Water Resources Institute
Annual Technical Report
FY 2006

Introduction

The University of Wisconsin Water Resources Institute (WRI) is based at UW-Madison as an academic unit of the university's Graduate School and works with its Office of Research & Sponsored Programs to ensure compliance with university, state and federal guidelines. WRI is housed in the UW-Madison Aquatic Sciences Center (ACS), the administrative home of both WRI and the UW Sea Grant Institute. The staff at ACS provides support for WRI administration, research and outreach activities. The WRI also supports a library containing more than 26,000 volumes covering all major water topics. With nearly 75% of its current base budget targeted for research, the WRI is supporting 24 individual research projects that address a wide range of water-related issues and problems. Research projects fall into the following four thematic areas: groundwater, surface water, groundwater/surface water interactions and drinking water initiatives. Participants in WRI-supported projects include faculty, staff and students at UW System campuses at Madison, Milwaukee, Stevens Point, Whitewater, LaCrosse and Parkside; UW-Extension; the Wisconsin State Laboratory of Hygiene; U.S. Geological Survey, and individuals in private industry. In May 1984, Comprehensive Groundwater Protection legislation for Wisconsin (1983 Act 410, Wisconsin Statutes) was signed into law. One of the provisions of the bill was to establish a state Groundwater Coordinating Council (GCC) appointed by the legislature and the governor. Advisory to the GCC is the Groundwater Advisory Council (GRAC), which is appointed by the UW-Madison Chancellor. Because groundwater protection is deemed a priority issue by the WRI, the GRAC serves as an important advisory committee for the WRI. Composed of a diversity of representatives with a great deal of scientific, political and administrative experience, the GRAC has helped the WRI identify current and anticipated water problems and issues and establish priorities for initiating research projects. Since July 1989, the state has provided line item funding for groundwater research to the UW System. This Groundwater Research Program, administered by the WRI, currently funds 14 projects that provide a balanced program of laboratory, field and computer modeling studies and applications designed to preserve or improve groundwater quality. Charged with the primary mission to plan, develop and coordinate research programs that address present and emerging water- and land-related issues, the WRI has developed a broadly based statewide program of basic and applied research that has effectively confronted a spectrum of societal concerns. Institute staff; UW System faculty, staff and students; state administrators and other public officials; industry, and the public have come to rely on the WRI for objective, timely scientific information about water resources issues. The WRI ensures that this information reaches these individuals through its strong information dissemination/technology transfer program. An integral part of the WRIs total program is the training of students. Research projects have provided support and training for graduate and undergraduate students pursuing degrees in a wide range of disciplines.

Research Program

As established by Wisconsin's Groundwater Law of 1984, the state provides $300,000 annually to the UW System to support groundwater research and monitoring. In 1989, the WRI became the UW System's lead institution for coordinating the calls for proposals and peer reviews for distribution of the funds. To avoid duplication and better target groundwater research funding, several other state agencies (the departments of Commerce, Natural Resources, and Agriculture, Trade and Consumer Protection) agreed to partner with the WRI to establish an annual Joint Solicitation for Groundwater Research and Monitoring. This annual solicitation has funded more than 300 groundwater research and monitoring projects since its inception and has helped establish Wisconsin as a leader in groundwater research. The results of the Wisconsin Groundwater Research and Monitoring Program (WGRMP) are recognized internationally, and WRI plays an important role in coordinating project reporting and making all technical reports available though our institute's library and website. Given the limited funding available through the annual 104(B) allocation, the Wisconsin WRI has decided to use its funds to participate in the WGRMP by supplementing this funding source and providing additional opportunities for groundwater research in the UW System. Our priorities for research are established annually by the Wisconsin Groundwater Research Advisory Council (GRAC) and included as part of the Joint Solicitation. The GRAC is our institute's advisory council and also convenes to make project funding decisions. All proposals submitted to the Joint Solicitation receive rigorous external peer review (coordinated by the WRI) and relevancy review by the Research Subcommittee of the state's Groundwater Coordinating Council. We believe that partnership with other state agencies provides us with the ability to fund highly relevant research and allows our limited funds for 104(B) to be leveraged to the fullest extent.

