University of Wisconsin Water Resources Institute
Annual Technical Report
FY 2003

Introduction

Research Program

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

Basic Information

Title:	Role of the Hyporheic Zone in Methylmercury Production and Transport to Lake Superior
Project Number:	2003WI45B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Geochemical Processes, Toxic Substances, Non Point Pollution
Descriptors:	mercury, sediment-water interface, hyporheic zone
Principal Investigators:	David Armstrong

Publication

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

D. E. Armstrong, University of Wisconsin-Madison
Funding Agency: UWS Groundwater Research Program

Project duration: July 2002 – June 2004

Project Description

This investigation focuses on the role of the hyporheic zone in the production and transport of methylmercury into surface waters. The objectives are: (1) to measure methylmercury levels and rates of mercury methylation and demethylation in contrasting hyporheic zones, and (2) to evaluate the potential flux of methylmercury from these zones through measurements of hydraulic conductivities and gradients. We have selected the Allequash Creek watershed as a site for investigation of hyporheic zones processes. This site, located in Vilas County, Wis., is also within the investigation areas for the UW-Madison NSF Long Term Ecosystem Research program and the USGS Water, Energy, and Biogeochemical Budgets program. This enables collaboration with scientists from these groups and use of USGS background information and groundwater sampling sites installed at the site. Measurements will include methylation and demethylation rates, mercury and methylmercury concentrations, and water levels in hyporheic zone waters. Measurements will be made seasonally during approximately three sampling trips per year over the two-year project period.

Project Update

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

In August 2003, use at the research site of a specifically constructed, trace metal-clean, close interval differential sampler allowed for sampling of mercury species concentrations in pore waters within the hyporheic zone sediment at five discrete depths to 15 cm. Sediment cores taken along with the pore water samples yielded additional insight into the partitioning of mercury species among the sediment and water phases. Additional sampling occurred in October and November of 2003, and April and June of 2004.

To assess the rates of methylation and demethylation, incubations using isotopically enriched mercury and methylmercury components to spike core samples at low concentration levels occurred in November 2003 and April 2004. In these experiments, isotopic MeHg 199 and inorganic Hg 201 injected into intact duplicate sediment cores and incubated at both 5 and 20 C for 12 hours provided contrasting samples for the determination of methylation and demethylation rates.

Use of a microelectrode apparatus for real-time determination of temperature, dissolved oxygen, pH, redox, and sulfide concentration within the hyporheic pore waters began with the April 2004 sampling event. Use of a HydroLab for collection of pH, specific conductivity, redox, temperature and dissolved oxygen continued as in 2003 on sampled wells and piezometer nests. Well water level measurements and piezometer nest head determinations continued during all sampling events for potential flux determinations.

Final analyses and data interpretation of samples collected through June 2004 are in process and will be included in the final project report.

Arsenic Contamination in Groundwater in Southeast Wisconsin

Basic Information

Title:	Arsenic Contamination in Groundwater in Southeast Wisconsin
Project Number:	2003WI47B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Hydrogeochemistry, Toxic Substances, Water Quality
Descriptors:	arsenic, groundwater, trace metals
Principal Investigators:	Jean Bahr, Madeline Beth Gotkowitz

Publication

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

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

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

Project Update

Groundwater Chemistry Sampling and Analysis

To date, 23 water samples from 16 sites have been collected. Additional sources of groundwater chemistry data include the Wisconsin Department of Natural Resources database and a private well sampling program conducted in cooperation with the Geneva Lake Environmental Agency. Approximately 10% of the wells in the study area have arsenic concentrations exceeding the new USEPA maximum contaminant level of 10 ppb. Maximum arsenic concentrations are on the order of 80 ppb. The groundwater chemistry data support previous observations that elevated arsenic concentrations occur in both glacial and shallow bedrock wells. The arsenic is dominantly As (III) (65%-100%).

Arsenic is commonly associated with oxide minerals. Under reducing conditions, oxide minerals are unstable, and arsenic may be released to ground water due to reductive dissolution oxide minerals. Groundwater chemistry data from southeastern Wisconsin show a negative correlation between arsenic and oxidation/reduction potential. This trend suggests that arsenic is more mobile under reducing conditions and indicates that reductive dissolution of oxide minerals may lead to the observed aqueous arsenic concentrations.

The groundwater chemistry data indicate that arsenic concentrations are higher in deeper wells and that more reducing conditions exist in deeper wells. Additionally, the major ion chemistry of deeper wells is different from the major ion chemistry of shallower wells. These observations indicate that different geochemical processes are occurring at different depths in the groundwater flow system and that arsenic is more mobile deeper in the system.

In August 2002, a monitoring well was installed in an arsenic-impacted area. Four samples taken from the monitoring well over the past 2 years show relatively constant arsenic concentrations. Time-series sampling was also conducted during a pump test in an arsenic-impacted well. Very little change in water chemistry was seen in 13 samples taken over 70 well volumes during this pump test. This temporal stability suggests that processes local to the well bore have little influence on arsenic concentrations.

Collection and Analysis of Geologic Samples

Rotosonic drilling and monitoring well installation were completed in an arsenic-impacted area. During drilling, 330 ft of core were collected. A detailed description of the core has provided a valuable record of the stratigraphy in the study area. One hundred eight samples from the core have been analyzed for whole rock geochemistry. Arsenic concentrations range from less than detection to 5 ppm in most samples. Higher concentrations of arsenic occur in an organic horizon in the glacial aquifer (21 ppm) and in residuum (weathered bedrock) (15 ppm) at the base of the glacial aquifer. The outwash and upper till units contain relatively little arsenic, while lower till units have low to moderate arsenic concentrations (less than detect to 7 ppm). Based on these data, there are three possible sources of arsenic in the core: 1) organic material, 2) residuum, and 3) low levels of arsenic dispersed throughout the clay and silt units in the glacial deposits. Although samples from the organic horizon had the highest arsenic concentrations, we do not believe this horizon is a significant regional source of arsenic to groundwater. Locally, such organic layers may be important As sources. However, the organic material was most likely deposited in small wetlands situated in topographic lows that are not laterally extensive. The Wisconsin Geologic and Natural History Survey provided additional funding for grain size analysis of 150 samples from the core and for carbon age dating the organic horizon (39,580 ± 800 ybp). X-ray diffraction is being used to identify potential arsenic-bearing minerals in the high-arsenic samples.

Hydrogeologic Characterization

A 19-hour pump test provided information about the groundwater flow system in the study area. During this test, approximately 20,000 gallons (73 well volumes) of water were discharged from a well that is open to the bottom of the Quaternary and top of the Silurian aquifers. Water chemistry was monitored in the pumped well, and water levels were monitored in two nearby wells: one open to the deep Quaternary (MW-1) and one open to the shallow Quaternary (MW-2). During the pump test, 5.2 m of drawdown occurred in MW-1, but there was no measurable change in water level in MW-2. These results indicate that there is little hydraulic connection between the upper part of the Quaternary aquifer and the lower Quaternary/upper Silurian aquifers.

Laboratory Experiments

A series of chemical extractions on select arsenic-rich core samples is being conducted. Each extraction is designed to dissolve specific minerals. The relative amounts of arsenic released during each extraction provide additional information about the solid phase associations of arsenic in the core samples. Preliminary results from these extractions indicate the majority of the arsenic is associated with oxide minerals.

We have developed preliminary plans for batch experiments. During these experiments, we will expose core samples to chemicals representative of compounds used by microbes to facilitate reduction and dissolution of oxide minerals. The amount of arsenic released from the core during these experiments will be indicative of whether reductive dissolution of oxide minerals may be responsible for the elevated arsenic concentrations observed in groundwater in southeastern Wisconsin. We plan to conduct these batch experiments after the sequential extractions are completed.

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

Basic Information

Title:	Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study
Project Number:	2000WI8G
Start Date:	9/1/2000
End Date:	8/31/2003
Funding Source:	104G
Congressional District:	WI-2
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Toxic Substances, Non Point Pollution
Descriptors:	mercury, hydrology, dissolved organic carbon, transport, wetlands, lakes
Principal Investigators:	james.p.hurley.1

Publication

1. Harris, R.C., J.W.M. Rudd, M. Amyot, C. Babiarz, K. Beaty, P. Blanchfield, A. (Drew) Bodaly, B. Branfireun, C.C. Gilmour, A. Heyes, H. Hintelmann, J. Hurley, C. Kelly, D. Krabbenhoft, S. Lindberg, M. Paterson, C. Podemski, K. Rolfhus, K. Sandilands, K. Scott, G. Southworth, V. St. Louis. 2001. METAALICUS: A Study to Determine the Relationship Between Mercury Deposition and MeHg Concentrations of Fish. Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments Sponsored by the U.S. Environmental Protection Agency. West Palm Beach, Florida. May.
2. Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott and V.L. St. Louis. 2002. Reactivity and mobility of new and old mercury in a boreal forest ecosystem during the first year of the METAALICUS study. Environmental Science and Technology. 36(23):5034-5040.
3. Babiarz C.L, J.P. Hurley, D.P. Krabbenhoft, C.C. Gilmour, and B.A. Branfireun. 2003. Application of ultrafiltration and stable isotope amendments to the partitioning of mercury in lake water and over land runoff. Science of the Total Environment. 304: 295-303
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6. Babiarz, C., J. Hurley, D. Krabbenhoft, T. Trinko, M. Tate, S. Chadwick, and D. Armstrong. An overview of the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States. American Water Resources Association. Minocqua, Wisconsin. February 27 & 28, 2003.
7. Babiarz, C., J. Hurley, D. Krabbenhoft, T. Trinko, M. Tate, S. Chadwick, and D. Armstrong. A Hypolimnetic Mass Balance of Mercury from a Dimictic Lake: Results from the METAALICUS Project. 12th International Conference on Heavy Metals in the Environment. Grenoble, France. May 26-30, 2003.
8. Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft, T. R. Trinko, M.T. Tate. Towards a Hypolimnetic Mass Balance: Results from the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS). Experimental Lakes Area, Canadian Dept of Fisheries and Oceans. June 24, 2003.
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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, U.S. Geological Survey, Kristofer R. Rolfhus, University of Wisconsin

Problem and Research Objectives

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

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

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

METAALICUS is a large, multidisciplinary, multi-investigator project, with an anticipated 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

1. Provide direct information on the effects of nonpoint atmospheric Hg deposition on bioaccumulation in predatory fish
2. Determine the relative importance of the watershed (including upland and wetland portions) and direct deposition in determining bioaccumulation of Hg in predatory fish of a lacustrine environment.
3. Provide (for the first time) direct measurement of ecosystem response times between Hg deposition and transport, and provide a direct comparison of the reactivity of Hg added via "new deposition" and Hg considered as the historic pool within the watershed.
4. To more definitively trace Hg processes and pathways at the ecosystem scale using 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 (nonradioactive) 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

Our Summer-Fall 2003 field season strategy had three new components compared to previous years of the METAALICUS study. One phase of our research has been to better understand the partitioning of mercury to various components in the waters from upland runoff, wetland runoff and in the lake. We have begun to use Chelex and DEAE resin techniques to characterize the relative strength of DOC ligands for mercury. The long term fate of Hg in this system may be dependent on the types and strength of binding to various ligands. Samples have been taken monthly at six depths that capture both the redox transition in the lake (~7m) and the gradient just above the sediment-water interface. In an effort to better understand the long term accumulation of Hg in the bottom sediments of our study lake, Lake 658, we have collected freshly fallen particulate matter in cylindrical chambers known as sediment traps. We have recently added a modified sediment trap in each basin to evaluate the concentration of pore water associated with freshly settled material. This is an extremely important value so that we can determine the diffusive fluxes out of sediments. The balance between sedimentation and remineralization (and flux out of sediments) determines the residence time of Hg in the system.

Our work also expanded within Lake 658 and we have refined our estimates of sedimentation processes in Lake 658. In particular we have synthesized data from 2001 and 2002 to better direct a hypolimnetic mass balance and better coordinate with other groups' data. Gross sedimentation to the sediment-water interface is captured by cylindrical sedimentation traps. Previous reports have documented that we could detect lake spike isotope in hypolimnetic traps within seven days of spiking, indicative of rapid particle partitioning in the epilimnion and transport to the sediment surface. We continue to estimate this downward flux on a biweekly basis in both basins of the lake. Figure 2 summarizes our initial estimates of HgT deposition to the sediment-water interface for 2001 and 2002. Gross sedimentation of ambient HgT was estimated at 22.8 and 18.1 ug/m^2 for the open water period, while rates for isotopic Hg were estimated at 5.9 and 5.4 ug/m^2. For the isotope, this represents about 25% of the spike.

Using Hg concentrations in solid phase sediments, coupled with Pb-210 and Cs-137 techniques for dating (P. Wilkinson, DFO) were able to provide the first estimates of net accumulation of ambient HgT in the bottom sediments of the west basin of Lake 658. The focus-corrected estimate of 12 ug/m^2-yr exceeds estimates of direct atmospheric deposition to the lake and when coupled with evasion losses, reflects the strong influence of the watershed in delivering ambient HgT to the lake. Gross sedimentation from the epilimnion exceeds net accumulation by about a factor of two, indicating that HgT is recycled at least once in the lake during the open water period. Over the next year, we hope to be able to estimate rates of net accumulation of the spike. We have also subcontracted with Dan Engstrom (Science Museum of Minnesota) to obtain additional cores in Lake 658 for dating and estimation of whole lake Hg accumulation.

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

Basic Information

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

Publication

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

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

Project duration: September 2001 – August 2003

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

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

Project Update

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

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

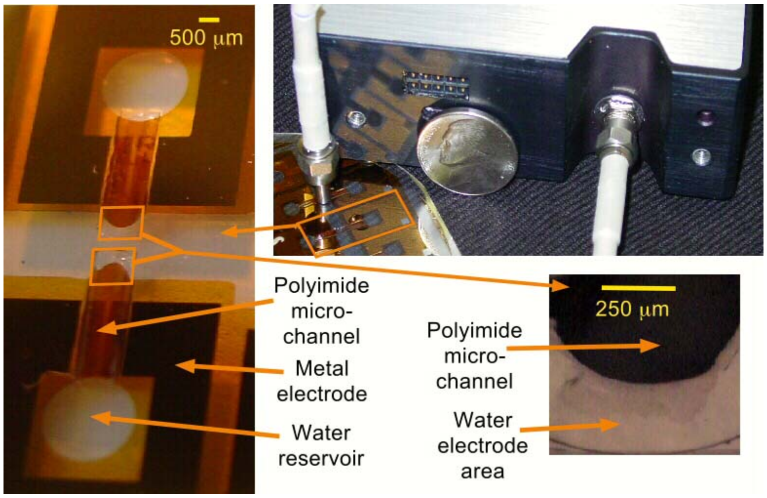

Fig. 1 Optical viewgraph of system and close-up view of the LEd-SpEC.

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

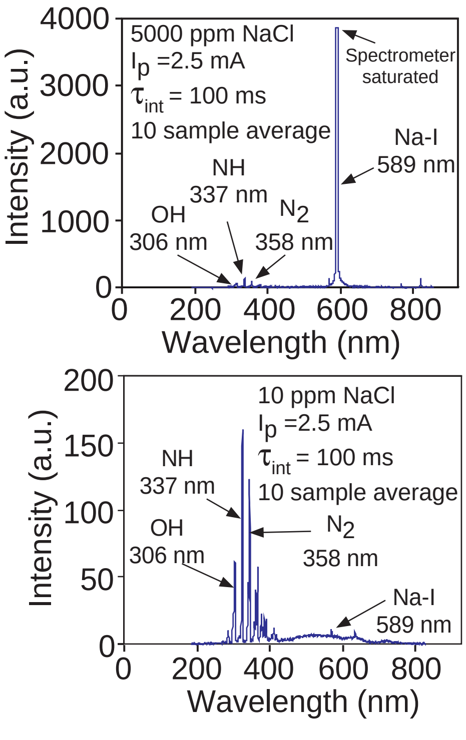

Fig. 2: Spectra for NaCl samples with concentrations of (a-upper) 5000 ppm, and (b-lower) 10 ppm.

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

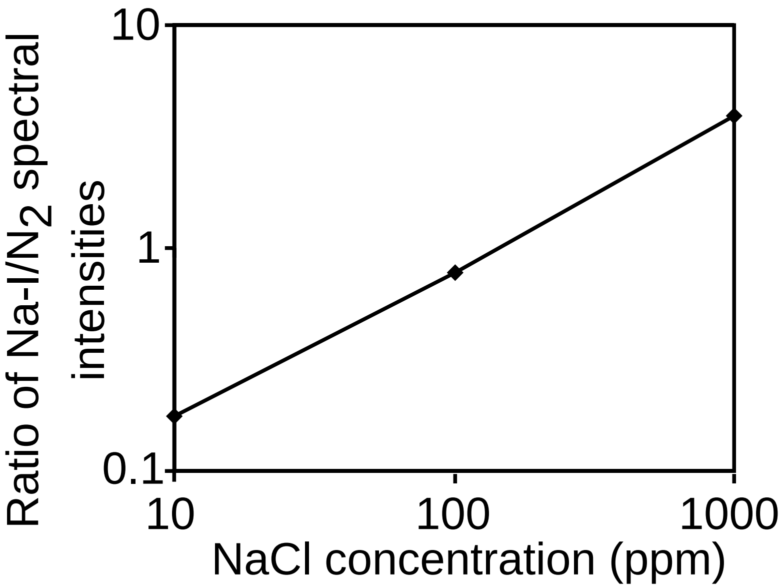

Fig. 3: Ratio of Na to N_2 spectral intensities as a function of NaCl concentration.

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

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

Field Evaluation of Raingardens as a Method for Enhancing Groundwater Recharge

Basic Information

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

Publication

1. Dussaillant, A. R., C. Wu, and K.W. Potter. 2004. Richards equation model of a rain garden. Journal of Hydrologic Engineering, ASCE. 9(3). pp. 219-225.
2. Dussaillant, A. 2002. Focused recharge in a rain garden: Numerical modeling and field experiments, Unpublished Ph.D. dissertation. Department of Civil & Environmental Engineering, University of Wisconsin-Madison. 139 pp.
3. Atchison, Duston, and K. W. Potter, "Bioretention Design Strategies Developed Using a Continuous Simulation Green-Ampt Model," poster presented at the 2003 Annual Water Resources Conference of the American Water Resources Association, San Diego, California, Hilton San Diego Resort, November 3-6, 2003.
4. Chow, Eric, and K. W. Potter, "Modeling Infiltration Practices at the Watershed Scale," poster presented at the 2003 Annual Water Resources Conference of the American Water Resources Association, San Diego, California, Hilton San Diego Resort, November 3-6, 2003.
5. Owen, Katherine E., Kenneth W. Potter, and Kent Brander, Does Development Type Influence Runoff Volume and Infiltration Performance? poster presented at the 2003 Annual Water Resources Conference of the American Water Resources Association, San Diego, California, Hilton San Diego Resort, November 3-6, 2003.

FINAL REPORT

FIELD EVALUATION OF RAIN GARDENS AS A METHOD FOR ENHANCING GROUNDWATER RECHARGE

Kenneth W. Potter
University of Wisconsin-Madison

This project was supported, in part, by General Purpose Revenue funds of the State of Wisconsin to the University of Wisconsin System for the performance of research on groundwater quality and quantity. Selection of projects was conducted on a competitive basis through a joint solicitation from the University and the Wisconsin Departments of Natural Resources; Agriculture, Trade and Consumer Protection; Commerce; and advice of the Wisconsin Groundwater Research Advisory Council and with the concurrence of the Wisconsin Groundwater Coordinating Council.

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PROJECT SUMMARY

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

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

Investigator: Kenneth W. Potter, Professor, Department of Civil & Environmental Engineering

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

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

Objectives: Before rain gardens can be widely implemented, they should be tested through carefully designed demonstration projects. The purpose of the proposed project was to construct an experimental rain garden for use in evaluating rain garden performance.

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

Three controlled experiments were performed during the period August 26 to September 1, 2002. In these experiments water was artificially supplied to the rain garden at a rate of seven gallons per minute until the ponding level reached 15 cm. (This supply rate corresponds to a rainfall rate of about one inch per hour when both roofs are contributing.) During the experiments soil water measurements were made with the TDR system, for comparison with model results.

Results and Discussion: The modeled and experimental results match well with respect to ponding times and overflow volumes. The model also does a reasonably good job of predicting the temporal pattern of soil moisture in the rain garden. However, the modeled volume of subsurface discharge from the rain garden was significantly larger than observed. It is believed that the discrepancy is due to leakage of water through the TDR access holes. This problem has subsequently been corrected.

Conclusions: An experimental rain garden has been constructed that allows measurement of all water budget terns except evapotranspiration. Experiments to date have demonstrated that a previously developed numerical model of rain gardens provides useful predictions of rain garden performance.

Related Publications: None.

Key Words: Rain gardens; artificial groundwater recharge

Funding: University of Wisconsin System

INTRODUCTION

For about half of Wisconsin, groundwater is the primary water source for human activities. In urbanized area, groundwater withdrawals significantly exceed groundwater recharge rates. For example, unit area groundwater withdrawals in the Madison area equal about 40 cm, an amount that is over twice the recharge rate. This does not generally pose a water supply problem, because groundwater readily migrates from the adjacent undeveloped area. However, groundwater pumping does cause environmental degradation.

