center's (OCLC) WorldCat.

The WRI Library is one of only two libraries established under the State Water Resources Research Institutes Program. The Library collection, electronic resources and services are built upon long-term cooperation and coordination with other University of Wisconsin and area libraries. Library staff participate in campus library groups, the Special Libraries Association, the Wisconsin Library Association, and other library organizations. Through this coordination, the librarian has built a unique collection and specialized services that do not duplicate the collections or services of other area libraries.

The WRIL depends on the resources of the UW-Madison Library System for access to many online water-related indices, databases, full text journals and documents. Also, the UW-Madison General Library System partially supports WRI Library participation in MadCat, the University online catalog. In return, WRI Library makes a unique collection of water-related documents available to the campus community and contributes toward making "Water Resources Abstracts" available online on campus.

The Library has also long cooperated with the Wisconsin Department of Natural Resources (WDNR) Library which depends on the library to collect water-related technical reports. To this end, WDNR contributes funds each year to support the

purchase of materials and the provision of library services to DNR personnel. Since August 1990, the Library has circulated and served as a depository for the reports of the WDNR Groundwater Management Practice Monitoring Grant Program. The Library has added these reports to Madcat, listed them in “Recent Acquisitions”, and provided staff to put project summaries on the Web.

Library Services: Staff will help users find information, use electronic resources, perform subject searches, answer reference questions, and obtain materials through interlibrary loan. The Library also distributes "Recent Acquisitions and Web Sites of Interest," monthly to approximately 300 university personnel, state agency staff, researchers, consultants, libraries, private organizations and interested citizens. The WRI Library Web Site (*http://wri.wisc.edu/library)* includes information about the library and library policies, links to renew and request books, an electronic reference service (AskWater), back files of "Recent Acquisitions and Web Sites of Interest", links to the UW online catalog and databases, guides to finding water-related information and jobs on the Web, and listings of water curricula and water-related tourism books.

Library Usage: Use of the WRI Library by faculty, students, federal agencies, private consulting firms, and others interested in water continues to increase. Although book circulation statistics for most libraries are declining due to greater use of the Web for information, WRIL circulation increased 16% over last year. During the period 3/00 – 2/01, library staff responded to 1250 requests for individual titles and subject searches. More than 630 UW-Madison faculty, staff, and students, WDNR staff, private consulting organizations, and members of the public contacted the WRIL last year.

Library circulation and use statistics only tell part of the story. Web Sites are becoming an important part of library services. Usage of the WRIL Web Site has also grown steadily over the reporting period. In March 2000, 757 people visited the Site or an average of 24 people per day. By February 2001, the number of visits had increased to 1148 or 41 visitors per day. Visitors also spent more time on average. The average visit in March 2000 was about 10 minutes long. By February 2000, the average was 15 minutes long.

New Library Activities: During the period 3/00-2/01, the Library staff added the following to the Web Site at *http://wri.wisc.edu/library*.

> "Guide to Finding Water-Related Information on the Web" (http://wri.wisc.edu/library/subject.html). includes links to water-related databases, journals, newsletters, professional organizations, laws, funding sources, etc. Although some resources are available only to UW-Madison faculty, staff, and students, many are available free to everyone on the Web.
>
> “Guide. To Finding a Water-Related Job on the Web" (http://wri.wisc.edu/library/finding_jobsall.html) contains links to Web Sites with information on deciding what you want to do, writing a resume, and interviewing tips as well as job postings.

"The Water Education Place" (http://wri.wisc.edu/library/WaterCurricula/index.html) is a guide to the WRI curricula collection and Web Sites for teachers and students.

Library staff have also begun to add the collection to the UW-Madison Circulation System so that anyone at any UW campus can check out WRIL books online. The books will be sent to the requester through a state-wide delivery system.

Water Resources Institute Publications

Results of WRI-supported research are published in a variety of forums. Much of the WRI research ultimately appears in refereed professional journals, although results of WRI research can also be accessed as technical reports, conference proceedings and abstracts, book chapters, or as dissertations and theses. A list of all publications resulting from WRI-supported research was added to the WRI Web Site during the past year. Copies of WRI publications are distributed upon request. A highlight during the past year was the production of the University of Wisconsin Water Resources Institute Program Directory. This directory provides a brief history of the Wisconsin WRI program, briefly describes all research projects supported through the WRI, and gives a general overview of the WRI program.