Monitoring Environmental Effects at an Established Phytoremediation Site

Basic Information

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

Publication

Monitoring Environmental Effects at an Established Phytoremediation Site

Phase III

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TABLE OF CONTENTS

Figures and Tables

PROJECT SUMMARY

Monitoring Environmental Effects at an Established Phytoremediation Site

Project I.D.: WR04R007

Investigators: William M. DeVita – Laboratory manager, Water and Environmental Analysis Laboratory, University of Wisconsin – Stevens Point.
Mark Dawson – Environmental Engineer, Sand Creek Consultants, Amherst, WI.

Period of Contract: July 1, 2004 – June 30, 2006

This study is a continuation of groundwater monitoring (contaminants and elevation), along with examination of mortality and estimated biomass production of hybrid poplars at an established phytoremediation site in Bancroft, WI in southern Portage County.

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

The study site is an active aerial agricultural chemical facility, located near Bancroft, Wisconsin, and has a history of soil and groundwater contamination. Dinoseb (2, sec-butyl-4,6-dinitrophenol) is the primary contaminant of concern. At the time this study was initiated, dinoseb-contaminated soil was unacceptable for conventional landfill disposal or landspreading. Sandy soil, shallow groundwater, and other factors make this a prime site to study the effects of phytoremediation.

Objectives - The objectives of this research were:

1) Assess mortality and biomass production of the established trees at the site in both the source area and downgradient area.
2) Investigate possible relationships between hydrologic response and transpiration rates at various times through the project duration (both daily and seasonal changes).
3) Monitor changes in the groundwater contaminant profile through the source and downgradient areas.

Methods - A total of 834 hybrid poplars and willows were planted in June 2000. An irrigation system and electric fence were installed to help establish the plantation. Mortality and estimated biomass production were measured following each growing season since 2000. A network of groundwater monitoring wells had been installed for contaminant testing and groundwater elevation monitoring using electronic data loggers. Contaminant monitoring occurred in the spring and fall of each year. Down-well data loggers provided continuous monitoring of groundwater elevation throughout the growing season. A complete weather station was located within 500 meters and all pertinent weather data was available for this project.

Previous studies have examined: transpiration rates of the hybrid poplars, groundwater response to transpiration, presence of contaminants in biological tissues, aquifer characteristics, hybrid poplar mortality rates, biomass production, and groundwater quality. This study examines mortality and biomass production, hydrologic response, and groundwater quality trends.

Mortality is assessed in the fall by visual inspection of the trees and evidence of viable leaves or leaf buds. Biomass is estimated through direct measurement of trunk diameter and height as recommended by U.S. Forest Service North Central Experimental Station. The equation for this estimation is d^2*h where d = diameter breast height, and h = total tree height. Groundwater quality trends are evaluated by comparing dinoseb concentrations in monitoring wells across the study area. Hydrologic response is monitored with the use of groundwater elevation dataloggers (Aquarod – Sequoia Scientific) in three areas of the property. Elevation is logged once every 30 minutes with 1 mm of accuracy. Weather data is gathered using a Davis Instruments weather station that logs data every 30 minutes.

Results and Discussion - Following six growing seasons, there were no significant differences in mortality of the two key poplar clones, NM-6 (39%) and DN-34 (40%) in the plot as a whole, nor in the contaminated (source) area of the plot (45% and 46%, respectively). There were, however, substantial differences in mortality between the source and downgradient areas (45% and 16%, respectively). Estimated biomass produced by the two clones was also significantly different, with 75% of the biomass produced by NM-6.

Groundwater was analyzed for dinoseb, which has historically been the main contaminant of concern at this site. Dinoseb concentrations in groundwater have fluctuated considerably, likely due to flushing actions from the soil associated with precipitation events. Samples from downgradient piezometers have steadily decreased in dinoseb concentration and have been recorded at less than detection limits (5.0 µg/L) since October 2004.