Under undeveloped conditions, springs, wetlands, streams, and lakes and their associated ecosystems depend on a constant supply of water discharged from groundwater. This water has important advantages over storm runoff. Its flow rate and temperature are nearly constant and its quality is generally excellent. Storm runoff, on the other hand is episodic, causes thermal pollution, and contains sediment, nutrients, and other contaminants. Urban development greatly reduces the discharge of groundwater to water bodies and aquatic ecosystems and at the same time increases the discharge of storm runoff. The net result is severe environmental degradation, even at relatively low levels of urbanization. This has been observed in southern Wisconsin as well as in other parts of the United States (Booth and Jackson, 1997).

One potential strategy for mitigating the depletion of groundwater is to direct runoff from impervious surfaces to highly pervious ones. This has been done for many years on Long Island through the use of infiltration basins (Aronson and Seaburn, 1974). However, infiltration basins are often not successful in Wisconsin, partly because of the difficulty in constructing effective basins in a landscape with complex glacial stratigraphy and predominantly silty soils.

Rain gardens, sunken gardens that receive stormwater runoff, appear to be a viable alternative to infiltration basins. While the latter are generally sited low in a watershed, where infiltration can be hard to achieve, rain gardens are constructed adjacent to impervious surfaces and hence are dispersed throughout the watershed. Furthermore, the use of many rain gardens rather than one infiltration pond makes it possible to account for site-specific hydrologic, stratagraphic, and water quality conditions.

In a previous research project, we developed a numerical model (RECHARGE) for use in the evaluation and design of rain gardens (Dussailant *et al.*, in press). RECHARGE models a three-layered rain garden, consisting of a rooting zone, a high conductivity storage layer, and a lower layer representing the *in situ* soil. The model is based on the Richards Equation, and includes the major relevant processes of interception and depression storage, runon from an impervious area, ponding and infiltration through a layered soil, and evapotranspiration, in a continuous simulation mode where the surface water and soil water flow are coupled. Application of the model using hourly rainfall data from Madison for the period 1992 to 1997 indicates that a rain garden can recharge groundwater during the rainfall season at a rate equal to about twice the average annual groundwater recharge for undeveloped portions of southern. Furthermore, this can be achieved with a rain garden with area equal to 10-20% of the area of the contributing impervious surface.

These preliminary results are very encouraging. In the case of new developments it is certainly feasible to construct rain gardens with area equal to 10% of the connected impervious area. In many developed areas it is should be possible to add rain gardens. Even a rain garden with area equal to five percent of the impervious area provides substantial groundwater recharge. However before rain gardens can be widely implemented, they should be tested through carefully designed demonstration projects. The purpose of the proposed project was to construct an experimental rain garden for use in evaluating rain garden performance.

PROCEDURES AND METHODS

Construction of Experimental Rain Garden

The experimental rain garden was installed in the Dane County Parks Lussier Family Heritage Center in Madison, Wisconsin. It is essentially a lysimeter with a surface area of 5.4 m^2 and containing 6.5 m3 of soil enclosed within a polyethylene liner (Figure 1). This liner hydraulically isolates the garden soil from the surroundings, permitting direct measurement of deep percolation. The liner consists of 40 mil LDPE, shaped to conform to the excavation.

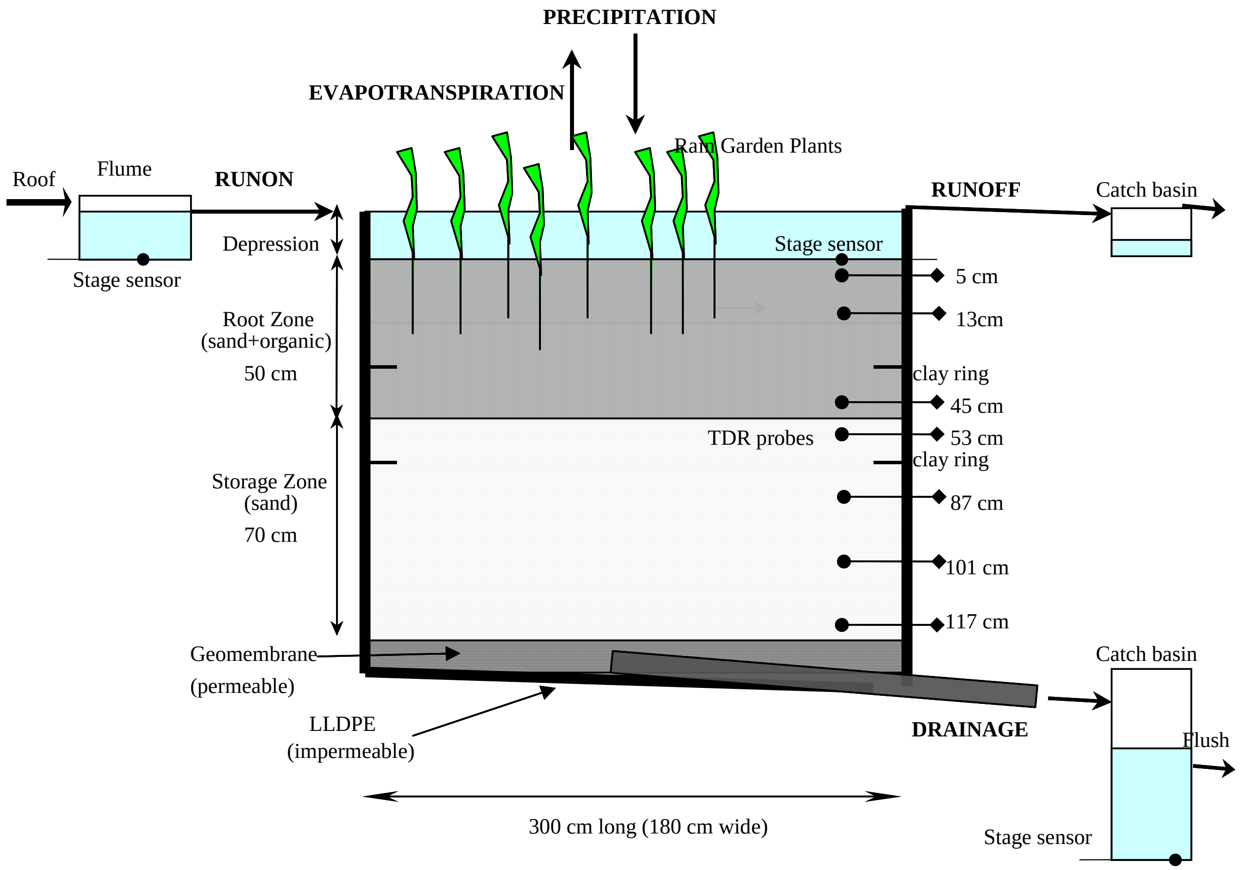

Figure 1. Conceptual diagram of experimental rain garden.

The root zone of the experimental rain garden is 50 cm deep, consisting of 60% sandy material and 40% peat moss, the latter providing moisture retention. A 70 cm storage zone underlies the root zone, consisting entirely of sand. The sandy storage zone is underlain by a permeable geomembrane consisting of a textile over plastic web. This allows for drainage without loss of sand. The storage zone soil was manually compacted using tampers, and two 3 cm-wide rings of benthonite clay were placed at depths of 30 and 70 cm to minimize sidewall preferential flow (Corwin, 2000).

Figure 2 shows a plan view of the rain garden and the flow distribution system. The rain garden is connected to two downspouts draining 50 m^2 of roof each. Valves allow for connection of one or both downspouts; hence the ratio of roof to rain garden area can be either five percent or 10%. Both downspouts are piped into a stilling basin filled with gravel so as to reduce turbulence and provide more favorable conditions for downstream flow measurement. Water entering the rain garden is distributed through a manifold of perforated pipes.

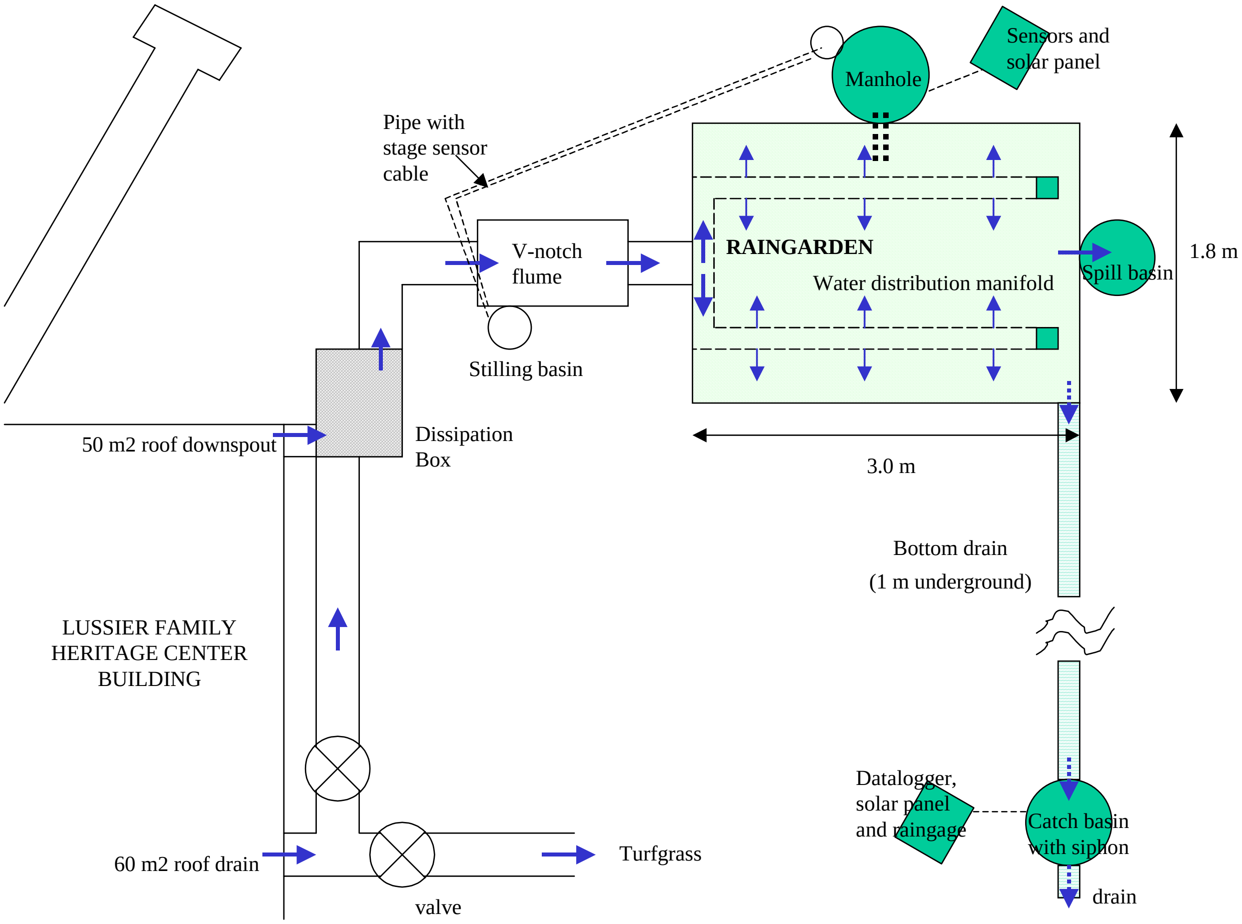

Figure 2. Conceptual plan view diagram of experimental rain garden.

Several sensor systems are used to measure terms of the water budget. Site rainfall is measured by a tipping bucket rain gauge located at the site. Flow from the roof downspouts to the rain garden passes through a prerated trapezoidal flume. A pressure transducer in the stilling well measures water levels in the flume. Another transducer monitors the depth of ponding in the rain garden so as to allow for measurements of changes in surface storage. Spillage from the rain garden is collected in a runoff catch basin, where it can be manually collected and quantified.

Time Domain Reflectometry (Benson and Bosscher 1999) is used to measure water storage in the rooting and storage zones of the rain garden. TDR probes were placed at seven depths (Figure 2) and connected to a SDM multiplexer, a Tektronix 1502B Time Domain Reflectometry (TDR) cable tester, and a CR-10 datalogger. The specific depths were selected so as to provide data spaced more densely close to interfaces and more sparsely in the bulk of the homogeneous layers. A manhole was installed on one side of the rain garden to provide access to the TDR probes.

Drainage from the rain garden flows through a drain to a PVC pipe that empties to a catch basin. This basin contains a siphon that empties when the basin accumulates 100 liters, triggering a switch, and a pressure transducer that monitors the changing head in the basin. These three sensors are connected to a CSI CR-10 datalogger powered by a solar panel and two rechargeable batteries.

The CR-10 dataloggers were programmed so as to read and store data as a function of water input frequency. Volumetric water content is computed assuming a Topp calibration (Topp, *et al.* 1980; Benson and Bosscher 1999).

Plant Selection

The plants chosen for the rain garden needed to be aesthetically pleasing and be able to withstand ponding times of one to two days. Plants meeting the second criteria were obtained from Kercher and Zedler (2001), which reports research on the tolerance of Wisconsin native plants to various hydrologic regimes. Table 1 provides a list of plants used in the rain garden.

Table 1. Experimental rain garden plants

Species name	Common name
Aquilegia canadensis	Columbine
Aster laevis	Smooth blue aster
Baptisia alba	White wild indigo
Baptisia bracteata	Cream wild indigo
Bolboschoenus fluvatilis	River bulrush
Caltha palustris	Marsh marigold
Iris versicolor	Wild iris
Liatris pycnostanchya	Prairie blazing star
Lobelia siphilitica	Great blue lobelia
Pycnanthemum virginianum	Mountain mint
Rosa blanda	Early fall rose
Silphium laciniatum	Compass plant
Zizia aurea	Golden alexanders

Calibration of Soil Water Characteristic Curves

About six months after the rain garden was constructed, soil cores were collected for estimation of soil water characteristic curves. Soil cores from the root and storage zones were prepared in the laboratory by compacting soil samples to the average dry unit density measured from undisturbed core samples. Porosity was estimated from bulk density laboratory determination. The soil properties were estimated using procedures described below.

Soil water characteristic curves, $\theta(h)$, were measured in a hanging column setup equipped with a Buchner funnel, specifically recommended for sandy soils (Khire 1995). Only desorption curves were measured. The data from the laboratory measurements and field data was fitted to the van Genuchten-Mualem equations (Mualem 1976; van Genuchten 1980), assuming no hysteresis.

Falling head permeameters were used to estimate saturated hydraulic conductivity, K_{sat}, using soil samples compacted to the same dry density as the undisturbed soil cores. The functions for unsaturated hydraulic conductivity, $K(h)$, and soil moisture capacity, $M(h)$, were determined using the parameters obtained from the curve fit for the soil water characteristic function.

Rain Garden Experiments

Three controlled experiments were performed during the period August 26 to September 1, 2002. In these experiments water was artificially supplied to the rain garden at a rate of seven gallons per minute until the ponding level reached 15 cm. (This supply rate corresponds to a rainfall rate of about one inch per hour when both roofs are contributing.) During the experiments soil water measurements were made with the TDR system, for comparison with model results.

Table 2 summarizes the conditions associated with each of the three experiments. No overspill was allowed - the inflow was shut off as soon as the ponding depth got to 15 cm. Water application rates were very similar (6.6-7.0 gal/min), but much less water was required in experiment 1 because the initial soil moisture was much higher.

Table 2. Experimental conditions

Condition	Experiment 1	Experiment 2	Experiment 3
Date	08/27/02	08/29/02	09/01/02
Initial condition	very wet	moderately wet	field capacity
Root Zone initial soil moisture (m^3/m^3)	0.10	0.10	0.13
Storage Zone initial soil moisture (m^3/m^3)	0.20-0.32	0.10-0.26	0.22
Inflow (gal/min)	6.8	6.6	7.0
Equivalent intensity at L=10% (cm/h)	2.51	2.44	2.54
Start time of application	16:00	15:00	12:17
End time of application	17:10	16:52	13:57
Water application time (h)	1.17	1.87	1.67
Total water applied (gal)	477.4	740.5	701.4

Model simulation input files were programmed so as to have the same initial condition as that given by the TDR data: soil moisture data was interpolated between probe nodes so as to provide a complete initial profile for RECHARGE runs. The spatial step used was 1 cm. We assumed a limiting bottom K_{sat}[3] of 5 cm/h for the rain garden during saturated conditions.

RESULTS AND DISCUSSION

Soil hydraulic parameters

Estimated densities and saturated hydraulic conductivities for the rain garden soils are given in Table 3. The estimated values are within the range common for sands. The storage zone is denser, which may partly explain the lower saturated hydraulic conductivity. The average value for each layer was used in the model simulations. Table 4 gives the parameters estimated based on the laboratory data and parameters based on both laboratory and field data.

Table 3. Soil parameters

Soil Characteristic	Root Zone Layer	Storage Zone Layer
Texture	60% sand, 40% peat moss	Mason's sand
Dry density (g/cm^3)	1.4	1.8
K_{sat} (cm/h)	80.4-85.9	26.9-47.0

Table 4. Mualem-van Genuchten parameters of the rain garden soil layers from laboratory data.

Soil Characteristic	Root Zone Layer	Storage Zone Layer
Texture	Sand with peat moss	Sand
α (cm^{-1})	0.033	0.032
n	3.594 (3.637)	3.250 (2.146)
$\theta_{residual}$	0.03	0.15 (0.10)
$\theta_{saturated}$	0.40	0.37
K_{sat} (cm/h)	83.1	36.9

Table 5 compares experimental parameters with the results obtained by model simulations. The model mimics the ponding times reasonably well (within a few minutes. In experiments 2 and 3, the model predicted that six percent and four percent of the input water would spill, while no spill occurred in the experimental rain garden.

Table 5. Experimental data vs. model parameters (values in parenthesis are the result of model simulations).

Parameters	Experiment 1	Experiment 2	Experiment 3
Start time of application	16:00	15:00	12:17
End time of application	17:10	16:52	13:57
Water application time (h)	1.17	1.87	1.67
Total water applied (gal)	477.36	740.52	701.40
Start time of ponding	16:53 (16:59)	16:08 (16:11)	13:20 (13:12)
End time of ponding	19:02 (18:59)	20:08 (19:54)	16:42 (16:58)
Total ponding time (h)	2.15 (2.0)	4.00 (3.7)	3.37 (3.7)
Ponded infiltration (cm/h)	5-6 (5.0)	5-7 (5.0)	5-7 (5.0)
Overspill runoff	no (no)	no (6% input)	no (4% input)
Max. ponding depth (cm)	15 (9.0)	15 (15.0)	15 (15.0)

Experiment 1 – August 27

Initial conditions were very wet - soil moisture in the root zone was around 0.1 m^3/m^3, while in the storage zone it was between 0.2 and 0.32 m^3/m^3. Figure 3 shows the TDR measurements compared with the RECHARGE model simulations. RECHARGE results follow the general data trends, particularly for the storage zone nodes. It does a poorer job with the more surficial nodes in the root zone, where it overestimates the time length of saturation by approximately half an hour, by prolonging the end time. For all the nodes, RECHARGE tends to react more rapidly to the wetting, reaching θ_{sat} approximately half an hour sooner than the data shows. This is likely due to uneven spreading in the rain garden.

The catch basin measured 0.66 m^3 at the end of the experiment, as compared to a model simulation of 0.87 m^3. This discrepancy is believed to be due in part to leakage through the TDR access holes.

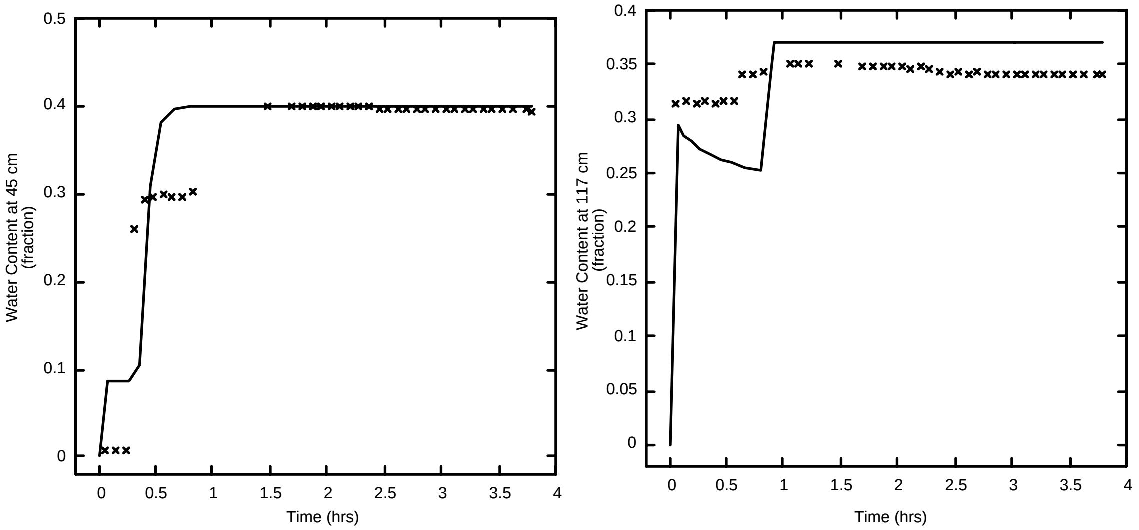

Figure 3. August 27 experiment: TDR field measurements of volumetric water content (X) compared to RECHARGE output, for probes in the root zone (45 cm) and the storage zone (117 cm).