Water Resources Institute Web Site

The WRI has maintained a Web site since 1995 to provide an efficient means for the transfer of water-related information. The site provides information about WRI programs and staff, water resources funding opportunities, conference information, project summaries, links to other water-related sources, and information about the WRI Library.

During the past year, WRI staff added the following to the Web Site:

Water Expertise Database (http://wri.wisc.edu/wriexpertise/index.asp) is a comprehensive listing of more than 800 water professionals in Wisconsin. It is searchable by last name of expert, area of expertise, and/or research interest.

WRI Publications (http://wri.wisc.edu/Publications/66-00pubs.html) is a listing of publications based on research supported by the Wisconsin Water Resources Institute from 1966-2001. Copies of publications can be obtained from the Library.

The Wisconsin Groundwater Research and Monitoring Project database (http://wri.wisc.edu/wgrmp/wgrmp.htm) was added to the Web. This Site presents summaries of groundwater research/monitoring projects completed since 1989. It can be browsed by title or broad subject classifications. Copies of the full reports are available from the Library.

The WRI Water Links (http://wri.wisc.edu/links.html) were updated to include links to Wisconsin water research, groundwater, State Government, and graduate education programs.

Use of the WRI Web Site has steadily increased from February 2000 through March 2001. In March 2000, 2885 people visited the Site or an average of 93 people per day. By February 2001, the number of visits had increased to 3674 or 131 visitors per day. Visitors also spent more time on average. The average visit in March 2000 was about 21 minutes long. By February 2000, the average visit was 27 minutes long.

Conferences, Meetings and Presentations

The Wisconsin Water Resources Institute co-sponsored the American Water Resources Association -- Wisconsin Section Annual Meeting on March 23 and 24, 2000 in Green Bay, Wisconsin. This meeting provided a forum for nearly 50 papers that covered a variety of water-related subjects and were presented during six technical sessions and a poster session. This meeting is unique because it encourages students to present papers or posters describing their original research. Awards are presented to the student papers judged to be "best." At the meeting, the WRI librarian in cooperation with Steenbock Agricultural Library staff made a presentation on "Finding a Water-Related Job on the Web".

The Wisconsin Water Resources Institute is also co-sponsoring the 2001 annual meeting of the Midwest Groundwater Conference. The WRI web site serves as the home for information on the conference and contains links for on-line registration and abstract submission. The institute is also responsible for all promotion and publication activities of the conference, to be held in Madison in late October 2001.

The Assistant Director for Research has also been named co-chair (along with D. Krabbenhoft, USGS-Middleton) of the Seventh International Conference on Mercury as a Global Pollutant. The conference, which attracts approximately 800 international researchers and mangers, will be held in Madison in summer of 2005.

USGS Summer Intern Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	4	5	0	11	20
Masters	0	2	0	8	10
Ph.D.	4	1	0	3	8
Post-Doc.	1	1	0	2	4
Total	9	9	0	24	42

Notable Awards and Achievements

Wes Dripps, a Ph.D. student in the Department of Geology and Geophysics at UW-Madison won the following awards for his work supported Section 104 G funding ("The Spatial Variability of Natural Groundwater Recharge" to M. Anderson): - American Geophysical Union, Hydrology Section Outstanding Student Paper Award, Spring 2001 annual meeting - American Geophysical Union, Hydrology Section 2000 Horton Grant - SW Bailey Distinguished Graduate Fellowship, Dept. of Geology and Geophysics, and The Graduate School, UW-Madison, 2000-01.

James Hurley, Assistant Director of Research, University of Wisconsin Water Resources Institute and Research Water Chemist for the Wisconsin Department of Natural Resources, was awarded the 2000 Steve Serns Research Award from WDNR for outstanding contributions to research.

The University of Wisconsin Water Resources Institute was chosen to co-host the Seventh International Conference on Mercury as a Global Pollutant. The conference, which attracts over 800 international experts, will be held in Madison, WI in August 2005.

Tim Eaton, a Ph.D. student in the Department of Geology and Geophysics at UW-Madison won the award for best student poster at the 37th annual meeting of the American Institute of Professional Geologists conference in Milwaukee (October 2000) for his poster "Importance of a sparse fracture network in the Maquoketa confining unit: evidence for preferential flowpaths". He is funded through Section 104 B on the project "Hydraulic Conductivity and Specific Storage of the Maquoketa Shale (Wang, Bradbury and Eaton)"

Publications from Prior Projects