Groundwater elevation declined steadily throughout the summer months with a maximum decline of 807 mm measured between May and September 2004. The majority of drawdown is most likely due to regional and local irrigation pumping systems. Groundwater recharge correlated with rainfall events. Diurnal water table fluctuations from transpiration were not observed due to rapidly rising (rainfall) and falling (groundwater pumping) of the water table.

Conclusions/Implications/Recommendations - Biomass calculations show that hybrid poplar NM-6 is more prolific than DN-34 in soil and groundwater severely contaminated with dinoseb, although similar morality levels were observed. A hybrid poplar plantation appears to have effectively reduced off-site migration of dinoseb with the groundwater; however, assimilation or a mechanism of degradation of dissolved dinoseb in relation to the trees was not established. Hybrid poplars were found to influence water table elevations; however, this influence was often obscured during periods of extensive groundwater pumping and large rainfall events that resulted in a rapidly rising and dropping water table.

Key words - dinoseb, phytoremediation, hybrid poplars, groundwater

Funding - Water Resources Institute, University of Wisconsin

INTRODUCTION

Phytoremediation has received widespread attention for offering the prospect of a low cost alternative to restoration or containment of contaminated soils and groundwater. Its effectiveness has been demonstrated for the remediation of volatile organic compounds (1), metals (2), petroleum hydrocarbons (3), some pesticides (4), and a wide array of industrial compounds (5).

Contaminated groundwater is often remediated by expensive pump-and-treat methods. A dense stand of trees can offer similar benefits in shallow aquifers, without the capital expenditures of pumps, extraction wells, and disposal of treated water. Additionally, phytoremediation offers degradation of many contaminants through various biological and chemical routes. While many laboratory studies of phytoremediation potential have been conducted, application of this technology in field studies is limited. Sites contaminated with agricultural chemicals are widespread around Wisconsin and the United States.

At the time this study was initiated, dinoseb-contaminated soil was regulated to be disposed at hazardous waste approved landfills. Cost for disposing of the volume of soil at this site extended into millions of dollars. Since this site is located in an isolated area, with no sensitive receptors downgradient, a low-cost alternative was proposed.

The objectives of this study were to monitor survival rates and estimate biomass production of two hybrid poplar clones when exposed to contaminants in soil and groundwater, correlate hydrologic response to rain events at various times through the project duration (both daily and seasonal changes), and determine changes in groundwater dinoseb concentrations through the study area.

The study site is located in south-central Portage County, Wisconsin, in the township of Pine Grove. An aerial agricultural spraying service has operated on this site for approximately 25 years and is currently enrolled in the Wisconsin Department of Agriculture, Trade, and Consumer Protection (DATCP) administered Agricultural Chemical Cleanup Program (ACCP).

Knowledge of groundwater contamination at this site dates back to 1985. Testing of spraying equipment and disposal of pesticide containers resulted in groundwater contaminated with dinoseb (2-sec-butyl-4,6-dinitrophenol) and other pesticides of lesser concentrations and toxicological concern. Dinoseb had been reported as high as 2000 µg/L (6) in groundwater samples from this site. This study has focused on the presence of dinoseb because of its toxicity, cancellation of use by U.S. EPA in 1986, and cost of disposal of dinoseb-contaminated soil.

As required by DATCP, buried pesticide containers were located by magnetic testing and excavated in May 2000. The area that was excavated is defined as the “source area” of the site map (Figure 1). This activity likely resulted in a release of more contaminants into the subsurface environment from residual chemicals in discarded containers. During container removal, topsoil was disturbed and often buried, leaving very sandy and contaminated soils on the surface. Geologic material at this site was identified as outwash sand. The depth to groundwater is approximately 2 meters below ground surface (bgs).