Experiment 2 – August 29

Initial conditions were wet, since a ponding event had occurred two days before. RECHARGE results resemble data measurements very closely (Figure 4) for all probes. The model predicts the onset of saturation very accurately, and also the root zone desaturation, while underestimating the length of the saturation times in the storage zone.

The catch basin measured 1.05 m^3 at the end of the experiment, as compared to model simulation of 2.00 m^3.

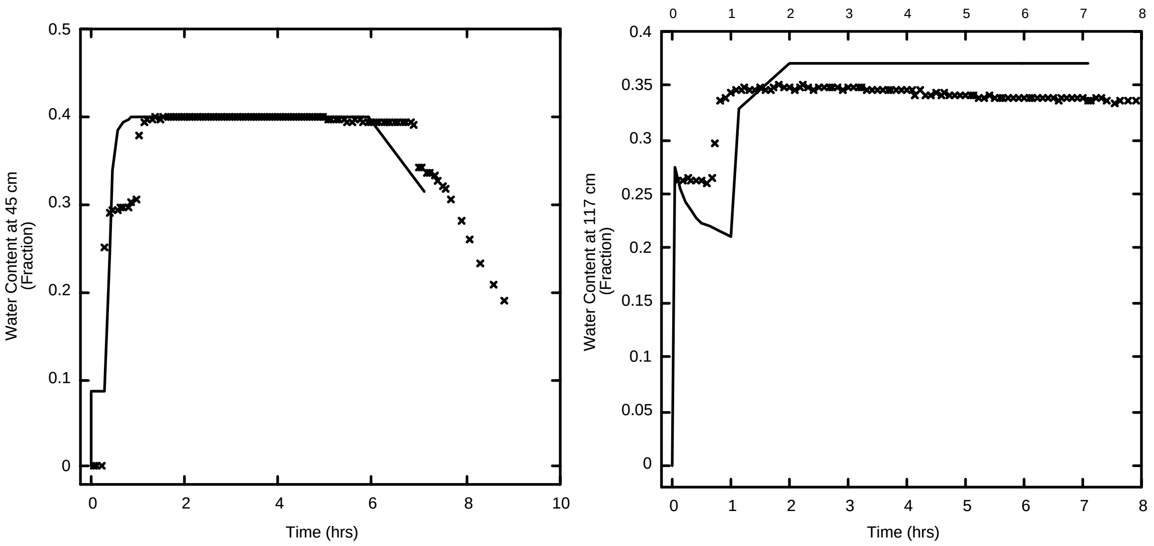

Figure 4. August 28 experiment: TDR field measurements of volumetric water content (X) compared to RECHARGE output, for probes in the root zone (45 cm) and the storage zone (117 cm).

Experiment 3 – September 1

Initial soil conditions for this experiment were approximately field capacity. RECHARGE matches the observed data well (Figure 5) for both the root zone and storage zone probe data. The model follows the data closely during the onset and the end of saturation for both soil layers.

The catch basin measured 1.03 m^3 at the end of the experiment, as compared to model simulation of 1.40 m^3.

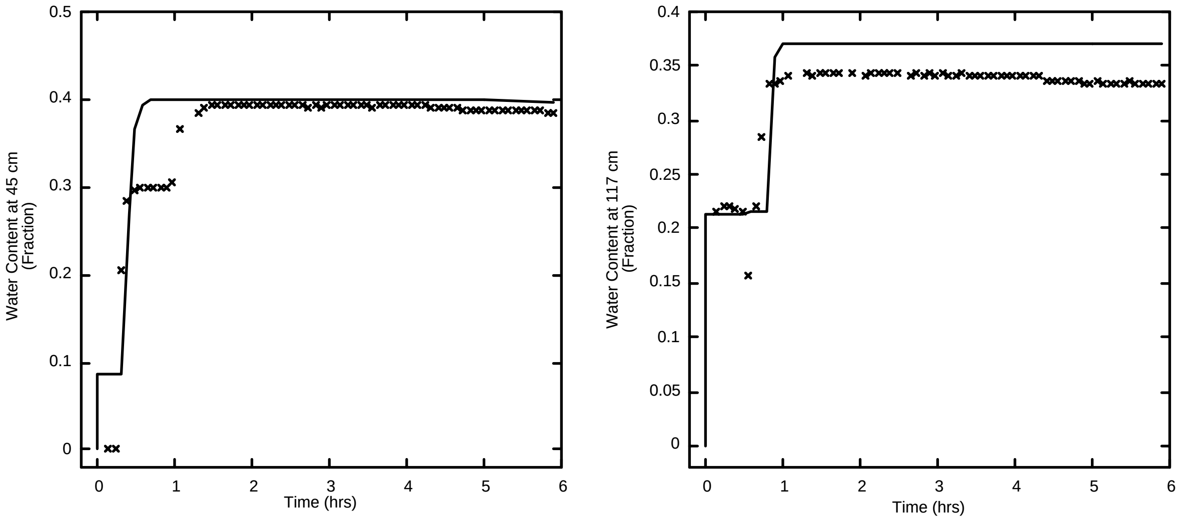

Figure 5**.** September 1 experiment: TDR field measurements of volumetric water content (X) compared to RECHARGE output, for probes in the root zone (45 cm) and the storage zone (117 cm).

CONCLUSIONS

An experimental rain garden has been constructed that allows for measurements of all water budget terms except evapotranspiration, which can be estimated by mass balance. Soil water measurements made during three experiments compare well to modeled values. However, the measured quantity of water draining the experimental rain garden was significantly less than the predicted amount, due mainly to leakage of water through the measurment ports. Once this problem has been corrected the experimental rain garden will be an excellent tool for understanding rain garden behavior and for testing numerical models.

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Removal of Arsenic in Groundwater Using a Novel Mesoporous Sorbent

Basic Information

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

Publication

1. Jang, M., E.W. Shin, J.K. Park, and S.I. Choi, Mechanisms of Arsenate Adsorption by Highly-Ordered Nano-Structured Silicate Media Impregnated with Metal Oxides. Environmental Science and Technology. 37(21); 5062-5070.
2. Eun Woo Shin, James S. Han, Min Jang, Soo-Hong Min, Jae Kwang Park, and Roger M. Rowell, Phosphorus Adsorption on Al-Impregnated Mesoporous Silicate: Surface Structure and Behavior of Adsorbents, Environmental Science and Technology, 38(3); 912-917
3. Min Jang. 2003. Arsenic Removal from Water Using Nano-Scale Metal Oxide Incorporated, Highly Ordered Mesoporous Silicate Media
4. Park, J.K. 2003. Removal of Arsenic in Groundwater Using Novel Mesoporous Sorbent Water Resources Institute, University of Wisconsin-Madison.

REMOVAL OF ARSENIC IN GROUNDWATER USING NOVEL MESOPOROUS SORBENT

CIVIL AND ENVIRONMENTAL ENGINEERING
(ENVIRONMENTAL PROGRAM)

UNIVERSITY OF WISCONSIN-MADISON

2003

This project was supported, in part, by General Purpose Revenue funds of the State of Wisconsin to the University of Wisconsin System for the performance of research on groundwater quality and quantity. Selection of projects was conducted on a competitive basis through a joint solicitation from the University and the Wisconsin Departments of Natural Resources; Agriculture, Trade and Consumer Protection; Commerce; and advice of the Wisconsin Groundwater Research Advisory Council and with the concurrence of the Wisconsin Groundwater Coordinating Council.

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PROJECT SUMMARY

PROJECT ID: R/UW-REM-006

INVESTIGATOR:

PRINCIPAL INVESTIGATOR: JAE K. PARK, PROFESSOR, CEE

RESEARCH ASSISTANT: MIN JANG, PhD, CEE

PERIOD OF CONTRACT: 7/01/2002~6/30/2003

BACKGROUND/NEED:

Through our batch tests, we found that this technique will be effectively applied for arsenic removal from groundwater. However, it is needed to conduct experimental works with a real groundwater contaminated arsenic species in order to design the POU/POE application of arsenic removal.

OBJECTIVES:

The objectives of this study were as follows: (1) to develop novel adsorbents through synthesizing highly ordered mesoporous silica SBA-15 and incorporating lanthanum oxide using an incipient-wetness impregnation technique; (2) to characterize the physicochemical properties of these media using several fine characterization techniques such as; XRD, N_2 gas *isotherm* analysis, and FTIR; (3) to evaluate the adsorption capacities through performing adsorption *kinetics* and *isotherms* of arsenate; and finally (4) to try to elucidate the adsorption behavior of the media in connection with the physicochemical characterization discovered by above fine tools.

METHODS:

Preparations of experimental procedure: Environmental Program Lab. (July/02~June/03)

Kinetics and isotherms: Environmental Program Lab. (Sep/02~May/03)

Analysis of physicochemical properties of media (Sep/02~June/03)

XRD: Materials Science and Engineering

N_2 gas isotherms: Water Chemistry

FTIR: Forest Product Lab.

HRTEM: Materials Science and Engineering

XPS: Materials Science and Engineering

Surface complexation modeling: Environmental Program Lab. (Jan/03~March/03)

RESULTS AND DISCUSSION:

XRD and N_2 *isotherm* results showed that an immoderate substitution of lanthanum into silica networks was occurred at 80 percent of lanthanum impregnation even though lanthanum was highly dispersed into the mesopore structures of SBA-15 without a formation of lanthanum oxide particles.

FTIR results showed that there was no structural collapse of silica frameworks at 80 percent lanthanum impregnation. This can be explained as a result of a partial substitution of lanthanum precursors with silicon, which could play an important role in structural stabilization as has been shown by other studies.

Although the arsenate adsorption densities increased with lanthanum impregnation up to 50% (the most efficient percentage of lanthanum impregnation), it abruptly decreased at 80% due to the substitution of lanthanum with silicon, leading to the overall reduction of arsenate adsorption capacity.

At the arsenate concentration of 0.667 mmol_{As}/L in this study, the adsorption capacity of 50% lanthanum-impregnated SBA-15 (designated to La_{50}SBA-15) was 1.651 mmol_{As}/g, (123.7 mg_{As}/g) which was about 10 or 14 times higher than the other referenced values of La(III) impregnated alumina (0.172 mmol_{As}/g) or La(III) impregnated silica gel (0.118 mmol_{As}/g).

CONCLUSIONS/IMPLICATIONS/RECOMMENDATIONS:

Nano-scale impregnation of lanthanum onto SBA-15 has a lot of advantages in terms of not only adsorption velocity and capacity but also cost benefits for small scale of POU/POE application of arsenate removal since a small amount of lanthanum precursor is needed for impregnation and the regeneration of the lanthanum-impregnated mesoporous media will be applicable due to excellent structural stability of lanthanum-impregnated SBA-15.

RELATED PUBLICATION:

SCI Paper

(1) Min Jang, Eun Woo Shin, Jae K. Park, and Sang I. Choi, Mechanisms of Arsenate Adsorption by Highly-Ordered Nano-Structured Silicate Media Impregnated with Metal Oxides, Accepted in *Environmental Science and Technology* (August 28, 2003).

(2) Min Jang, Park, Jae K., Eun Woo Shin, Lanthanum Functionalized Highly Ordered Mesoporous Media for Arsenic Removal, Submitted to *Environmental Science and Technology*.

US Patent

Jae K. Park and Min Jang, “Removal of Arsenic and Other Anions Using Novel Adsorbents,” Patent (U.S. Patent) proceeding.

Presentation

Min Jang, Eun Woo Shin, and Jae K. Park, Removal of Arsenic Using Mesoporous Silicate Media Impregnated Metal Oxides Nano-Particles, WEFTEC, Research Section 41, Chicago.

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1.2 INTRODUCTION

As a medium having higher sorption capacity than activated alumina, lanthanum oxide has higher isoelectric point (IEP) of 11.1 than activated alumina (9.2) (Misra and Nayak, 1995). It is also one of the cheapest rare-earth elements, is extracted from bastnaesite and monazite (Tokunaga *et al.*, 1999b), and has been known as nontoxic and environmental friendly (Tokunaga *et al.*, 1999a). For these reasons, many researchers have investigated the precipitation and/or adsorption processes (Wasay *et al.*, 1996a; Tokunaga *et al.*, 1997) using lanthanum compounds for the removal of oxyanions such as selenium and arsenic species. Wasay *et al.* (1996a and 1996b) studied the adsorption process of a lanthanum-impregnated silica gel and La(III)-impregnated alumina to remove fluoride, phosphate, selenite, and arsenate ions. A wet impregnation method was used to incorporate lanthanum ions on the surface functional groups. Their adsorption *isotherm* results showed that the adsorption of each anion followed the *Langmuir isotherm* without interferences of other anions such as Cl^-, Br^-, I^-, NO_3^-, and SO_4^{2-}.

Up to now, using the characteristics of mesoporous materials, there has been a great deal of some efforts to develop several types of adsorbents for removal of arsenic or other toxic elements. Fryxell *et al.*, synthesized copper chelated ethylenediamine (EDA) immobilized mesoporous silicate as anion adsorbent. In their synthesis procedure, they used the mesitylene organic solution to expand pore structures and cetyltrimethylammonium chloride/hydroxide as pore templating agent (Fryxell *et al.*, 1999). After grafting the ethylenediamine (EDA) silane onto the surface of mesoporous silica, Cu (II) ions were bonded to create octahedral complexes. Their media had positively charged hosts with three-fold symmetry which match the geometry of tetrahedral anions, so that they showed high selectivity of anions as well as high sorption capacity of about 140 mg (arsenate)/g. Yoshitake *et al.*, attempted to synthesize several types of cations (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and H^+) coordinated aminosilane-functionalized MCM-41, SBA-1, and MCM-48, inspecting the arsenate adsorption properties (Yoshitake *et al.*, 2002; Yoshitake *et al.*, 2003). They found that Fe/NN-MCM-41 had a distribution coefficient of more than 2.0×10^5 even at below 100 mg/L of arsenate concentration and showed the highest arsenate adsorption capacity of 2.5 mmol_{As}/g. However, as described above, both cases tried to utilize complicated synthesis procedures, in which expensive and toxic chemicals were used, resulting in a significant limitation for a large-scale application. Accordingly, in this study, simplified and economic synthesis routes of adsorbents, which still have high adsorption capacities of anionic toxic species, were investigated. Using amphiphilic triblock copolymers as a structure-directing template agent, the mesoporous silica molecular sieves SBA-15 were successfully synthesized under hydrothermal conditions (Zhao *et al.*, 1998). The uniform two dimesional hexagonal (space group *p6mm*) mesopore channels of SBA-15 can be tailored by changing synthesis conditions. The objectives of this study were as follows: (1) to develop novel adsorbents through synthesizing highly ordered mesoporous silica (SBA-15) and incorporating lanthanum oxide using an incipient-wetness impregnation technique; (2) to characterize the physicochemical properties of these media using several fine characterization techniques, such as XRD, N_2 gas *isotherm* analysis, and FTIR, (3) to evaluate the adsorption capacities through performing adsorption *kinetics* and *isotherms* of arsenate; and finally (4) to try to elucidate the adsorption behavior of the media in connections with the physicochemical characterization discovered by above fine tools.

1.3 PROCEDURES AND METHODS

Synthesis of lanthanum-impregnated SBA-15 and conductivity tests

SBA-15 was synthesized using triblock copolymer (Pluronic P123, $EO_{20}PO_{70}EO_{20}$, Aldrich®) as a structure-directing reagent and tetraethyl orthosilicate (Aldrich®) as a silica precursor. A 4-gram triblock copolymer was dissolved in 60 mL of deionized water for 30 min and a 2 M hydrochloric acid solution was added. The mixed solution was stirred for 30 minutes. Tetraethyl orthosilicate (TEOS) was then added to the mixture and heated at 35°C for 20 hrs. The mixture was transferred into a Teflon bottle and heated at 90°C for 24 hrs without stirring. The solid product was then filtered with a 0.45-μm filter paper and dried at room temperature under vacuum before calcination. The mole fraction of each component for as-synthesized SBA-15 was 1 mol TEOS: 5.854 mol HCl: 162.681 mol H_2O: 0.0168 mol triblock copolymer. The calcination was performed in an oven at 550°C for 6 hrs in air to remove the triblock copolymer organic component. The calcined SBA-15 was preserved at room temperature under vacuum. $La(NO_3)_3 \cdot xH_2O$ (x = 3~5, Aldrich®) was selected as lanthanum precursor to incorporate into SBA-15 through use of an incipient wetness impregnation technique (Jang *et al.*, 2003). The mixture was dried in the hood at room temperature for 1 day. To compare the IR spectra, lanthanum oxide was synthesized by the same lanthanum precursor with the following procedure. A 100 mL solution of lanthanum precursor was prepared with a concentration of 3 $mole_{La}$/L of deionized water. The solution was then dried in an oven at 105°C for one day. All solids were then calcined in an oven at the programmed temperature of the range starting from room temperature to 550°C at a rate of 0.5°C per minute, and preserved for 4 hours. After calcinations, the solids were kept inside a vacuum chamber.

In order to find the optimum temperature for completing the oxidation of lanthanum precursors, calcinations was conducted with different temperatures, followed by conductivity test. The SBA-15 impregnated with highest impregnated percentage (80%) of lanthanum precursor was calcined in an oven at the programmed temperature of the range from room to planned temperatures at a rate of 0.5°C/min. The solids were then calcined at final temperature for 4 hours. After calcination, solids were kept on a vacuum chamber before conductivity tests. The conductivity tests were conducted according to the procedure described by Jang *et al*, (2003).

Characterization of LaSBA-15

A Stoe High Resolution X-Ray Diffractometer (Microphotonics, Allentown, Pa.) equipped with Cu Kα radiation (40 kV, 25 mA) was used to obtain x-ray diffraction patterns in a short range (0.8°~2.1°) for a series of lanthanum-impregnated SBA-15 and calcined SBA-15. A wide range (10°~70°) of x-ray diffraction pattern was conducted for La_{80}SBA-15, which has the largest portion of lanthanum (44.4 percent) based on the mass of media. N_2 gas adsorption-desorption *isotherms* were performed at 77 K using a Micromeritics ASAP 2400 analyzer (Norcross, Ga.). Media were dehydrated at 393 K for 1 day before performing *isotherm* tests. The BET specific surface area (A_{BET}) was calculated by the linear part of the BET equation in the range of relative pressure range from 0.05 to 0.2. The primary mesopore size distributions (PSD) of media were obtained using Barrett, Joyner and Halenda (BJH) method with the corrected Kelvin equation of the adsorption branch of the hysteresis loop of the nitrogen adsorption *isotherm*, which can accurately calculate pore size distribution under the assumption of a cylindrical shape of pores (Kruk and Jaroniec, 1997; Newalkar *et al.*, 2001a; Newalkar *et* *al.*, 2001b). The pore diameter corresponding to the maximum of PSD is denoted as W_{KJS}. The primary mesopore (V_p) was estimated using the β_s plot method, which is an easily determined alternative to α_s plot method ($\alpha_s = v_{ads}$ $(P/P_0)/v_{ads}$ (0.4)). Based on Frenkel, Halsey and Hill (FHH) theory, the v_{ads} of α_s equation is replaced by the statistical thickness of the adsorbed gas layer to have a following equation: $\beta_s = [\ln(0.4)/\ln(P/P_0)]^{(1/2.7)}$ (Lukens *et al.*, 1999). Micropore volume (V_{micro}) and area (A_{micro}) were obtained by *t*-plot method. The total pore volumes (V_t) were determined at 0.99 of relative pressure. IR spectra were obtained by a Mattson Galaxy 5020 FTIR spectrometer (Mattson Instruments, Madison, Wis.) to get the information of the change of functional groups onto the oxide surface and structural stability after lanthanum impregnation at room temperature. Potassium bromide was used to mix with samples.

Arsenate Adsorption *Kinetic* Tests

Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$, Sigma®) was used as the arsenate source for a stock solution without any modification. A stock solution of arsenate (133 mmol/L) was prepared with 0.01 *M* $NaNO_3$ solution based on deionized water. A Photronix® reagent grade water system was used to prepare all of deionized water. Granular activated alumina (AA-400G, ALCAN®, 8×14 mesh) was selected as a commercialized product for arsenic removal to compare the adsorption *isotherm* and *kinetic* data with various amounts of lanthanum-impregnated SBA-15. The specific surface area of activated alumina was 350~380 m^2/g (ALCAN, 1997).

Arsenate *kinetic* studies were conducted with various amounts of lanthanum-impregnated SBA-15 and granular activated alumina. An aliquot of 1,000 mL of deionized water prepared with 0.01 *M* $NaNO_3$ was poured into a reaction bottle for each *kinetic* study. After adding arsenate stock solution to make the initial arsenate concentration of 0.267 $mmol_{As}/L$, the solution was stirred with a magnetic stirrer at a velocity of 500 rpm. The pH of the solution was adjusted to 7.2±0.02 with an automatic pH titrator and the temperature was maintained at 20±0.5°C for one hour before a 0.15 gram of media was added. In order to maintain a constant pH during *kinetic* studies, the automatic titrator was installed in the reactor and connected with a pH electrode and small tubes running from two pumps, titrating with small volumes of acid (HNO_3, 0.01 *M*) and base (NaOH, 0.01 *M*) stock solution. One of the two pumps, connected to either the acid or base stock solution, was operated when the pH drifted ±0.02 pH units from the initial pH. An aliquot of 5 mL of suspensions was withdrawn at 2~60 minute intervals and filtered through a 0.45-μm Uniflo® filter unit for arsenate analysis. It was found that the pseudo-second order *kinetic* equation agreed with many adsorption processes using heterogeneous materials, of which chemisorptions are the rate-controlling step (Ho and McKay, 1998; Reddad *et al.*, 2002). Therefore, all of the *kinetic* data were fitted with a pseudo-second *kinetic* model to measure the rate constants, initial sorption rates, and adsorption capacities of arsenate.

Arsenate Adsorption *Isotherm* Tests

Granular activated alumina, SBA-15, and the most efficient lanthanum percentage, 50 percent, impregnated SBA-15 were used for *isotherm* tests. In this test, the initial arsenate concentration was fixed at 0.267 or 0.667 mmol/L, and masses of media were varied. A 50 mL of $NaNO_3$ (0.01 *M*) solution prepared with deionized water was poured into a polyethylene bottle. Then, arsenate stock solution and media were added to achieve target arsenate concentrations as well as the pH of the samples was adjusted to 7.2±0.02 with acid and base stock solutions while mixing with magnetic stirrer. All samples were mixed in a rotary shaker at 150 rpm and 20±0.5°C. After 8 hrs of shaking, the pH of the samples was readjusted to 7.2±0.02

with the pH automatic titrator using small volumes of acid and base stock solutions. All samples were then shaken in the rotary shaker until equilibrium state was reached. After 24 hrs of shaking, 5 mL was withdrawn and filtered with a 0.45-μm Uniflo® filter unit. All *isotherm* data were fitted with *Freundlich* and *Langmuir isotherm* models to evaluate several parameters.

Arsenic Analysis

A Varian AA-975 Atomic Absorption Spectrophotometer and a GTA-95 Graphite Tube Atomizer with programmable sample dispenser (Palo Alto, California) were used for arsenate analysis of samples. In this analysis, 20 mg/L nickel solution was used as a matrix modifier. The detection limit of AAS-graphite was 0.0474 μg/L.

1.4 RESULTS AND DISCUSSION

Conductivity tests

Figure 1 shows the conductivities of 80 percent lanthanum-impregnated SBA-15 calcined at different temperatures. As the calcinations temperature increased, the conductivities decreased because more lanthanum ions were oxidized as a result of the higher temperature. The conductivity of material calcined at 550°C was the same as that of deionized water, indicating the complete oxidation of lanthanum precursor. Therefore, all lanthanum-impregnated SBA-15 used in all subsequent experiments was synthesized using a final temperature of 550°C.

X-ray diffraction

Figure 2 (A) shows x-ray diffraction results of SBA-15 and various amounts of lanthanum-impregnated SBA-15 in the range of 0.8° and 2.1°. Calcined SBA-15 displayed a well-resolved pattern at very low 2θ with a sharp peak at 0.92° and two weak peaks at 1.60° and 1.84°. This x-ray diffraction pattern was similar to the reported SBA-15 pattern (Zhao *et al.*, 1998). The XRD peaks of SBA-15 can be indexed to a hexagonal lattice with a *d*(100) spacing of 95.93 Å, corresponding to a unit cell parameter a_0 of 110.78 Å obtained by the following equation: $a_0 = 2 \times d_{100} / \sqrt{3}$. With increase of lanthanum impregnation percentages onto SBA-15, the peak intensities at *d*(100) decreased gradually and the width of peak shapes broadened, indicating that a wide range of pore structures can be developed with increase of lanthanum impregnation (Nooney *et al.*, 2001). Figure 2 (B) shows the change of *d*(100) space with the increase of lanthanum-impregnated percentages. The *d*(100) space or unit cell parameter (a_0) of La_{10}SBA-15 was not different from calcined SBA-15. However, the *d*(100) spaces were linearly decreased to 89.33 Å (La_{50}SBA-15) with increase of lanthanum impregnation. Accordingly, lanthanum oxide was coated into mesopore structures of SBA-15 to have a smaller unit cell parameter. Sauer *et al.*(2002) also found a similar trend in their synthesis of europium doped yttria (YOX)-dispersed SBA-15. However, with increase to 80%, the *d*(100) space increased again to 91.94 Å. This phenomenon could be caused by an immoderate substitution of lanthanum into silica networks at 80 percent of lanthanum impregnation percentage. The increase of *d*(100) space or unit cell parameter by substitution of other metals into mesoporous silica has been observed by other researchers (Dapurkar and Selvam, 2001; Kuang *et al.*, 2001; Newalkar *et al.*, 2001b). A wide-angle of x-ray diffraction analysis was performed for highest amount (80 percent) of lanthanum-impregnated SBA-15 in this study. Figure 2 (C) shows the wide-angle of x-ray diffraction patterns for La_{80}SBA-15. For the x-ray diffraction of La_{80}SBA-15, even though the weight percentage of lanthanum element impregnated into SBA-15 was 44.4% in the solid (0.444 g (lanthanum)/g of media), there was no distinct peak; instead, very weak and wide range of peaks were found in the range of 25~32°, indicating that nano-scale of lanthanum oxide was homogeneously dispersed into the mesopore structures of SBA-15 and no large size of lanthanum oxide particles were formed outside of SBA-15 (Sauer *et al.*, 2002; Yang *et al.*, 2003).

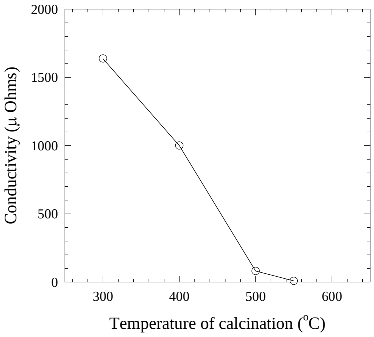

FIGURE 1 Conductivity tests of 80 percent lanthanum-impregnated SBA-15 treated with different calcination temperatures

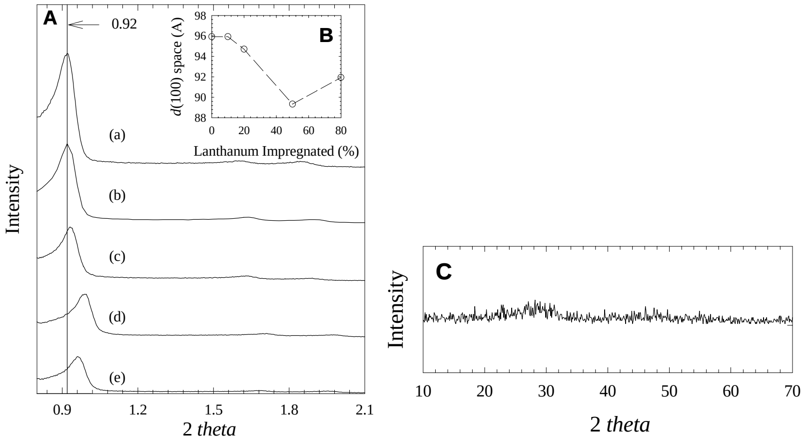

FIGURE 2 (A) Low-angle XRD measurements of SBA-15 (a), La_{10}SBA-15 (b), La_{20}SBA-15 (c), La_{50}SBA-15 (d), and La_{80}SBA-15 (e), (B) change of *d*(100) space with different lanthanum impregnation percentages, (C) a wide-angle of x-ray diffraction analysis performed for La_{80}SBA-15.

Nitrogen adsorption-desorption *isotherm*

Figure 3 (A) shows the nitrogen adsorption-desorption *isotherms* of calcined SBA-15 and various amounts of lanthanum-impregnated SBA-15. According to IUPAC (International Union of Pure and Applied Chemistry) classification, all *isotherms* show a typical Type IV model and have a H1 hysteresis loop, which is representative for mesopores (Sing *et al.*, 1985). The adsorbed volume of all *isotherms* sharply increased at relative pressure (P/P_0) of about 0.64, presenting capillary condensation of nitrogen within uniform mesopore structures (Kruk and Jaroniec, 1997). The inflection position of the relative pressure is related to a diameter in the mesopore range and the sharpness of these steps indicates the uniformity of the mesopore size distribution (Luan *et al.*, 1999; Newalkar *et al.*, 2001a). Up to 50 percent of lanthanum impregnation, the sharpness of inflection steps decreased gradually; however, it was largely declined at 80 percent. Also, inflection positions were slightly shifted toward lower relative pressure in the range of 0.4~0.8 with higher impregnation percentages of lanthanum. Therefore, it can be surmised that more heterogeneity of pore size distribution occurred for 80 percent lanthanum-impregnated SBA-15 even though the exact change of mesopore diameters could not be detected from the nitrogen *isotherms*. To investigate the change of primary mesopore size distribution (PSD) with lanthanum impregnation, the KJS approach was conducted for the nitrogen *isotherms*. From the nitrogen *isotherms*, the PSD plots were derived from the adsorption branch of the nitrogen hysteresis because the network penetration effects of polyethylene oxide (PEO) chains of the triblock copolymer template within the silica framework of SBA-15 cannot fully be excluded on the desorption branch (Sauer *et al.*, 2002). Table 1 shows the physical parameters of nitrogen *isotherms* for all media such as BET surface area, total pore volume, micropore area and volume, primary mesopore area, volume, and size, as well as *d*(100) spacing (Å) and unit cell parameter (a_0, Å) obtained by XRD analysis. Except primary mesopore sizes and unit cell parameters, most parameters obtained from nitrogen *isotherms* decreased with increase in lanthanum impregnation percentages even though the decrease trends of each parameter were different. The reductions of primary mesopore surface area and volume indicate the formation of lanthanum oxides within mesopore structures (Morey *et al.*, 2000). As a special aspect, micropores of about 160 m^2/g were developed in the SBA-15 because there are some evidences of microporous corona effect resulted by the partial embedding of the PEO chains in the silica walls (Kruk *et al.*, 2000; Sauer *et al.*, 2002). The reduction of micropore and primary mesopore volumes of different amounts of lanthanum-impregnated SBA-15 is shown at Figure 3 (B). With 20 percent of lanthanum impregnation, micropore volume decreased significantly to 21 percent while primary mesopore volume decreased to 69.5 percent. Moreover, the primary mesopore volumes were linearly reduced from 10 percent to 80 percent lanthanum impregnation while micropore volume reductions were not much changed with higher lanthanum impregnation than 20 percent. Accordingly, micropore volume can be saturated with fewer amounts of lanthanum impregnation than primary mesopore. Overall results showed that most adsorption active surface sites of lanthanum-impregnated SBA-15 could exist at mesopore phase, excluding micro- and macro-pore structures. The pore size distribution of calcined SBA-15 and various amount of lanthanum-incorporated SBA-15 obtained from adsorption *isotherm* branches were shown in Figure 4. All media showed a sharp PSD. As shown in Figure 4, a broad maximum peak (73.1 Å) for SBA-15 was changed to be sharp and shifted to have a smaller maximum peak of 60.9 Å with 10 percent lanthanum impregnation even though the adsorbed volume of maximum peak was not much reduced. With increase in lanthanum impregnation up to 50 percent, the maximum peaks were more sharpened and their adsorbed volumes gradually decreased. When the lanthanum impregnation was increased to 80 percent, the maximum peak of PSD was changed again to be broadened and shifted to have a larger pore (63.1 Å) than that of 50 percent. Moreover, its adsorbed volume was abruptly decreased, representing more heterogeneous pore structures than other media. The increase in primary mesopore size might be linked with the increase of *d*(100) shown with XRD analysis, which can be caused by the fact that lanthanum precursors are substituted into silicon to expand the unit cell at 80 percent of lanthanum impregnation.

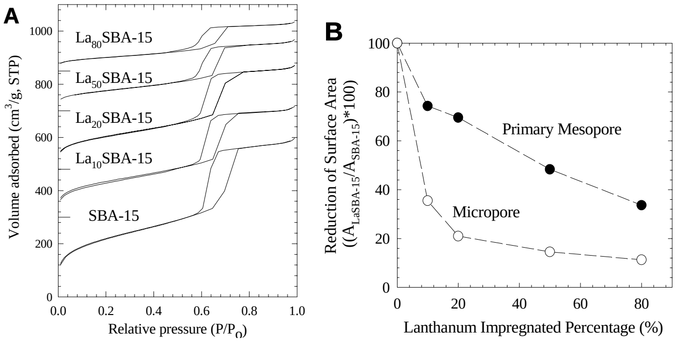

FIGURE 3 (A) Nitrogen adsorption-desorption *isotherms* of SBA-15, La_{10}-, La_{20}-, La_{50}-, and La_{80}SBA-15, (B) Reductions of primary mesopore and micropore volumes according to lanthanum impregnation percentages

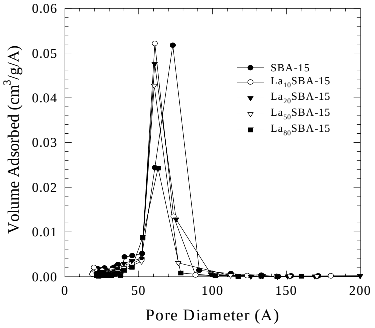

FIGURE 4 Pore size distributions of La_{80}SBA-15, La_{50}SBA-15, La_{20}SBA-15, La_{10}SBA-15, and SBA-15 obtained from adsorption branches

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Figure 5 (A) shows the IR spectra of uncalcined and calcined La_{20}SBA-15. The strong peaks in the IR band of 1250~1700 cm^{-1} of uncalcined La_{20}SBA-15 disappeared completely for calcined La_{20}SBA-15. The vibration mode of nitrate can be broadly assigned for the IR band of 1650~750 cm^{-1}, especially a number of peaks in the NO_2 stretching region of 1250~1700 cm^{-1} suggests the presence of nitrate ions (Klingenberg and Vannice, 1996). From this result, it is concluded that nitrate ions of lanthanum precursor were totally decomposed with a calcination procedure employed. Figure 5 (B) shows the IR patterns of calcined SBA-15, LaSBA-15, and lanthanum oxide in the wave number of 400~1600 cm^{-1}. The three peaks at 465 cm^{-1}, 800 cm^{-1}, and 1085 cm^{-1} corresponded to rocking, bending (or symmetric stretching) and asymmetric stretching of the intertetrahedral oxygen atoms in the SiO_2 structure, respectively, for the IR patterns of calcined SBA-15 (Primeau *et al.*, 1997; Morey *et al.*, 2000). The peak at 960 cm^{-1} was also assigned to the stretching of nonbridging oxygen atoms ($Si\text{-}O^{\delta-}$) of a Si-OH stretch (Morey *et al.*, 2000). The peaks of 1085 cm^{-1} and the shoulder part in the IR bands of 1100~1300 cm^{-1} corresponded to the concerted (Si-O-Si) stretches, which were as a result of partial ordering of the silicate framework at the pore surface (Morey *et al.*, 2000). With an increase of lanthanum-impregnated percentages up to 20 percent, there were no peaks in the IR band of 1300~1600 cm^{-1}, exhibiting the phase of lanthanum oxide (La-O-La), although the absorbance intensities of 960 cm^{-1} decreased, implying that Si-OH groups were consumed to transform to Si-O-La bonds. From this result, it can be suggested that the monolayer phase of lanthanum oxide might be dominated at 20 percent of lanthanum impregnation. At 50 percent of lanthanum impregnation, however, the peak of 960 cm^{-1} disappeared completely, but the very small peaks in the IR band of 1300~1600 cm^{-1} appeared, indicating that more lanthanum precursors than needed for a complete consumption of Si-OH were involved for the multilayer of La-O-La bonds. Therefore, the multilayer phase of lanthanum oxide might be dominated at 50 percent lanthanum impregnation. It can be concluded from the above facts that the silanol groups on SBA-15 served as active sites for lanthanum incorporation and were consumed. With higher lanthanum impregnation than 50 percent, the IR peaks of 1300~1600 cm^{-1} were increased more , showing the lanthanum oxide phase clearly, which was also observed by other researchers (Klingenberg and Vannice, 1996). Even at the highest impregnation percentage (80 percent) of lanthanum, however, the IR peak of 1085 cm^{-1} and shoulder part in the IR bands of 1100~1300 cm^{-1} did not decrease. Accordingly, it can be surmised from this result that there was no structural collapse of pore structures occurred by the attacks of lanthanum precursors for Si-O bonds of mesoprous frameworks although a partial substitution of lanthanum with silicon occurred at 80 percent as proved by XRD and PSD analysis. For the case of aluminum impregnation (Shin *et al.*, 2003) in our study, the declinations of 1085 cm^{-1} and shoulder part in the IR bands of 1100~1300 cm^{-1} were distinctly occurred at 30 percent of aluminum impregnation. The structural collapse was also proved by XRD, PSD, and TEM analysis. In the *kinetic* studies of phosphate adsorption by use of aluminum impregnated SBA-15, much lower adsorption capacity was achieved at 30 percent of aluminum impregnation (Shin *et al.*, 2003). Therefore, structural collapse seems to be a significant factor for hindering the arsenate adsorption. Surprisingly, lanthanum was a good candidate of functioning materials for the mesoporous silicate supports in terms of structural stability as shown by other studies (Kloetstra *et al.*, 1997; Zhang and Pinnavaia, 1998; Melo and Urquieta-Gonzalez, 2001).

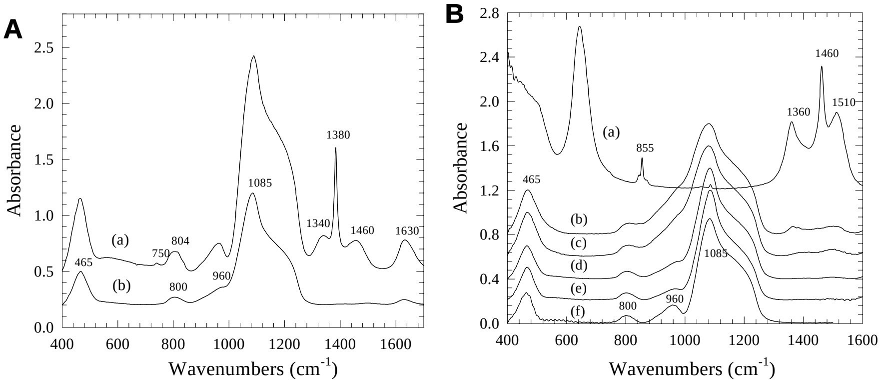

FIGURE 5 (A) FTIR spectra of uncalcined La_{20}SBA-15 (a) and calcined La_{20}SBA-15 (b), (B) FTIR spectra of lanthanum oxide (a), La_{80}SBA-15 (b), La_{50}SBA-15 (c), La_{20}SBA-15 (d), La_{10}SBA-15 (e), and SBA-15 (f)

Kinetic Studies of Arsenate Adsorption

Figure 6 (A) shows the arsenate adsorption *kinetics* of activated alumina and various amounts of lanthanum-impregnated SBA-15 as well as their fitting curves of pseudo-second order *kinetic* model. In comparison with activated alumina, more rapid and higher sorption capacities were obtained even at 10 percent lanthanum-impregnated SBA-15. Higher adsorption capacities were achieved; longer equilibrium times were taken for all *kinetics*. Since the q_{eq} values obtained by the pseudo-second order *kinetic* model were overestimated due to a few data of more extended time than 400 minutes and a trend of adsorption capacities was similar to the trend of arsenate adsorption capacities at 400 minutes (designated to $q_{(t=400)}$), the initial sorption rate (v_0) and $q_{(t=400)}$ values in accordance with the lanthanum impregnation percentages were expressed in Figure 6 (B). The $q_{(t=400)}$ values linearly increased to 1.66 $mmol_{As}/g$ (124.4 mg_{As}/g) with an increase of lanthanum impregnation up to 50%, but slightly decreased to 1.54 $mmol_{As}/g$ (115.4 mg_{As}/g) at 80 percent while the initial sorption rate sharply increased to 0.016 $mmol \cdot g^{-1} \cdot min^{-1}$ at 20 percent and further increased to 0.023 $mmol \cdot g^{-1} \cdot min^{-1}$ at 50 percent, but decreased to 0.020 $mmol \cdot g^{-1} \cdot min^{-1}$ at 80 percent. Figure 6 (C) shows the changes of arsenate adsorption densities and surface loadings with an increase of lanthanum impregnation percentages. The arsenate surface loading linearly increased as the lanthanum impregnation percentages increased while arsenate adsorption densities increased up to 50 percent of lanthanum impregnation, however, abruptly decreased at 80 percent impregnation. Correspondingly, there was a most efficient amount of lanthanum impregnation percentage that had the maximum arsenate adsorption capacity by increase of active sorption sites although the surface area of media decreased with increase of lanthanum impregnation. However, the occurrence of substitution with silicon in addition to the reduction of surface area might give a significant hindrance of arsenate adsorption capacity since a partial portion of lanthanum immobilized at the silica framework will not be functioning as active sorption sites for arsenate removal and the exchanged silicon can obstruct the active sites of lanthanum. Therefore, despite of the fact that a larger lanthanum was impregnated in SBA-15 than 50 percent, the reason for the decrease in the overall adsorption capacity of La_{80}SBA-15 might be due to not only a decrease of surface area but also silicon substitution, which were proved by the XRD and N_2 gas *isotherm* analysis. As a result of *kinetic* studies, the most efficient percentage of lanthanum impregnation was 50 percent in terms of arsenate adsorption speed and capacity. La_{50}SBA-15 also had about 10, 38, and 13 times higher $q_{(t=400)}$ ($mmol_{As}/g$), arsenate adsorption density ($mmol_{As}/mmol_{Me}$), and surface loading ($mmol_{As}/m^2$), respectively, than activated alumina. Although the active sites of activated alumina might be larger than that of La_{50}SBA-15 due to a larger surface area, it can be surmised by the following explanation that the lanthanum oxide incorporated SBA-15 was much more active than activated alumina in terms of physical and chemical properties. First, a large number of active sites for arsenate removal were achieved by the nano-scale dispersion of lanthanum precursors onto a highly ordered mesopore structures. Second, since most lanthanum active sites of SBA-15 exists in a relatively uniform hexagonal-open mesopore size distribution excluding micro- and macro-pores, the arsenate accessibility of lanthanum-impregnated SBA-15 was much better than that of activated alumina that has amorphorous matrices of aluminum oxides containing bottleneck shapes of pore structures hindering the accessibility of arsenate molecules to the active sites of the media (Kim, 2001).