PROCEDURES AND METHODS

In June 2000, trees were obtained from the U.S. Forest Service (USFS) through the U.S. Department of Energy Biofuels Feedstock Development Program. Trees were obtained as 20 cm cuttings and soaked in water for 5 days to promote root growth. Trees were planted in 12 rows in the main block (source area, clonal test plot, and downgradient plot) and 6 rows in the control plot. Rows were oriented in an east-west alignment. All trees were planted with 1.5 meter spacing between trees and 3 meters between rows. Prior to planting, 1 meter by 5 cm holes were augered into the soil to loosen the root zone. This approach was used to encourage root growth toward the water table. The hole was backfilled with native soil and cuttings were inserted into the loosened soil with the terminal bud just above the soil surface. A total of 834 trees were planted in this manner. Plots were divided as follows:

- Source area – 12 rows each consisting of 40 trees, planted in 3-row blocks of hybrid poplars DN-34 or NM-6.
- Clonal test plot – 12 rows each consisting of 11 trees, planted in 4-row blocks that were repeated three times randomly through the plot. One block consisted of DN-17 (hybrid poplar), D-105 (eastern cottonwood), SX-61 and SV-1 (both hybrid willows). Data from this clonal test plot are reported elsewhere (7, 8).
- Downgradient plot – 12 rows with 10 trees each, planted in 3-row blocks of DN-34 or NM-6.
- Control plot – 6 rows consisting of 17 trees, planted in 4 blocks. One block of 27 trees consisted of DN-34 that received two manure applications throughout the first year, while a second block of 27 DN-34 did not receive the manure treatment. A third block of 24 NM-6 received manure while the fourth block of 24 NM-6 did not. Results from manure application are reported elsewhere (7, 8).

Groundwater Monitoring Wells

A total of 27, 1.9 cm PVC monitoring wells with 30 cm screens were installed. Eight of these were nested wells consisting of two or three wells. Nested wells are identified on Figure 1 as having an “A, B, or C” letter designation. Monitoring wells identified in this manner as having a letter “A” were installed 30 cm below the water table, “B” were 60 cm below and “C” 90 cm below. Monitoring wells MW-3, 4 and 5 were installed with a 5-foot screen. Three wells (MW-14, 15, and 16) are 5 cm diameter observation wells with 1-meter screens. These wells contain groundwater elevation data loggers described later.

Monitoring wells DP-1 and DP-1P were installed during a previous ACCP investigation. DP-1 is a water table monitoring well with 0.75-meter screen and DP-1P is a piezometer with a 0.75-meter screen approximately 5.25 meters bgs. DP-1PP (6.75 meters bgs), and DP-1PPP (7.7 meters bgs) were installed with this study to ensure contaminated water was not exiting the site below the shallower wells. These wells, along with monitoring wells MW-1 through MW-12, were used to collect groundwater samples for pesticide analysis.

Groundwater sample collection

Groundwater elevation was measured before sample collection. A minimum of 30 cm of water in the well was required to insure that the surface of the water table was being sampled. If 30 cm of water was not available in “MW1-A”, for example, elevation of “MW1-B” would be measured and if enough water was present, it was sampled. Wells were purged to insure a minimum of three volumes of water were flushed through the well before collection in a one-liter, amber, borosilicate glass bottle. Because of extremely high (> 1 mg/L) concentrations of dinoseb in some wells, sample tubing was dedicated to each well or well nest sampled.

Groundwater Analysis

Samples were analyzed by the Water and Environmental Analysis Laboratory at University of Wisconsin- Stevens Point using a modification to EPA Method 8270. This method employs high resolution gas chromatography with mass spectrometry. Initially, samples were analyzed for a wide variety of nitrogen and phosphorus containing pesticides. While other low levels (<2 µg/L) of pesticides were detected, this study focused on dinoseb at levels greater than 5 µg/L.

Groundwater Elevation Monitoring

Groundwater elevation monitoring was conducted on all monitoring wells by measuring the depths to water from the top of well casing to the nearest 3 mm using an electronic water level indicator. The well casing elevations were determined using a laser level accurate to 3 mm feet over a distance of 30 meters (100 feet).