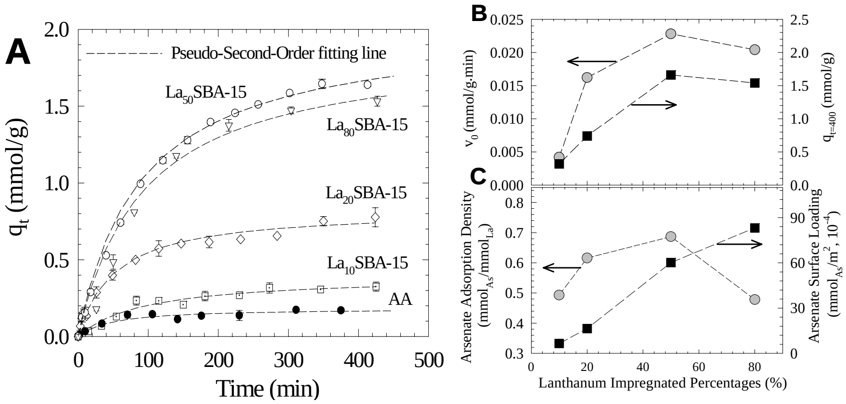

FIGURE 6 (A) Arsenate Adsorption *Kinetics* with LaSBA-15 and activated alumina (AA-400G, ALCAN®) (pH 7.2±0.02), (B) Initial sorption rate (v_0) and q_{eq} (mmol$_{As}$/g), (C) Arsenate adsorption density and surface loading.

Arsenate Adsorption *Isotherms* with LaSBA-15

Figure 7 shows the arsenate adsorption *isotherms* of activated alumina, SBA-15, and La$_{50}$SBA-15 at an initial arsenate concentration of 0.267 or 0.667 mmol$_{As}$/L. At an initial arsenate concentration of 0.267 mmol/L, SBA-15 and activated alumina had arsenate adsorption capacities of less than 0.06 and 0.12 mmol/g, respectively, while La$_{50}$SBA-15 (about 1.2 mmol/g) showed about 20 and 10 times higher adsorption capacities than SBA-15 and activated alumina, respectively. Therefore, the lanthanum oxide species incorporated onto the mesopore phase of SBA-15 were the most dominated active sorption sites for arsenate removal. Moreover, as similar to the magnification of adsorption capacities for both La$_{50}$SBA-15 and activated alumina in *kinetic* studies, La$_{50}$SBA-15 showed much more active sorption capacities than activated alumina, although absolute values of *isotherms* were different with those of *kinetics* due to a different experimental setup. With an increase in initial arsenate concentration, the adsorption capacity of La$_{50}$SBA-15 increased to about 1.6 mmol$_{As}$/g (119.9 mg$_{As}$/g) at 0.11 mmol$_{As}$/L. In spite of the fact that any mechanistic implication cannot be obtained from the determination coefficients of both *Langmuir* and *Freundlich* models because both models had very similar determination coefficients (Table 1) (Sposito, 1984), the q$_{max}$ values of *Langmuir* model were used to get the values of arsenate adsorption density (mmol$_{As}$/mmol$_{La}$) and arsenate surface loading (mmol$_{As}$/m^2, BET). La$_{50}$SBA-15 showed about 9, 34, and 12 times higher for q$_{max}$ (mmol$_{As}$/g), arsenate adsorption density (mmol$_{As}$/mmol$_{Me}$), and surface loading (mmol$_{As}$/m^2), respectively, than activated alumina, demonstrating a consistency with previous *kinetic* results. In Table 3, *isotherm* results of La$_{50}$SBA-15 were compared with other studies in which lanthanum was impregnated onto an alumina (Wasay *et al.*, 1996b) or silica gel (Wasay *et al.*, 1996a). Although the results of other studies showed no interference of other anions such as Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, and SO$_4^{2-}$ for arsenate removal, the adsorption capacity (1.651 mmol$_{As}$/g) of La$_{50}$SBA-15 obtained at lower arsenate concentration (0.667 mmol$_{As}$/L) in this study was about 10 or 14 times higher than the referenced values of La(III) impregnated alumina (0.172 mmol$_{As}$/g) or La(III) impregnated silica gel (0.118 mmol$_{As}$/g) at 1 mmol$_{As}$/L or 0.5~2 mmol$_{As}$/L of initial arsenate concentations, respectively. Accordingly, the nano-scale impregnation of lanthanum onto SBA-15 has a lot of advantages in terms of not only adsorption velocity and capacity but also cost benefits for small scale of POU/POE application of arsenate removal since a small amount of lanthanum precursor is needed for impregnation and the regeneration of the lanthanum-impregnated mesoporous media will be applicable due to excellent structural stability of lanthanum-impregnated SBA-15.

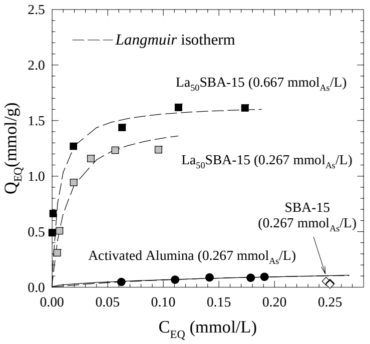

FIGURE 7 Arsenate Adsorption *Isotherm* of La_{50}SBA-15 and activated alumina (AA-400G, ALCAN®) at 0.267 $mmol_{As}$/L or 0.667 $mmol_{As}$/L of arsenate initial concentrations.

TABLE 1 Determination Coefficients (R^2), Several Parameters for the Fit of Arsenate Adsorption Isotherm Data to Both Freundlich and Langmuir Isotherms, and Comparison with Other Studies

Adsorption *isotherms* and parameters		This study			References	
		Activated alumina	La_{50}SBA-15		La(III)- alumina[c]	La(III)- silica gel[d]
As(V) conc. (mmol/L)		0.267	0.267	0.667	1	0.5~2
Langmuir	*b* (L/mmol)	5.98	77.52	167.37	19.7	-
	q_{max} (mmol/g)	0.172	1.516	1.651	0.172	0.118
	$q_{max}{}^{a}$	0.019	0.63	0.68	–	–
	$q_{max}{}^{b}$	4.9~4.5	54.9	59.8	56.8	4.03
	BET (m^2/g)	350~380[g]	276	276	45.1	293
	R^2	0.976	0.993	0.922	-	-

[a] arsenate adsorption density ($mmol_{As}/mmol_{Me}$), [b] surface loading (mmol/m^2) (×10^{-4}), [c] lanthanum(III) impregnated alumina (Wasay *et al.*, 1996b), [d] Lanthanum (III) impregnated silica gel (Wasay *et al.*, 1996a), [g] obtained from the reference (ALCAN, 1997).

CONCLUSIONS AND RECOMMENDATIONS

Although the lanthanum oxide was highly dispersed into the mesopore structures of SBA-15 without producing lanthanum oxide particles at 80%, a partial substitution of lanthanum into silica networks was observed by XRD and N_2 gas *isotherm*. According to a result of FTIR, however, there was no structural collapse of silica frameworks at 80 percent since a partial of lanthanum precursors substituted with silicon might play an important role of structural stabilization as has been proved at other studies. In the arsenate adsorption kinetics, due to the partial substitution of lanthanum at 80 percent, the arsenate adsorption densities abruptly decreased at 80 percent., leading to the overall reduction of arsenate adsorption capacity. The most efficient impregnated percentage, 50 percent, was used for arsenate isotherms tests. Therefore, lanthanum impregnated SBA-15 can be used to remove arsenic in groundwater effectively.

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Yoshitake, H.; Yokoi, T.; Tatsumi, T.; Adsorption Behavior of Arsenate at Transition Metal Cations Captured by Amino-Functionalized Mesoporous Silicas. Chem. Mater., 2003; Vol. 15, pp 1713-1721.

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1.6 APPENDIX A:

- **SCI Paper**

(1) Min Jang, Eun Woo Shin, Jae K. Park, and Sang I. Choi, Mechanisms of Arsenate Adsorption by Highly-Ordered Nano-Structured Silicate Media Impregnated with Metal Oxides, Accepted in *Environmental Science and Technology* (August 28, 2003).

(2) Eun Woo Shin, James S. Han, Min Jang, Soo-Hong Min, Jae Kwang Park, and Roger M. Rowell, Phosphorus Adsorption on Al-Impregnated Mesoporous Silicate: Surface Structure and Adsorption Behavior, Submitted to *Environmental Science and Technology*.

(3) Min Jang, Park, J. K., Eun Woo Shin, Lanthanum Functionalized Highly Ordered Mesoporous Media for Arsenic Removal, Submitted to *Environmental Science and Technology*.

- **US Patent**

Jae K. Park and Min Jang, "Removal of Arsenic and Other Anions Using Novel Adsorbents," Patent (U.S. Patent) proceeding

- **Presentation**

Min Jang, Eun Woo Shin, and Jae K. Park, Removal of Arsenic Using Mesoporous Silicate Media Impregnated Metal Oxides Nano-Particles, WEFTEC, Research Section 41, Chicago.

1.7 APPENDIX B:

(1) Eun Woo Shin, James S. Han, Min Jang, Soo-Hong Min, Jae Kwang Park, and Roger M. Rowell, Phosphorus Adsorption on Al-Impregnated Mesoporous Silicate: Surface Structure and Adsorption Behavior, submitted to *Environmental Science and Technology*.

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

Basic Information

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

Publication

1. Rayne, T.W., S.J. Gaffield and K.R. Bradbury. 2003. Linking Groundwater Recharge, Flow, and Stream-Temperature Models to Simulate the Effects of Local Land-Use on a Stream. Geological Society of America Abstracts with Programs. 35(6). p. 529.

PROJECT SUMMARY

Title	Impacts of Land Use and Groundwater Flow on the Temperature of Wisconsin Trout Streams
Project I.D.	WRI #: R/UW-GSI-005, GCC #: 02-GSI-3
Investigator(s)	*Principal Investigators:* Stephen J. Gaffield, Hydrogeologist, Wisconsin Geological and Natural History Survey Lizhu Wang, Supervisory Research Biologist, Michigan Department of Natural Resources *Other Contributors:* Todd W. Rayne, Professor, Hamilton College Department of Geology Kenneth R. Bradbury, Hydrogeologist, Wisconsin Geological and Natural History Survey
Period of Contract	July 1, 2001 – June 30, 2003
Background/Need	Groundwater discharge to streams is critical for maintaining coldwater fisheries. Habitat management is made difficult by a lack of detailed understanding of the controls over summer stream temperature.
Objectives	We evaluated the utility of models of stream temperature, groundwater flow, and groundwater recharge as decision-making tools for stream and watershed management.
Methods	We adapted the method used in the existing stream-temperature models SSTEMP and SNTEMP for application to small Wisconsin streams. Our stream-temperature model predicts water temperature as a function of groundwater inflow, channel shape, weather conditions, and shade from riparian vegetation. We tested model parameters previously calibrated for the Driftless Area to determine their suitability for use in the Northern Lakes and Forests, the North-Central Hardwood Forest, and the Southeast Wisconsin Till Plain Ecoregions of Wisconsin. Model simulations were compared to field data collected from five streams in the summer of 2001. For one of these streams, Rowan Creek in Columbia County, we linked the stream-temperature model to models of groundwater recharge and groundwater flow. By jointly using these three models, we evaluated the impact of future land-use changes on the infiltration of rain and snowmelt into the soil, stream baseflow supplied by the groundwater flow system, and stream temperature.

Results and Discussion

The stream-temperature model matched measured temperatures for three streams reasonably well, but it performed poorly for two streams with extensive wetlands. Assumptions upon which the model is based may not be valid for wetland stream channels.

Linked models of groundwater recharge, groundwater flow, and stream temperature for Rowan Creek predicted changes in stream temperature of up to 0.8°C related to drought, conversion from native vegetation to agricultural land use, and groundwater extraction from a well near the stream. Simulations of increased urban and suburban land covers predicted little change in temperature.

Conclusions, Implications, and Recommendations

Our stream-temperature model is well suited for assessment of many small Wisconsin streams. Where extensive wetlands are present, caution must be used in applying the model because it may not adequately represent the processes controlling stream temperature. More research is needed to determine the best approach for simulating the temperature of streams flowing through large wetlands.

The linked models indicate that daily mean stream temperature is rather insensitive to changes in the groundwater flow system related to human activities. Daily maximum temperature is likely to be more sensitive, but is not simulated by our technique. Human land use can have numerous other impacts on stream habitat that are not represented by our models, including changes in channel width, burial of pools and gravel spawning beds by sediment, and inflows of runoff heated by paved surfaces.

Key Words

Stream temperature; groundwater; recharge; land use; coldwater fisheries; mathematical models

Funding

University of Wisconsin System

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

Basic Information

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

Publication

1. Li, Z., D. Alessi, and L. Allen. (2002) Influence of Quaternary Ammonium on Sorption of Selected Metal Cations onto Clinoptilolite Zeolite. J. Environ. Qual. 31,1106-1114.
2. Willms, C., Z. Li, L. Allen, and C. V. Evans. 2004. Desorption of Cesium from Kaolinite and Illite Using Alkylammonium Salts. Applied Clay Science. 25(3-4). pp. 125-133.

Project Summary

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

Project ID: R/UW-REM-005

Investigators: Dr. Christine V. Evans, Professor of Geology, and Dr. Zhaohui Li, Associate Professor of Geology, Department of Geosciences, University of Wisconsin-Parkside

Period of Contract: 07/01/2001 – 06/30/2003

Background/Need: At some heavy industrial sites and DOE nuclear weapon manufacture and test sites, high concentrations of heavy metals and radionuclides in soils impose potential threat to groundwater. Soils with large surface areas and high cation exchange capacities may accumulate significant amounts of heavy metals and radionuclides, requiring eventual soil excavation and *ex situ* extraction of the heavy metals and radionuclides. Cesium and lead are two relatively common contaminants that are particularly difficult to extract from clay and oxide fractions of soils. Thus a search for an inexpensive, yet effective method, to remove heavy metals from soil becomes more imminent.

Objectives: The objectives of this research are to test the heavy metal removal efficiency using long chain cationic surfactants and to study the influence of surfactant chain length of several quaternary ammonium surfactants, the initial surfactant concentration, the initial heavy metal loading and initial solution pH and ionic strength on Pb and Cs removal from kaolinite and illite at batch scale, and then to conduct column leaching experiments to verify the batch results at different initial Pb and Cs loading.

Methods: Laboratory batch sorption was performed to determine the sorption maxima of Pb and Cs on kaolinite and illite. Then the clays were modified to 3, 15, and 100 percent of their metal sorption capacity. Desorption of Pb and Cs by cationic surfactant with different hydrophobic chain lengths (8, 12, and 16 carbons in the tail group, respectively) was determined against time, solution pH and ionic strength. For column studies, contaminated clays were leached with water and surfactant solution, and effluent metal concentrations were analyzed by atomic emission for Cs and ICP for Pb. Greenhouse studies were conducted by growing mustard and chard plants in Pb-modified soils at three levels of loading. The cationic surfactant was added to one set of replicates during normal watering procedures.

Results and Discussion:

Desorption of Cs$^+$ from Cs$^+$-preloaded kaolinite and illite at different loading levels followed different trends. In general, Cs$^+$ was more readily removed from kaolinite than from illite. Surfactant chain lengths have strong influences on Cs$^+$ desorption from kaolinite. As the surfactant chain length increased, the percentage of Cs$^+$ removal from kaolinite increased. In contrast, initial surfactant concentrations have a greater influence on Cs$^+$ removal from illite. As the surfactant concentration increased, the percentage of Cs$^+$ desorption increased. For kaolinite, when surfactant concentrations were the same, a higher percentage of Cs$^+$ desorption was achieved when Cs$^+$ loading was low. As the Cs$^+$ loading on kaolinite increased, the percentage of Cs$^+$ desorption decreased. In contrast, a higher percentage of Cs$^+$ desorption was obtained from illite when Cs$^+$ loading was high. The percentage of Cs$^+$ desorption decreased as the Cs$^+$ loading on illite decreased. For kaolinite and illite with higher Cs$^+$ loading, the percentage of Cs$^+$ removal increased logarithmically with the increase in HDTMA/Cs$^+$. A minimum value of 30 for the HDTMA/Cs$^+$ ratio is required to achieve 80 percent Cs$^+$ removal from kaolinite.

Column results show that a 100 percent increase in Cs$^+$ removal was achieved when a 6 m*M* HDTMA solution was used as the leaching solution compared to water. Contrast to the batch study, a higher percentage of Cs$^+$ removal from kaolinite was achieved by both surfactant solution and water when the Cs$^+$ loading on kaolinite was high.

Plant sorption results showed that both mustard and chard absorbed Pb somewhat proportionally to the amount in the soil. For both plant types, plant sorption of Pb increased substantially at the medium and high levels of Pb-loading when the surfactant was added.

Conclusions/ Implications/ Recommendations:

The research shows that the cationic surfactant, particularly HDTMA, drastically increase the Pb and Cs desorption from kaolinite surfaces. The greenhouse study shows that the cationic surfactant also increases plant sorption of Pb from Pb-loaded soils.

Key Words: Desorption, Heavy Metal, Illite, Kaolinite, Surfactant.

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

Co-occurrence and Removal of Arsenic and Iron in Groundwater

Basic Information

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

Publication

PROJECT SUMMARY

Concurrent Iron and Arsenic Removal During Iron Oxidation and Filtration

PROJECT No. R/UW-REM-007

Paul M. McGinley, Assistant Professor of Water Resources; Jesse Baumann, Undergraduate
Research Assistant; Eric Frank, Undergraduate Research Assistant; and
Richard Stephens, Laboratory Manager, Center for Watershed Science and Education
University of Wisconsin-Stevens Point

CONTRACT PERIOD: July 2001-June 2003

Background and Need

New regulations and a greater understanding of the health effects of arsenic exposure will lead many water suppliers to consider reducing arsenic concentrations in their drinking water. For some, that will be mandated because they currently exceed the new maximum contaminant level of 0.01 mg/l, for others, arsenic removal may be a consideration when evaluating the overall impact of future modifications to water quality. Concurrent iron and arsenic removal may provide an opportunity for many small water systems to simultaneously address a significant aesthetic water quality problem and provide risk reduction from arsenic exposure. Iron is a relatively ubiquitous groundwater constituent and its presence can preclude the effective use of some technologies without pre-treatment. However, previous research and field experience has shown that the formation of iron oxyhydroxides through precipitative iron removal generates an adsorptive media that can accumulate arsenic. Subsequent removal of the precipitated iron can also remove the arsenic. Unfortunately, current information on arsenic removal does not provide a clear discussion of the limitations and advantages of concurrent arsenic and iron removal particularly for small groundwater systems using conventional, low-residence time, oxidation/filtration systems. The research described here was designed to increase our understanding of the possibilities and limitations of conventional technologies for addressing arsenic in small water systems with an emphasis on Wisconsin water systems.

Objectives

This project had two primary objectives. The first was to provide a detailed laboratory and field demonstration of iron and arsenic removal that was directed towards identification of kinetic and speciation concerns for oxidation/direct filtration processes. The second was to evaluate other considerations that might generally apply to the utility of coincident iron and arsenic removal for Wisconsin water suppliers.

Methods

The laboratory evaluation of iron and arsenic removal focused on the rate of simultaneous iron and arsenic removal in reactors that mimicked conditions typically encountered at small water systems. A natural groundwater was spiked with arsenic and iron concentrations and over time the filterability of the iron and arsenic were evaluated. Removal of both arsenite (As(III)) and arsenate (As(V)) were evaluated separately and in combination at an iron concentration of 2 mg/l and a pH of 7.0 and 7.5. The field investigation investigated the concurrent removal of iron and arsenic at two water systems in full-scale systems. Those systems were designed for iron removal and had not adjusted their processes to optimize arsenic removal. Arsenic analysis was by both graphite furnace atomic absorption spectrometry (GFAAS) and inductively couple plasma (ICP-OES). Arsenic speciation was determined by acidifying the filtered sample and then separating As(III) and As(V) with an ion exchange resin before analysis. The final evaluation of considerations for concurrent arsenic and iron removal used available information on iron and arsenic co-occurrence, characteristics of the water systems, and the nature of other likely water quality problems at Wisconsin public water systems. Although the work used data collected at Wisconsin water systems, the results were developed to be applicable to many regions of the Midwestern U.S. and provide a matrix of considerations that can be applied generally.

Results and Discussion

The laboratory and field investigations confirmed the utility of iron removal for the treatment of arsenic. At iron concentrations commonly encountered in groundwater systems (1-2 mg/l), removals of relatively low concentrations of arsenic (< 0.05 mg/l) ranged from approximately 60-80%. The laboratory investigation of coincident iron and arsenic removal rates confirmed this removal could largely be achieved within 10-15 minutes for As(V) at these conditions, and followed closely the rate of iron removal. The rate of As(III) removal during iron oxidation/precipitation at pH 7 and 7.5 was considerably slower. Although the laboratory results confirmed an increase over time in the filterability of the As(III) suggesting accumulation by precipitating iron, the rate was much slower than that observed for As(V).

Conclusions

The results of this research confirm the utility of coincident iron and arsenic removal for the treatment of groundwater containing arsenic. In groundwater systems treating water through relatively short residence times, the oxidation/precipitation/filtration treatment process can effectively remove As(V). The rate of arsenic association with precipitating iron did not appear a significant limitation with respect to As(V), but may be a consideration with respect to As(III), particularly for those systems with very short hydraulic residence times. Future work will investigate the extent to which these kinetic limitations might be observed at the field-scale.

Related Publications and Presentations

Technical Presentation: Iron and Arsenic: What's the Connection. Presented at the Wisconsin Water Association Annual Meeting, September 2002, Wisconsin Dells, Wisconsin.

Poster Presentation: Wisconsin State Environmental Health Meeting: Arsenic Removal with Iron (w/undergraduate student Jesse Baumann), September 2003

Poster Presentation: Arsenic Removal During Iron Treatment (w/undergraduate student Jesse Baumann) at the American Water Resources Association Wisconsin Section Meeting, Lac du Flambeau, February 2003.

Technical Presentation: Removal of Arsenic with Iron. Presented to the Wisconsin Department of Natural Resources Bureau of Drinking and Groundwater, Madison, April 24, 2003.

Keywords: Arsenic, Drinking Water, Iron

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

Basic Information

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

Publication

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

R/UW-SAM-002

by

Bryant A. Browne, Associate Professor of Soil and Water Resources
Nathan M. Guldan, Graduate Student
College of Natural Resources, University of Wisconsin-Stevens Point

Contract: July 1, 2001 – June 30, 2003
Funding: University of Wisconsin System (UWS)
Focus Area: SAM
Key Words: Denitrification, Nitrate, Groundwater Age, CFCs, Spatial Scale, Temporal Scale, Baseflow Water Quality

Background/Need

Nitrate (NO_3^-) concentrations in groundwater fed streams are frequently lower than concentrations in groundwater beneath adjacent agricultural recharge areas. The cause of this discrepancy and similar discrepancies for other chemicals poses a key question for understanding how agricultural practices affect water quality in many river systems. Unfortunately, conventional stream monitoring approaches are insufficient to address this question.

Two factors that contribute to differences in groundwater NO_3^- concentrations between recharge areas and stream discharge points are: 1) the transformation of NO_3^- to gaseous forms (nitrous oxide, nitrogen gas) by denitrifying bacteria and 2) the amount of time it takes groundwater to move through the landscape from recharge areas to discharge points (lag time). To predict how these factors affect baseflow water quality a better understanding of the spatial and temporal scales of groundwater/surface water interactions is needed.

Objectives

The objectives of this study were to characterize the spatial and temporal scales of groundwater discharge to a 4th order stream within an agricultural basin and to quantify the influence of groundwater denitrification on baseflow NO_3^- concentrations.

Methods

This study was conducted in the Tomorrow/Waupaca River Watershed which is located in parts of Portage, Waupaca, and Waushara Counties in central Wisconsin. A network of miniature wells (minipiezometers) along 1st through 4th order stream corridors was established to map the primary discharge areas. The well screens were installed at a depth of approximately 70 cm below the streambed in order to sample groundwater immediately before it discharged to the stream. Groundwater samples were collected from the minipiezometers in late summer and fall 2002 to map the chemical characteristics of discharge to the stream network. Surface water samples were collected on October 19, 2002 to create a corresponding map of the baseflow water quality. Groundwater gas samples were collected from each minipiezometer in late summer and fall 2002 to determine the amount of denitrification occurring and to determine the lag time of the groundwater using chlorofluorocarbons (CFCs).

Results and Discussion

Baseflow was primarily derived from zones of discharge within 1st and 2nd order drainage corridors. Discharge occurred at a spatial scale of < 50,000 m cumulative stream length. Beyond 50,000 m cumulative stream length there was little communication between groundwater and surface water.

Contemporary baseflow was comprised, on average, of groundwater recharged nearly three decades ago, and reflected a temporal scale spanning nearly a half century. The mean lag time of groundwater discharge measured by apparent CFC age-dating was 28 (± 12) yrs.

Contemporary baseflow NO_3^- concentrations were strongly affected by denitrification in groundwater. The concentration of denitrified N was more or less constant across the 50-yr temporal scale. Denitrification reaction progress (percent of groundwater NO_3^- converted to harmless N_2 gas) was nearly complete (86%) in older groundwater (> 32 yr), which contributes about one-third of the discharge to the TWR, due to low O_2 and the availability of e^- donors. But reaction progress declined dramatically in younger groundwater (< 32 yr) in association with rising NO_3^- concentrations, higher O_2, and limited availability of e^- donors. Overall, more than half (59%) of the NO_3^- carried in groundwater was transformed to harmless N_2 gas by denitrifying bacteria before its release to baseflow.

Current concentrations of total NO_3^- (NO_3^- + denitrified N) in discharge to the TWR reflected land use practices between 1950 and the early 1990s, and strongly parallel the historical rise of N-fertilizer use. Using lag time distribution and denitrification data, stream baseflow NO_3^- concentrations were projected over a 110-yr period centered on the present (2002). Predicted baseflow NO_3^- concentrations were consistent with available historical baseflow data (1975, 1995, 2002). Projections for the future under a stable land use scenario suggest that rising baseflow NO_3^- concentrations will plateau between 2005 and 2020.

Conclusions/Implications/Recommendations

The lag time between groundwater recharge and groundwater discharge to baseflow dominated streams has confounded attempts to use conventional baseflow water quality monitoring approaches to assess relationships between land use practices and water quality in river systems.

In this study, we show that a basin-scale synoptic survey (combining water quality and recharge age-date measurements) at the groundwater/surface water interface is a highly effective tool for deciphering relationships between historic land use and contemporary and future baseflow water quality.

Similar lag time/denitrification studies should be performed in other basins where a longer baseflow water quality record will allow a more rigorous validation of baseflow projections against historical data.

Related Publications

None at this time.

Determination of Aquitard and Crystalline Bedrock Depth Using Time Domain Electromagnetics

Basic Information

Title:	Determination of Aquitard and Crystalline Bedrock Depth Using Time Domain Electromagnetics
Project Number:	2002WI54O
Start Date:	7/1/2002
End Date:	6/30/2003
Funding Source:	Other
Congressional District:	2nd
Research Category:	Not Applicable
Focus Category:	Geomorphological Processes, Groundwater, None
Descriptors:	stratigraphy, geophysics, time domain electromagnetic method
Principal Investigators:	David John Hart

Publication

1. Anderson, M.L., D.J. Hart, and D.L. Alumbaugh, Use of the Time-Domain Electromagnetic Method for Determining the Presence and Depth of Aquitards, abstract in American Water Resources Association Wisconsin Section, 27th Annual Meeting, 2003.
2. Anderson, M.L. Use of the Time-Domain Electromagnetic Method for Determining the Presence and Depth of Aquitards, Masters Thesis, University of Wisconsin, 2003. pp. 143.

Project Summary

Project Title Determination of Aquitard and Crystalline Bedrock Depth Using Time Domain Electromagnetics

Project Number R/UW-HDG-006

Investigators

Principal Investigators:
David Alumbaugh, Associate Professor of Geological Engineering, and Civil and Environmental Engineering, University of Wisconsin-Madison
David Hart, Assistant Professor, Wisconsin Geological and Natural History Survey

Research Assistant:
Megan Anderson, Master's Student, Geological Engineering, University of Wisconsin-Madison

Background/Need

As groundwater needs and concerns have increased, larger and more complex groundwater flow models have been developed to address the problems associated with the exploitation of this precious resource. One of the first steps in creating a useful groundwater flow simulation for the Wisconsin region is the development of a conceptual model that includes hydrostratigraphic units, e.g., shale aquitards, sandstone aquifers, and streambed deposits in tills. The depth, thickness, and extent of these units are usually determined from geologic logs, but in locations where the logs are sparse or nonexistent, the modeler is left with the difficult choice of deciding stratigraphic placement at depth. Time domain electromagnetics is a geophysical tool that showed promise in filling in the gaps in the geologic record so that better flow models and understanding of geology can be realized. However, this tool needed further analysis to determine its accuracy under Wisconsin geologic conditions. Guidelines were needed to set boundaries on what structures the method is capable of resolving.

Objectives

The objective of this study was to provide an assessment of the Time Domain Electromagnetic (TEM) method as a hydrostratigraphic mapping tool and to delineate the shaley facies of the Eau Claire Formation.

Methods

The shaley facies of the Eau Claire Formation, an important regional aquitard in southern and southwestern Wisconsin, served as the test case in this study. We used borehole geophysics to measure the thickness, depth, and resistivity of the Eau Claire shale at four locations. First, those measured values were employed in a forward modeling exercise to determine the theoretical limits of the thickness, depth and resistivity of a shale unit that might be resolved using TEM. Following the forward modeling, we conducted 16 TEM surveys in Dane, Sauk, La Crosse, and Trempealeau counties using a Zonge NT-20 transmitter with a loop size of 100 m. Five TEM surveys were conducted at locations where the Eau Claire shale is constrained by well logs and in areas where the method was challenged due to the shale being thin and/or deep. Multiple surveys were conducted at Pheasant Branch Conservatory, the location where the method was pushed to its limit of resolution with the shale depth and thickness. These surveys allowed us to calibrate and test the method. Finally, 11 additional surveys were conducted at locations where the presence of the Eau Claire shale was unknown. The data collected in the field surveys were analyzed using the WinGLink geophysical software package.

Results and Discussion

The method successfully detected the presence of the Eau Claire shale when the unit was thick and/or shallow, but the method did not always correctly delineate the depth and thickness of the shale. At sites where the Eau Claire shale was present along with a second conductor, e.g., conductive lake sediments, or the deep Mount Simon, the inversion results typically indicated the presence of the deeper conductor, the Mount Simon shale, as well as a second conductor that was sometimes too shallow to be the Eau Claire shale.

Conclusions and Implications

By comparing the geologic structure predicted by the TEM surveys with known geologic structure, this study was able to measure how well the TEM survey could reproduce the known geologic structures. The method is useful for determining whether or not a shale is present and can give a general indication of depth and thickness, but should not be used without a geologic control point. The reliability of the method is significantly lessened by the presence of a second conductor at depth. TEM surveys with different loop sizes might possibly reduce this error. A smaller loop could more accurately characterize the shallower conductor. That information could then be incorporated into the analysis of the data from the larger loop.

Key Words

TEM surveys, electromagnetic, aquitard, Eau Claire shale, inversion, nonuniqueness

Funding

University of Wisconsin – Water Resources Institute

F Test for Natural Attenuation in Groundwater: Application on Benzene

Basic Information

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

Publication

PROJECT SUMMARY

Title: **F Test for Natural Attenuation in Groundwater: Application on Benzene**

Project I.D.: R/UW-REM-008

Investigator(s): Principal Investigator(s):
Fe S. Evangelista, Associate Professor, Mathematical and Computer Sciences Department, UW-Whitewater ;
Aristeo M. Pelayo, Hydrogeologist, RR/3, WDNR

Period of Contract: July 1, 2002 – June 30, 2003

Background/Need: Chapter NR 726, Wis Adm. Code, allows closure of a petroleum site contaminated above NR 140 groundwater enforcement standards when natural attenuation (NA) has been demonstrated as an effective remedial option. The primary evidence for NA is contaminant concentration data that show a decreasing trend over time. However, the concentrations may be affected by the fluctuation of the water table such that conclusions from trend analysis and rate of degradation may be premature. A statistical F-test procedure was developed to determine the significance of water-table fluctuations in evaluating NA sites
.

Objectives: To investigate the utility of an F-test in analyzing the statistical significance of including both groundwater elevation and time as predictors of benzene concentration. The conclusions of the test would be compared to the conclusions from the Mann-Kendall and Mann-Whitney nonparametric tests.

Methods: Data from the web-accessible WI GIS registry of closed sites were reviewed. Sites were chosen based on the presence of both groundwater elevation and benzene concentration data, and the absence of any active remediation system during the monitoring period. The data was analyzed using the F-test technique, the calculation of the apparent half-life $t_{1/2}$, (*negative* when benzene is increasing) from the slope of the ‘*t*’-only regression line; and trends concluded from two nonparametric tests–Mann-Kendall (M-K), and Mann-Whitney U (M-W)–for wells where a negative $t_{1/2}$ was obtained.

Results and Discussion: Thirty wells were chosen from 25 NA sites. Twelve (12) wells were identified where the F-test concluded that the line ‘*t*’-only model is preferred. This implies that straightforward trend analysis of the concentration data is acceptable for these wells. Fifteen (15) sites had wells where at least one of the following was observed: (a) the value of $t_{1/2}$ is negative indicating an increasing trend, (b) the plane model or line *‘z’* model is preferred by the F-test, or (c) the F-test is inconclusive but the line *‘z’* model’s R^2 is larger than that for the line *‘t’* model. The latter two conditions imply that the variable ‘z’ cannot be ignored and points to the influence of groundwater elevation on benzene concentration. Consequently, the time-trend analysis of the data, including conclusions from nonparametric statistical tests may be spurious. The report includes a detailed analysis of four sites to demonstrate the range of results and insights that can be gained in using the F-test technique.

Conclusions/Implications/ Recommendations: The F-test is an analytic tool that could be used to screen sites before the calculation of a degradation rate from the linear regression of concentration *vs.* time or the use of a nonparametric test to show trends. When the F-test shows that groundwater elevation is significant (plane, ‘*z*’-only, and inconclusive but ‘*z*’-only has larger R^2), then we know that this *invariant* factor is affecting the concentrations; and hence, a nonparametric test is not appropriate. On the other hand, when the F-test shows that *‘z’* can be ignored (*i.e.*, test result of either: *‘t’*-only , or inconclusive but the *‘t’*-only has larger R^2), then nonparametric statistics may be more appropriately used.

Key Words: Benzene, Least-square regression, Natural Attenuation, Statistical F-Test

Funding: University of Wisconsin System

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

Basic Information

Title:	Monitoring the Effectiveness of Phytoremediation and Hydrogeologic Response at an Agricultural Chemical Facility
Project Number:	2002WI56O
Start Date:	7/1/2002
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Agriculture, Groundwater, Solute Transport
Descriptors:	phytoremediation, pesticides
Principal Investigators:	William DeVita

Publication

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

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

Project duration: July 2002 – June 2004

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

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

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

Project Update

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

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

Project Update:

As of June 1, 2004, the following objectives tasks have been completed as part of the proposed activities.

- Mortality was determined and biomass was estimated in October 2003 and compared to previous annual growth.
- Monitoring wells have been sampled in May 2004 (data is not yet available)
- Site maintenance has been ongoing.
- Groundwater elevation has been determined to be diurnal. In conjunction with another funding source, sap flow through the poplar’s sapwood was monitored and determined to by synchronous with the change in groundwater elevation.
- Sap flow is considered equal to transpiration and determined to average 13.5 liters per day in 10 of the larger trees on this site in October 2003.
- Water usage estimates have been made based upon transpiration and biomass.

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

Basic Information

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

Publication

1. E. Lee, M.A. Anderson, W.A. Zeltner, Arsenic Removal Strategies Using Novel Adsorbent Material, American Water Works Association 2003 Annual Conference, Proceeding Paper, Anaheim, Ca., 6/15 6/19/2003.
2. E. Lee, M.A. Anderson, W.A. Zeltner, Photoactive Removal of As (III) From Water Using Novel Active Material, American Water Works Association 2003 Annual Conference, Proceeding Paper, Anaheim, Ca., 6/15 6/19/2003.
3. Eunkyu Lee, M. Anderson, and W. Zeltner, Arsenic Removal Strategies Using Novel Adsorbent Material, American Water Works Association 2003 Annual Conference, Proceeding Paper, Anaheim, Cal., June 15-19, 2003.
4. Eunkyu Lee, M. Anderson, W. Zeltner, Photoactive Removal of As(III) From Water Using Novel Active Material, American Water Works Association 2003 Annual Conference, Proceeding Paper, Anaheim, Cal., June 15-19, 2003.

Project Summary

Title:	**Photocatalytic Adsorption Media and Processes for Enhanced Removal of Arsenic from Groundwaters**
Project I.D.:	**R/UW-WSP-001**
Investigators:	**Marc A. Anderson (Principal Investigator)** Professor, Environmental Chemistry and Technology Program University of Wisconsin – Madison
	Eunkyu Lee Research Assistant, Dept. of Civil and Environmental Engineering University of Wisconsin – Madison
	Walter A. Zeltner Associate Scientist, Water Science and Engineering Laboratory, University of Wisconsin – Madison
	Timothy J. Lee Research Assistant, Dept. of Civil and Environmental Engineering University of Wisconsin – Madison
Period of Contract:	July 2002 – June 2003

Objectives:

The main objective of this study is to validate the new technologies we have developed in our laboratory for arsenic removal and to develop parameters for scaling these techniques to use in the field.

Methods:

Aluminum oxide (Al_2O_3), spinel ($MgAl_2O_4$), titanium dioxide (TiO_2) and mixed sols were synthesized by sol-gel technology and coated on glass beads. The synthesized media were tested in batch, column, and differential column batch reactors using synthetic solutions and groundwater samples from Danvers, Ill.

Results and Discussions:

Many arsenic removal processes have been found to be ineffective for arsenite, As(III), which is uncharged at the pH of drinking water. Removal of As(III) is generally accomplished by oxidizing it to arsenate, As(V), which can be removed by adsorption or ion-exchange mechanisms.

Previous researchers have found that the TiO_2/ultraviolet photocatalytic process effectively converts As(III) to As(V). However, most of these studies were performed with TiO_2 nano-particle suspensions. Removal of these particles later in the treatment process could be problematic. During the authors' testing, a heterogeneous photocatalytic adsorbent (Al_2O_3/TiO_2) was synthesized by sol-gel techniques and shown to effectively remove As(III) without requiring a separate oxidation process. This composite acts as a photocatalyst that can oxidize As(III) to As(V), with the latter species being adsorbed by the adsorbent. The materials (Al_2O_3/TiO_2) were mixed as a stable suspension (sol) that was used to coat glass beads. After the coated beads were fired, the resulting thin films served as both a photocatalyst and an adsorbent. It was found that the TiO_2 photocatalyst oxidizes As(III) at the same rate at a lower dissolved oxygen DO level (~ 1 mg/L) as at a higher DO level (7 mg/L).

Conclusions/ Implications/ Recommendations:

This study indicates that photocatalytic adsorption may prove to be an effective single-step method for removing arsenite without requiring separate oxidation and adsorption processes. Mixed coated media have been shown to remove arsenite more effectively than either pure Al_2O_3 or TiO_2. Photocatalytic oxidation of arsenite was found to be effective for both synthetic solutions and groundwater samples from Danvers, Ill. The photooxidation rate was not changed at a lower dissolved oxygen level, and the rate of arsenite oxidation in synthetic solutions and in groundwater samples was comparable. The photooxidation rate was not changed even after 6000 hours operation without regeneration. Arsenic adsorption on the surface of the photocatalyst did not interfere with the arsenite oxidation rate, therefore, this device is possible to use as a photocatalytic adsorption process. This test shows the potential for this combined oxidation-adsorption process, although further development and optimization is required.

Related Publications: None at present.

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

Funding: University of Wisconsin Water Resources Institute

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

Basic Information

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

Publication

1. Wilcox, J.D. 2003. Variability of groundwater chemistry in an agricultural setting and implications for assessing impacts of land use change. University of Wisconsin-Madison. M.S. Thesis. 121p.
2. Wilcox, J.D., K.R. Bradbury, J.M. Bahr, and C.L. Thomas. 2003. Variability of groundwater quality beneath an unsewered rural subdivision. Geological Society of America Abstracts with Programs (November 2003).
3. Wilcox, J.D., J.M. Bahr, K.R. Bradbury, and C.L. Thomas. 2003. Variability in groundwater chemistry beneath agricultural and rural residential land uses. Wisconsin Ground Water Association Annual Conference Program.
4. Wilcox, J.D., C.L. Thomas, K.R. Bradbury, and J.M. Bahr. 2003. Spatial and temporal variability of groundwater chemistry beneath agricultural land: Implications for assessing environmental impacts of a new unsewered subdivision. American Water Resources Association Wisconsin Section 27th Annual Meeting Program and Abstracts.

PROJECT SUMMARY

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

Project ID: **R/UW-OSW-001**

Investigator(s): Dr. Kenneth R. Bradbury, Hydrogeologist/Professor, Wisconsin Geological and Natural History Survey, University of Wisconsin-Extension

Jeffrey D. Wilcox, Research Assistant, Department of Geology and Geophysics, University of Wisconsin-Madison

Period of Contract: July 1, 2001 to June 30, 2003

Background/Need: Urban development of rural areas is a significant land-use issue in Wisconsin and in many other parts of the United States. Septic tank and leach field treatment of wastewater can release contaminants such as nitrate, bacteria, viruses, and hazardous household chemicals to groundwater systems, posing potential threats to nearby wells and surface water. Potential groundwater contamination is often cited as justification for discouraging or prohibiting new unsewered rural developments, particularly in environmentally sensitive areas with high water tables or shallow bedrock, yet few field studies are available to document groundwater impacts.

Objectives: This project was initiated as a long-term monitoring study to document groundwater conditions before, during, and after construction of an unsewered rural subdivision that employs alternative on-site wastewater treatment technologies.

Methods: Site investigations consisted of hydrogeologic studies and water sampling with the goals of understanding the geology of the site, local groundwater movement, and background groundwater quality. Shallow piezometers and deeper bedrock wells were used to characterize the field site and to sample for major ions, indicator species, and atrazine. Isotopes of nitrogen were used to distinguish nitrate sources.

Results and Discussion:

Two aquifers are present at the site – a shallow unlithified aquifer composed of glacial sediment and a bedrock aquifer. Water levels in site wells ranged from 7 to 54 feet below the land surface. Most recharge occurs during the spring months, with declining water levels the rest of the year. During spring recharge, the aquifer responds rapidly to precipitation, snowmelt, and ground thaw, although the magnitude of this response varies with location across the field site. Prior to subdivision construction almost all of the water samples collected from shallow wells at the Savannah Valley site showed evidence of human impact, as median values of nitrate-N (6.2 mg/L), sodium (17.0 mg/L), chloride (19.3 mg/L), and conductivity (821 µS/cm) were much higher than would be expected in an undeveloped area. Significant temporal and spatial variability in groundwater chemistry existed across the field site prior to subdivision construction. This variability can be explained by 1) seasonal variations in recharge, 2) local loading patterns, 3) aquifer heterogeneities, and 4) surface topography. Groundwater nitrate beneath the Savannah Valley subdivision site appears to have originated from both synthetic and organic (cow manure) fertilizers, as the measured $\delta^{15}N$ values fall between the typical values for the two sources.

Conclusions/Implications/ Recommendations:

For this study we installed monitoring equipment and acquired nearly two years of groundwater monitoring data prior to the construction of new homes at a rural subdivision site in south-central Wisconsin. The most important finding is the high variability - in both space and time - of groundwater quality across this relatively small subdivision site. Concentrations of chemical parameters just below the water table exceeded drinking water standards for nitrate and atrazine in some wells and showed evidence of land-use impacts (agricultural use and highway salting) in many wells. Concentrations in deeper bedrock wells, although lower and less variable, also showed evidence of impacts from land use. Groundwater monitoring should continue at the Savannah Valley site as the subdivision is developed and septic systems come into use. The background data collected prior to development provides a necessary benchmark against which to compare future land-use impacts.

Key Words: Groundwater, subdivisions, nitrate, land use

Funding: University of Wisconsin System, Madison Area Builders Association

Design and Evaluation of Rain Gardens for Enhancement of Groundwater Recharge

Basic Information

Title:	Design and Evaluation of Rain Gardens for Enhancement of Groundwater Recharge
Project Number:	2003WI58O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Water Quantity, Water Supply
Descriptors:	raingarden, recharge, urban hydrology
Principal Investigators:	Kenneth W. Potter

Publication

Design and Evaluation of Rain Gardens for Enhancement of Groundwater Recharge

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

Project Duration: July 2003–June 2005

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

Project Update:

We have been collecting data from the experimental rain garden since the fall of 2003. No problems were encountered during intermittent snowmelts during the winter and spring. Even with very large rainfalls in the late spring of 2004, the rain garden did not overflow.

We have made significant improvements to our computer model for designing and evaluating bioretention cells (RECARGA), including capacity for handling underdrains. We have also created a version of the model that does not require that the user have any proprietary software.

We have completed several drafts of a technical manual for the design of bioretention cells. Currently we are checking and refining the design charts that are provided in the manual.

We have also provided the Wisconsin Department of Natural Resources with infiltration design tools that it is using to enforce new rules requiring stormwater infiltration.

Evaluation of Contamination of Groundwater around Landfills

Basic Information

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

Publication

Evaluation of Contamination of Groundwater Around Landfills

T. B. Edil, University of Wisconsin-Madison, Civil and Environmental Engineering;
C. H. Benson, University of Wisconsin-Madison, Civil and Environmental Engineering;
and
J. Connelly, Wisconsin Department of Natural Resources, Bureau of Waste Management
Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2005

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

Project Update:

Analysis of the data presented in the WDNR Groundwater Environmental Management System (GEMS) database indicates that more than half of the 675 licensed landfills in the state show some presence of volatile organic compounds (VOCs) in the landfill leachate, lysimeters, or monitoring wells. To maintain a representative, yet manageable data set, sites with lysimeters were selected for further analysis. All of the 675 sites were viewed to determine that 88 sites were constructed with one or more lysimeter(s) as a component of the landfill and were thus further analyzed for VOC concentrations. Thirty-eight of the 88 sites had detects of one or more VOC at or above the limit of detection. At the 38 sites with detects there were 91 lysimeters because of multiple cells/lysimeters at particular sites. Concentrations of each of the 47 VOC monitored for by the WDNR were analyzed at all of the 91 lysimeters to determine which VOC's were most prevalent. The aforementioned analysis indicated that there were approximately 1,800 data points above the limit of detection consisting of 39 different VOC's. Also, there were 215 detects, at 26 different lysimeters, above the DNR enforceable standard. The concentration of the points above the enforceable standard ranged from being at the enforceable standard to 10 or more times that of the enforceable standard. Two hundred twenty-eight plots were made to determine the concentration variation versus elapse time for each VOC detected at each of the 91 lysimeters. The aforementioned analysis was performed to determine if there were any trends in the data through time. Graphical results show that the data is highly variable and no temporal trends were seen.

Data pertaining to VOC concentrations in the leachate at the 91 cells with lysimeters was analyzed to determine if the concentrations in the lysimeters could be expected. Leachate data was plotted using the same scale as was used for the lysimeter's data to determine if there were any trends or if any correlation could be made between the leachate and lysimeter data (at each landfill cell and for each compound). Five hundred seven plots were made and are currently being compared with the plots made for the lysimeter data to determine if there is any correlation between the two data sets. Also, VOC concentrations in the leachate will be used as initial concentrations for the transport modeling phase of this project.

Also, data on chloride concentration variation at each of the sites with lysimeter data is being examined to help determine if there is a predominant mode of transport through the liner system.

Results from the aforementioned analyzes will be compared with the construction documentation for each site to draw conclusions about what, if any, correlation can be made between VOC concentration and liner type (i.e., if there is a statistically significant difference in VOC concentrations at clay-lined versus composite-lined sites).

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

Basic Information

Title:	Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics in Subsurface Environments
Project Number:	2003WI60O
Start Date:	7/1/2003
End Date:	6/30/2005
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Surface Water, Waste Water
Descriptors:	antibiotics, environmental fate
Principal Investigators:	Joel Alexander Pedersen

Publication

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

K. G. Karthikeyan, University of Wisconsin-Madison, Biological Systems Engineering
and
J. A. Pedersen, University of Wisconsin-Madison, Soil Science
Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2005

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

Project Update:

This report summarizes our progress during the first year (July 2003 - June 2004) of our 2-year research project.

I. Sorption of Antibiotics to Mineral Surfaces:

Prior to initiating sorption experiments with mineral-associated humic substances, we investigated the effect of solution chemistry on antibiotic sorption to the pure mineral phases. Association of tetracycline (TC) and ciprofloxacin (CIP) to hydrous oxides of Al (HAO) and Fe (HFO) and sorption of sulfamethazine (SMZ) to smectitic clays and natural organic matter were investigated.

For both HAO and HFO, sorption of TC was slightly pH-dependent below pH 7 above which it decreased with increasing pH. Ligand-promoted dissolution, more pronounced between pH 4 and 7, occurred during TC sorption to these minerals. Ligand-promoted dissolution was more significant for HAO than HFO and was attributable to the difference in labile surface sites between these sorbents. TC sorption was quite rapid and equilibrium was achieved after 4 h. However, soluble metal (Me - Al or Fe) concentrations attained equilibrium only after 24 h. Ligand-promoted dissolution appears to be a two-step process; initially 1:1 Me-TC soluble complexes were formed and as the reaction progressed 2:1 Me-TC complexes existed. Increasing ionic strength decreased sorption only at higher sorbate-to-sorbent ratios suggesting the dominance of inner-sphere type complexes at low surface coverages. Spectroscopic evidence indicates that amide and carbonyl functional groups of TC could be responsible for sorption to mineral surfaces.

Ciprofloxacin is one of the most active fluoroquinolone antibiotics and is among the compounds detected in wastewater influent and effluent samples in our statewide survey of treatment plants in Wisconsin. Loss of CIP from solution was measured using liquid scintillation counting (LSC) and compound-specific HPLC analysis to accurately quantify sorption and also monitor transformation of the parent compound. Results indicate that CIP sorption to HAO and HFO has a strong pH-dependence with maximum sorption occurring in the pH range where the zwitterionic form is predominant. There is no significant difference in sorption extents quantified using LSC and HPLC, indicating that CIP is stable in solution. Sorption isotherms obtained at three different ionic strength values (0.01, 0.1 and 0.5 M NaCl) could be adequately described using the Langmuir isotherm equation. The extent of CIP sorption is independent of changes in ionic strength, suggestive of the formation of inner-sphere type complexes with the hydrous oxides of Fe and Al. Spectroscopic analysis, using FTIR equipped with a photo-acoustic detector, indicates that carboxylic group in CIP could be responsible for sorption to hydrous oxides.

We investigated the adsorption of sulfamethazine (SMZ) to the clay minerals montmorillonite (SWy-2, SAz-1) and kaolinite (KGa-1b) and Pehokee peat. By using [3,5-^{3}H]-SMZ, we were able to examine SMZ adsorption to a smectite (SWy-2) homoionic in Na^{+}, Mg^{2+}, K^{+}, Ca^{2+} at environmentally relevant concentrations as a function of pH and ionic strength. Different characteristic clay minerals, Na-saturated KGa-1b, SAz-1 and charge-reduced clay were used to elucidate the adsorption mechanisms. The General Linear Model was used to obtain distribution coefficients (K_d) for the cationic, neutral and anionic SMZ species. The value of K_d for cationic species adsorption to montmorillonite (SWy-2, SAz-1) was one to two orders of magnitude greater than that for neutral species. Increases in solution ionic strength suppressed adsorption at lower pH values and increased adsorption at lower proton activities. The adsorption of SMZ^{+} to Na-KGa-1b was negligible; the sorption of SMZ^{0} to Na-KGa-1b was comparable to that to Na-SWy-2. Overall SMZ sorption to smectitic clays was low, except at pH values less than approximately 3.5. Distribution coefficients for sorption to Pehokee peat were an order of magnitude higher than for clay minerals.

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

II. Association of Antibiotics with Dissolved Organic Matter:

We have conducted preliminary work on the association of antibiotics with dissolved organic matter (DOM) using equilibrium dialysis. To date we have focused on validating our experimental design. Although equilibrium dialysis has been used extensively for determining K_{DOC} values, a series of validation experiments is required to determine and account for the behavior of DOM and the antibiotics in the experimental apparatus. For example, we have examined DOM diffusion kinetics across the dialysis membrane and the amount of contamination from the dialysis tubing itself. We have developed procedures to minimize DOM leakage during experiments. We have also examined and developed a solution to quenching of scintillation by humic acids. We are currently completing the final stage of method validation for our SMZ experiments: determining SMZ sorption to dialysis tubing and closures and examining the kinetics of SMZ diffusion across the dialysis membrane.

Coupled Modeling of Gravity and Aeromagnetic Data for Analysis of the Waukesha Fault, Southeastern Wisconsin

Basic Information

Title:	Coupled Modeling of Gravity and Aeromagnetic Data for Analysis of the Waukesha Fault, Southeastern Wisconsin
Project Number:	2003WI61O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Models, None, None
Descriptors:	hydrogeology
Principal Investigators:	John D Skalbeck

Publication

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

J. Skalbeck, University of Wisconsin-Parkside, Department of Geosciences
Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2004

Increased concerns recently about the quantity and quality of groundwater resources in Wisconsin have brought about the need for better understanding of the subsurface geologic lithology and structure that controls groundwater flow. Geoscientists, engineers, and community planners often rely on numerical models for groundwater flow to effectively manage this vital resource. These models are typically based on correlating sparse data that are often located large distances apart and are limited in depth. The limited spatial data typically requires simplification of the conceptual model that may add uncertainty to the simulation results and the accuracy of a groundwater model. We propose incorporating potential fields (gravity and aeromagnetic data) modeling into the toolbox of the groundwater modeler to better constrain the conceptual model of a hydrogeologic system. The area near the Waukesha Fault in southeastern Wisconsin provides an excellent research opportunity for our proposed approach because of the strong gravity and aeromagnetic anomalies associated with the fault, the apparent complexity in fault geometry, and uncertainty in Precambrian basement depth and structure.

This study will provide a better-constrained subsurface geologic model of the area adjacent to the Waukesha Fault through coupled (simultaneous) modeling of gravity and aeromagnetic data. To our knowledge, coupled modeling of these two potential field data sets simultaneously has not been conducted to date. Strong interest in the Deep Sandstone Aquifer System of southern Wisconsin is prevalent due to extensive drawdown and reduction in groundwater quality. Results from this proposed study may also be useful for evaluating the conceptual model that provided the foundation for the regional groundwater model for southeast Wisconsin. Additionally, with excellent coverage of aeromagnetic and gravity data throughout Wisconsin, successful results from this study would encourage application of potential fields modeling in other groundwater research. Coupled modeling of gravity and aeromagnetic data greatly constrains the possible non-unique solutions that are inherent in any geophysical modeling method. The study will benefit hydrogeologist and groundwater resources managers working in southeastern Wisconsin. In addition, results of this study will illustrate that potential fields modeling is an important tool that can be incorporated into other groundwater studies in Wisconsin.

Project Update:

Normal vertical displacement along the Waukesha Fault produces strong gravity and aeromagnetic anomalies and abundant geologic log data that allows for well-constrained coupled modeling of gravity and aeromagnetic (potential fields) of subsurface geology in southeastern Wisconsin. Compiled gravity and aeromagnetic maps for Wisconsin from the U.S. Geological Survey (USGS) provides well-documented data for this study.

A geologic model was first constructed along a northwest-southeast profile to include lithologic depths from the only well (USGS Test Well, Zion, Ill.) in the study area that penetrates the entire Cambrian-Ordovician aquifer system to reach the Precambrian basement. Lithology depths from the USGS well log database used to construct the southeastern Wisconsin regional numerical groundwater flow model provide additional constrains on possible model configurations. Previous local and state-wide studies provided initial density and magnetic susceptibility data for geologic formations that were adjusted to optimize the model fits this well-constrained profile.

Models of two parallel profiles were constructed using the optimized density and magnetic susceptibility values obtained from the first profile and lithologic depths from the USGS well log database. Preliminary model results from these profiles suggest vertical offset of Precambrian basement from 700 to 800 m along a high angle normal fault. Based on thickness of the Cambrian Mount Simon sandstone, preliminary results also suggest that most of the offset occurred during the Cambrian.

What Happens as the Confined Cambrian-Ordovician Aquifer in Southeastern Wisconsin Begins to be

Basic Information

Title:	What Happens as the Confined Cambrian-Ordovician Aquifer in Southeastern Wisconsin Begins to be
Project Number:	2003WI62O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Quantity, None, None
Descriptors:	aquafer, physical sandtank model, unsaturated conditions
Principal Investigators:	Timothy T. Eaton

Publication

What Happens When the Confined Cambrian-Ordovician Aquifer in SE Wisconsin is "Dewatered?"

T. Eaton, University of Wisconsin-Extension, Wisconsin Geological and Natural History Survey

Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2004

The Cambrian-Ordovician aquifer has long been an important source of municipal water supply in SE Wisconsin, and pumping has drawn down the potentiometric surface of the deep aquifer system by over 400 ft during the 20th century. Regional flow modeling and limited well data suggest that static water levels may be locally below the base of the Maquoketa Formation that forms the regional aquitard. The objectives of this proposal are 1) to investigate how unsaturated conditions might develop in a scaled physical sand-tank model, 2) to attempt to verify the development of such hydrogeologic conditions in the field, and 3) to predict the long-term impact on water supply and quality by observing the evolution of head in the vicinity of model pumping wells. Use of a physical sand-tank model presents an opportunity to investigate a phenomenon that is not commonly addressed by conventional computer flow models. Head data collected as unsaturated conditions develop in an appropriately instrumented physical model will be useful for future specialized computer simulation of geochemical processes (PHREEQE-C) or saturated/unsaturated conditions (HYDRUS, SUTRA).

Project Update:

The physical sand-tank model has been constructed and tested, and is now being used to investigate the distribution of head when model pumping wells are discharging. Glass beads sieved to within a size range of 0.125-0.106 mm, rather than natural sand, were needed to approximate the hydraulic conductivity of the Cambrian-Ordovician aquifer.

Preliminary sand-tank model operation was filmed, and analysis shows the spatial extent over time of drawdown below the elevation of measurement points while model wells are being pumped. Since wellhead valves were closed during this experiment, no air was permitted to enter the aquifer system, and heads below measurement points indicate pressures below atmospheric.

An additional experiment is planned while pumping model wells with wellhead valves open, better representing real-world conditions, to investigate desaturation processes. Field installation of multi-evel piezometers below the Maquoketa aquitard at a site in southeastern Wisconsin is currently being completed. These piezometers will allow long-term monitoring of the development of unsaturated conditions in the field.

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

Basic Information

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

Publication

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

M. Anderson, University of Wisconsin-Madison, Geology and Geophysics
Funding Agency: UWS Groundwater Research Program

Project Duration: July 2003–June 2004

As water resources become stressed in the State of Wisconsin owing to increased demand for municipal water, aquifer storage and recovery (ASR) may become an increasingly viable option. In ASR, excess water is stored in aquifers when demand is low and withdrawn for use when demand increases. In this research, groundwater flow and transport models of ASR systems were developed for three representative hydrogeologic settings in Wisconsin: a confined sandstone aquifer representative of conditions in SE Wisconsin, an unconfined glacial drift aquifer representative of the surficial aquifer in SE Wisconsin, and an unconfined fractured dolomite aquifer representative of conditions around Sturgeon Bay. The groundwater flow code MODFLOW and the transport code MT3DMS, as well as the particle tracking code MODPATH were used to simulate storage and recovery cycles in the systems. Sensitivity to regional hydraulic gradient, dispersivity, effective porosity, and zones of high hydraulic conductivity, as well as pumping rates and storage times were investigated. A better understanding of the effects of these hydrogeologic parameters and conditions as well as pumping rates and storage times will help guide future planning and implementation of ASR systems in Wisconsin.

Project Update:

We decided to focus most of our efforts on modeling the confined sandstone aquifer representative of conditions in the area around Waukesha, Wisconsin. There is an ASR system currently in operation in nearby Oak Creek, Wisconsin, and the city of Waukesha is considering implementing ASR. Furthermore, ASR is almost always designed for confined aquifer systems. Results for this setting show that recovery efficiency is most sensitive to the ambient groundwater velocity of the system. Groundwater velocity is controlled by the regional hydraulic gradient, hydraulic conductivity and effective porosity. In simulations using particle tracking without mixing between the ambient groundwater and the injected water, effective porosity is the most sensitive parameter. When mixing between injected and ambient groundwater is included using the transport model MT3DMS, dispersivity (the mixing parameter) is the most sensitive parameter. In the particle tracking simulations, recovery efficiency varied inversely with hydraulic gradient and directly with storage period, effective porosity and volume of injected water; injection and recovery rates did not affect recovery efficiency. In the transport simulations, recovery efficiency varied inversely with dispersivity, hydraulic gradient and storage period and directly with volume of injected water. Increasing the hydraulic conductivity of a layer initially caused an increase in recovery efficiency, which leveled off and then decreased as hydraulic conductivity increased.

Modeling of the unconfined systems is currently underway. Preliminary results show similar trends in sensitivity of recovery efficiency to hydrogeologic parameters and conditions. The unconfined systems, however, exhibit significant mounding and locally high hydraulic gradients around the ASR well when large volumes of water are injected owing to the high storage coefficients that characterize unconfined systems.

Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation

Basic Information

Title:	Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation
Project Number:	2003WI64O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Water Quality
Focus Category:	Treatment, Groundwater, Water Quality
Descriptors:	remediation
Principal Investigators:	Zhaohui Li

Publication

Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation

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

Project Duration: July 2003–June 2005

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

Project Update:

Oxidative dechlorination of chlorinated solvents by permanganate is an emerging technology for remediation of groundwater contaminated with dissolved chlorinated contaminants. During the first year, the enhancement of trichloroethylene (TCE) and perchloroethylene (PCE) degradation by permanganate in aqueous solution in the presence of surfactant was evaluated through a continuous stir batch reactor system with the presence of permanganate as the limiting reagent and free phase TCE or PCE. The TCE and PCE degradation was determined by continuously monitoring the amount of chloride produced, which was then reverted to the rate of permanganate consumption. It was found that the chloride production, an indication of TCE degradation, followed a pseudo-first-order reaction kinetics with respect to $KMnO_4$ in the presence of free phase TCE. When no surfactants were present, the observed pseudo-first-order rate constant (k_{obs}) was 0.08–0.19 min^{-1} and the half-life ($t_{1/2}$) was 4–9 min for MnO_4^-. When the surfactant concentration was less then its critical micelle concentration (CMC), the k_{obs} values increased to 0.42–0.46 min^{-1} and the $t_{1/2}$ reduced to 1.5–1.7 min for MnO_4^-. As the surfactant concentration was greater than the CMC, the k_{obs} values increased to 0.56–0.58 min^{-1} and the $t_{1/2}$ reduced to 1.2–1.3 min. The reaction rate also increased when ninate 411, another type of anionic surfactant, at concentrations of 0.1, 0.3 and 1.0% were present in the system. The results showed that combination of permanganate with a proper type of surfactant could speed up contaminant removal.

Contrast to the much greater enhancement for TCE oxidation, the enhancement of PCE oxidation by $KMnO_4$ in the presence of SDS was less obvious. The k_{obs} without SDS was 0.006 min^{-1} compared to 0.007 – 0.008 min^{-1} when 35 and 10.5 mM SDS were present. The $t_{1/2}$ was 124 min when SDS was absent. The $t_{1/2}$ was reduced to 98 – 83 min when 35 and 10.5 mM SDS were present.

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

Basic Information

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

Publication

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

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

Project Duration: July 2003–June 2005

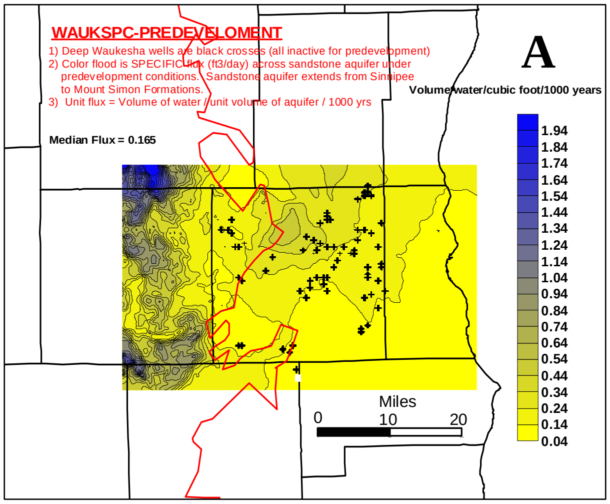
A major issue facing water managers and users in eastern Wisconsin is a high, and in certain wells, increasing concentration of TDS and radioactivity in the deep sandstone aquifer. At present, the source and movement of these contaminants is uncertain. Our current level of understanding of conditions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

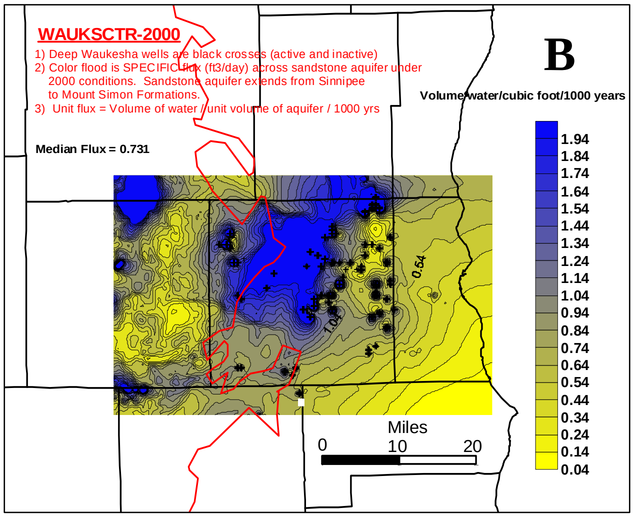
Project Update:

A graduate student has been identified for this project and has begun work on multiple aspects of this project. Several tasks are concurrently underway. Many of these tasks rely on “wells-of-opportunity,” ie., those that are open for repairs or are newly constructed. Specific tasks that are currently on-going include:

- Reevaluation of dynamic flowmeter logs previously obtained from various municipalities. This is a critical ingredient in extracting vertically discrete information. By July 2004, a newly completed well in Pewaukee will be pump-tested and we will perform geophysical and flowmeter logging and collect vertically discrete samples.

- An inset model has been built that focuses on Waukesha County. This inset model uses head boundaries from the SEWRPC regional flow model (ref.) This model will be used to further refine the flow regime within Waukesha County and test the hypothesis that upwelling of deep radioactive water is occurring. The regional model itself has also been used to ascertain the extent of changes to the regional flow regime that have been engendered by pumpage in SE Wisconsin. One example of the changes engendered is shown in the accompanying figure. Map A shows the gallons of water moving through a given unit of aquifer per 1,000 years (the specific flux) before pumping began in SE Wisconsin. Map B shows the specific flux for current conditions (year 2000). The primary pool of radium in the system is on the solids and the extra "flushing" of the aquifer due to increased pumping is a key factor in determining the causes of high radium in the water.





- Ultrafiltration and analysis of samples collected from select pairs of wells is underway to test for the possibility that colloids are partially responsible for the transport of radium in the aquifer. The selected wells exhibit different radium levels yet are of similar construction, geographic location and water chemistry.

- Petrographic, X-ray diffraction and cation exchange analyses are being performed on a suite of aquifer solids obtained during the drilling of a new well in Pewaukee. This will provide information on the solid phases that is critical for realistic geochemical modeling.

Providing Communities with the Groundwater Information Needed for Comprehensive Planning

Basic Information

Title:	Providing Communities with the Groundwater Information Needed for Comprehensive Planning
Project Number:	2003WI66O
Start Date:	7/1/2003
End Date:	6/30/2004
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Quantity, Hydrology, Models
Descriptors:	comprehensive planning, recharge
Principal Investigators:	Douglas S. Cherkauer

Publication

Providing Communities with the Groundwater Information Needed for Comprehensive Planning

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

Project Duration: July 2003–June 2005

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

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

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

A call for volunteers has identified 35 well owners who have joined our monitoring study. We measure water levels in their wells bimonthly, producing both a series of water table maps and well hydrographs. Four sets of water levels have been collected to date. In addition groundwater discharge as stream baseflow is being monitored at six sites.

Over 550 WCRs have been used to generate 22 hydrogeologic cross sections through the study area. A sequence of five pairs of glacial tills and outwashes overlies dolomite bedrock, producing a complex aquifer system of interwoven sand and gravel atop porous and fractured dolomite.

Recharge rates have been estimated using GIS information on land cover, drainage system, soil properties and hillslope. The process was developed in an earlier Joint Solicitation project. The recharge values will be verified against rates obtained by analysis of the well hydrographs at the 35 monitoring locations.

At present, the hydrogeology, surface hydrology and recharge are being incorporated into a groundwater flow model for the study area. It will be calibrated to the heads observed in the monitored wells and to the fluxes measured at our stream gaging sites.

The information generated by this project is being included in Element 5 of the Comprehensive Plan, which the town is currently developing. We have been asked to present our results to the public via both newsletter and public meetings, and ultimately it will be placed on the town's Web page. Based on feedback to date, it appears that both the citizenry and leadership are very supportive of crafting a plan which will protect the quantity and quality of the ground water resource.

Information Transfer Program

University of Wisconsin-Water Resources Institute - Information Transfer

Basic Information

Title:	University of Wisconsin-Water Resources Institute - Information Transfer
Project Number:	2002WI2B
Start Date:	3/1/2003
End Date:	2/28/2004
Funding Source:	104B
Congressional District:	WI - 2nd
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Anders W. Andren, JoAnn M. Savoy

Publication

1. Anderson, Marc A., Eunkyu Lee, Walt Zeltner, and Timothy J. Lee. 2003. Photocatalytic adsorption media and processes for enhanced removal of arsenic from groundwaters. Water Resources Institute, University of Wisconsin-Madison. 12p.
2. Anderson, Megan L., David J. Hart and David Alumbaugh. 2003. Determination of aquitard and crystalline bedrock depth using time domain electromagnetics. Water Resources Institute, University of Wisconsin-Madison. 15 p.
3. Bradbury, Kenneth R. and Jefffrey D. Wilcos. 2003. Impacts of privately sewered subdivisions on groundwater quality in Dane county, Wisconsin. Water Resources Institute, University of Wisconsin-Madison. 16 p.
4. Browne, Bryant A.. 2003. A basin scale denitrification budget for a nitrate contaminated Wisconsin aquifer : A study at the groundwater/surface water interface. Water Resources Institute, University of Wisconsin-Madison. 15 p.
5. Browne, Bryant A. and Nathan M. Guldan. 2003. Monitoring and scaling of water quality in the Tomorrow-Waupaca watershed. Water Resources Institute, University of Wisconsin-Madison. 19 p.
6. Cherkauer, Douglas S. and Craig J. LaCosse. 2003. Causes of historical changes in groundwater recharge rates in Southeastern Wisconsin. Water Resources Institute, University of Wisconsin-Madison. 17 p.
7. Dodson, Stanley. 2003. Effect of clean and polluted groundwater on reproduction and development on Daphnia. Water Resources Institute, University of Wisconsin-Madison. 16 p.
8. Evangelista, Fe.S. and Aristeo M. Pelayo. 2003. F-test for natural attenuation in groundwater:

Application on benzene. Water Resources Institute, University of Wisconsin-Madison. Water Resources Institute, University of Wisconsin-Madison. 1 vol.

9. Evans, Christine V. and Zhaohui Li. 2003. Removal of heavy metals and radionuclides from soils using cationic surfactant flushing. Water Resources Institute, University of Wisconsin-Madison. 15 p.
10. Gaffield, Stephen J., Todd W. Rayne, Lizhu Wang and Kenneth R. Bradbury. 2003. Impacts of land use and groundwater flow on the temperature of Wisconsin trout streams. Water Resources Institute, University of Wisconsin-Madison. 19 p.
11. Hunt, Randall J. Investigation of changing hydrologic conditions in the Coon Creek watershed in the Driftless area of Wisconsin. Water Resources Institute, University of Wisconsin-Madison. 16 p.
12. Park, Jae K. 2003. Removal of arsenic in groundwater using novel mesoporous sorbent. Water Resources Institute, University of Wisconsin-Madison. 16 p.
13. Potter, Kenneth W. 2003. Field evaluation of rain gardens as a method for enhancing groundwater recharge. Water Resources Institute, University of Wisconsin-Madison. 15p.
14. 2003 Annual Meeting of the Wisconsin Section of the American Water Resources Association (AWRA) Call for Papers: Gathering of the Waters. 2003. Water Resources Institute, University of Wisconsin-Madison. 2 p.
15. 2003 Annual Meeting of the Wisconsin Section of the AWRA Program Highlights and Registration: Gathering of the Waters. 2003. Water Resources Institute, University of Wisconsin-Madison. 2 p.
16. 2003 Annual Meeting of the Wisconsin Section of the AWRA Program Highlights and Registration: Gathering of the Waters. 2003. Water Resources Institute, University of Wisconsin-Madison. 2 p.
17. 2003 Annual Meeting of the Wisconsin Section of the AWRA Announcement and Abstracts: Gathering of the Waters. 2003. Water Resources Institute, University of Wisconsin-Madison. 55 p.
18. University of Wisconsin Aquatic Sciences Center. Liquid Assets: Wisconsins Water Wealth. 2003. Aquatic Sciences Center, University of Wisconsin-Madison. 32 p.
19. Recent Acquisitions and Web Sites of Interest. Monthly 3/2003 - 9/2003. Water Resources Library, University of Wisconsin-Madison. Various.
20. UW Water Resources Library Launches Online Information Resource. Press release. 2003. Water Resources Institute, University of Wisconsin-Madison. 1 p.
21. New Studies to Analyze Role of Antibiotics, Other Issues Regarding Wisconsins Water Supply. Press Release. 2003. Water Resources Institute, University of Wisconsin-Madison. 1 p.
22. Wisconsins Water Library. Bookmark. 2003. Water Resources Institute, University of Wisconsin-Madison.
23. Water Wealth, Water Woes. Fact Sheet. 2003. Water Resources Institute, University of Wisconsin-Madison. 2 p.
24. Arsenic. Fact Sheet. 2003. Water Resources Institute, University of Wisconsin-Madison. 2 p.
25. Groundwater Drawdown. Fact Sheet. 2003. Water Resources Institute, University of Wisconsin-Madison. 2 p
26. Park, Jae K. and Min Jang. Removal of Arsenic and Other Anions Using Novel Adsorbents. 2003. P02222US Patent, Applied at September 18, 2003.

Besides sponsoring conferences, maintaining a Web site, issuing publications, and supporting a library, WRI embarked upon several new information dissemination or outreach activities during the past fiscal year.

Wisconsin's Water Library

Established in 1964 by the UW Water Resources Institute, the Water Resources Library (WRL) is one of many UW-Madison libraries. The library has a unique collection of almost 30,000 volumes of water-related information, a curriculum collection, dozens of educational videos, and over 60 journals and 100 newsletters.

During 2003, the WRL developed Wisconsin's Water Library (*www.aqua.wisc.edu/waterlibrary*) as a special Year of Water outreach project and became the first Wisconsin academic library to make its collection available online to the public. Books and other library materials may be checked out by any Wisconsin resident free of charge and are sent to the user's local public library for pick up and return. The online library also includes "Ask a Librarian," a help-feature for visitors.

The Water Library was chosen as the Great Lakes Information Network "Web Site of the Month" in April 2004. Articles about this new resource have appeared in newsletters or on Web sites sponsored by the Wisconsin Department of Public Instruction, the Wisconsin Department of Natural Resources, UW-Madison Libraries, Milwaukee Public Library and 15 other organizations.

Partners

UW-Madison Libraries
Wisconsin Public Libraries
Wisconsin Libraries Delivery Network
Wisconsin Academy of Sciences, Arts and Letters
UW Sea Grant Institute
Wisconsin Department of Public Instruction Division for Libraries, Technology & Community Learning
Wisconsin Department of Natural Resources

Promotional Materials Developed

Bookmark
Press release
Email news release

Wisconsin's Water Library for Kids

WRL applied for and received a grant from the Friends of UW-Madison Libraries to purchase K-8 materials for Wisconsin's Water Library. Library staff with the assistance of an advisory committee selected materials for the "kids" section of the Water Library and to support Madison JASON. Madison JASON is a UW Sea Grant-sponsored program dedicated to improving science, math, and technology education for students in grades 4-9.

Additional Partners

UW-Madison Cooperative Children's Book Center,
Friends of UW-Madison Libraries
Madison Jason
Wisconsin Department of Natural Resources
Dane County UW Extension Natural Resource/Community Development Educator

Wisconsin teachers, home schoolers and school librarians statewide

Digitization of WRI and Selected DNR Groundwater Research Reports

The Water Resources Library partnered with UW System Digital Collections Center to digitize WRI and selected DNR groundwater research/monitoring final reports funded under the Joint Solicitation for Groundwater Research and Monitoring Projects. The final reports are now available online at the WRI Groundwater Research and Monitoring Program Web site (*www.wri.wisc.edu/wgrmp/wgrmp.htm*) and the UW Ecology and Natural Resources Collection (*webcat.library.wisc.edu:3200/EcoNatRes/*). This digitization project allows us to make the full text of important groundwater research available online to a broader audience.

Partners

University of Wisconsin Digital Collections Center
Wisconsin Department of Natural Resources

Wisconsin Water Policy Inventory

During the past year, staff in cooperation with a University of Wisconsin-Madison graduate seminar developed the Wisconsin Water Policies Inventory (*www.aqua.wisc.edu/waterpolicy*), a Web-based tool for researching the state's major policies pertaining to water. This project, undertaken for the Year of Water observance, enables Wisconsinites to browse state policies by category or to search using keywords. Steve Born, UW-Madison professor of planning and environmental studies, co-directed the project with Elisa Graffy, U.S. Geological Survey policy specialist. Wisconsin citizens should now be able to easily find state laws, rules and programs that govern Wisconsin's water resources.

Partners

UW Sea Grant
UW-Madison Dept. of Urban and Regional Planning
UW-Madison Gaylord Nelson Institute for Environmental Studies
Students of URPL/IES Class 865
Wisconsin Academy of Sciences, Arts and Letters
U.S. Geological Survey, Water Resources Discipline, Wisconsin District

Groundwater Fact Sheets

Water Resources Institute staff published three fact sheets dealing with the Institute and groundwater problems in Wisconsin. The fact sheets were issued in both hard copy and *.pdf format. They can be viewed online at *www.wri.wisc.edu*.

Water Wealth, Water Woes
An introduction to the Wisconsin Water Resources Institute, one of 54 Water Resources Research Institutes nationwide dedicated to research, outreach and education to solve state, regional and national water problems.

Groundwater Drawdown
Large-scale pumping of groundwater has caused large drawdowns – long-term drops in groundwater levels – in the Lower Fox River Valley, southeastern Wisconsin and Dane County. Drawdowns can cause serious economic, health and environmental problems: wells run dry and must be drilled deeper; concentrations of arsenic, radium, salts and other naturally occurring substances can reach unhealthy levels; and streams, lakes and wetlands lose water or dry up, depriving fish, birds, amphibians and mammals of vital habitat.

Arsenic

Elevated levels of arsenic have been detected in public and/or private drinking water systems in 30 of Wisconsin's 72 counties. Long-term exposure to arsenic in drinking water has been linked to cancer of the skin, bladder, prostate, lungs, nasal passages, kidneys and liver.

Wisconsin's Year of Water Activities

The Wisconsin WRI has been an active participant in the Wisconsin Academy of Sciences, Arts and Letters' 2003 "Year of Water" observance. During the past year, WRI helped support a full-time associate position at the academy to coordinate Year of Water activities, consisting of nearly 100 events throughout the state. Wisconsin WRI staff contributed directly to the development of a *Waters of Wisconsin* report, released on Earth Day 2003, which summarizes the status of Wisconsin's surface and groundwater resources, defines current and future issues, and recommends and lays the groundwork for developing a comprehensive state policy on water quality, use and sustainability—a key provision in Governor Doyle's "Grow Wisconsin" job creation plan.

Ongoing Activities

Wisconsin WRI Web Site:

The WRI Web Site (*wri.wisc.edu*) introduces users to the Wisconsin program and includes a variety of information for those interested in water-related issues and research. The site includes information about current and previous projects, funding opportunities, conferences, the Water Resources Library, and WRI publications. Other features include the directory of Wisconsin water experts and the Wisconsin Groundwater Research and Monitoring Program projects database developed in cooperation with the Wisconsin departments of Natural Resources; Agriculture, Trade & Consumer Protection; and Commerce.

Publications

From March 2003 through February 2004, institute staff published 13 final reports from WRI-funded projects as well as several other conference, program-related and library publications. Besides staff activities, much WRI-funded research appeared in refereed professional journals, as well as technical reports, conference proceedings and abstracts, book chapters, and dissertations and theses.

UW Water Resources Library

UW Water Resources Library is a unique collection of more than 30,000 volumes covering all major water topics. It is particularly strong in Wisconsin and Great Lakes water resources issues, groundwater protection, wetlands issues, and the impacts of agricultural chemicals. The library also has an extensive collection of publications from other state Water Resources Research Institutes and subscribes to more than 30 journals and receives more than 100 newsletters. As detailed above, the library launched Wisconsin's Water Library during the past fiscal year to make its resources available to all Wisconsin residents, began building a Water Library for Kids and undertook a project to digitize the Wisconsin Groundwater Research and Monitoring Program projects.

Conferences

Conference: American Water Resources Association – Wisconsin Section 27th Annual Meeting: "Gathering of the Waters"
Lead Sponsor: American Water Resources Association, Wisconsin Section

Co-Sponsors: UW Water Resources Institute; Wisconsin Department of Natural Resources; UW-Stevens Point Center for Watershed Science and Education; and U.S. Geological Survey, Wisconsin District
Attendance: 150

WRI continues to co-sponsor this annual meeting, which is unique in that it encourages students to present papers or posters describing their original research. Students funded through the Wisconsin Groundwater Research and Monitoring Program are particularly encouraged to present results of their research

Student Support

None

Notable Awards and Achievements

Publications from Prior Projects

1. 2001WI35O ("Effect of Clean and Polluted Groundwater on Reproduction and Development of Daphnia") - Articles in Refereed Scientific Journals - Kashian, Donna R., Stanley I. Dodson. 2004. Effects of Vertebrate Hormones on Development and Sex Determination in Daphnia magna. Environmental Toxicology and Chemistry. 23(5). pp. 1282-1288.