Groundwater fluctuations were monitored in MW-14, MW-15 and MW-16 (5 cm diameter PVC monitoring wells with 1-meter screens) using AquaRods (Sequoia Scientific, Redmond, WA). This device measures capacitance (translated into groundwater elevation) at selected time intervals or changes in groundwater elevation. This study utilized 1-meter rods with accuracy of 1 mm. One data logger was located in the center of the main plot (MW-14), a second data logger was located on the north edge of the main plot (MW-15), and the third data logger was located south of and away from the control plot (MW-16).

Mortality and Estimated Biomass Production

Mortality and estimated biomass were determined concurrently at the end of each growing season. Mortality was determined by visual inspection of the tree and presence of buds. Estimated biomass was determined by the formula $d^2 * h$ where d = diameter and h = height. Initially, because of the small sizes of the trees, diameter was measured at the tree's base. However, for the duration of this study, diameter has been measured at breast height (dbh) as that is a more conventional forestry measurement. Biomass data from previous studies at this site should not be used as comparisons because measuring techniques were altered.

RESULTS AND DISCUSSION

Mortality and Estimated Biomass Production

Numerous variables will affect survival and estimated biomass production of these new trees. With the limited resources available, it is not reasonable to assess all possible variables. Differences in soil conditions (texture, nutrient content, and contaminant concentration) exist within the study site. Random differences also exist from weed growth, damage from deer browsing, girdling by rabbits/voles and damage from site maintenance equipment. Examination of the control plot as well as the downgradient plot facilitates the interpretation of mortality and estimated biomass production throughout the study site.

Total mortality of the NM-6 and DN-34 clones within the main study block (source area plus downgradient area) was 39%. Segregation of these areas reveals significant differences. Total mortality of the two poplar clones in the source area was 45%, while downgradient mortality was 16%. Total control plot mortality of 24% was also lower than the source area but similar to downgradient mortality. Differences in source area compared to downgradient and control plot mortality may indeed be due to contaminants present since other variables such as soil type exist across the entire site.

Differences between mortality of NM-6 and DN-34 in the source area were insignificant (39% versus 40% respectively) as was mortality in the downgradient area (13% versus 18% respectively). Closer examination of the source area reveals great differences in mortality across the study site (see Figures 3 and 4.) Numbering the rows from north (row 1) to south (row 12), it is evident that rows 3 through 8 experienced the greatest losses with row 5 demonstrating 83% mortality of the DN-34 clone. Rows 3 through 8 all experienced mortality of greater than 50% in the source area. This area, as noted on Figure 1, is considered the source area where buried containers were excavated and topsoil disturbed.

Mortality of clonal varieties DN-34 and NM-6 within the three plots they were planted (source, downgradient, and control) is illustrated in Figure 3. Greater mortality in the source area is evident when compared to the downgradient and control areas. It is uncertain whether mortality in the source area was due to toxic conditions in the soil or groundwater. Trees in the source area are exposed to dinoseb in groundwater (as evident by MW-3, 10 and 11) as are trees downgradient (MW-5, 6 and 7). Wells located in the middle of the site (MW-4 and 9) are also highly contaminated, yet trees downgradient of these wells have much higher survival rates. It is possible that soil in the source area remains as the key to mortality and trees are affected as their roots are exposed to pockets of highly contaminated soil, or as contaminants are mobilized from soil into the root zone. It may also be possible that once contaminants are mobilized to the saturated zone, they do not migrate back into the capillary fringe. Regardless, mortality of both the NM-6 and DN-34 clones was greater in the source area than either the downgradient and control plots.

Biomass is often evaluated through harvesting of the trees. This was not an option for continuation of this study, so biomass production was estimated by measuring tree diameter at breast height (d) and height (h), then calculated by taking diameter squared multiplied by the height of the tree ($d^2 * h = cm^3$). If more than one shoot was present, then multiple measurements were made on each tree and summed to obtain estimated biomass. This method of biomass estimation has been utilized by U.S. Forest Service and measurements were taken in October of 2004 and 2005.

Figure 4 illustrates total estimated biomass production within the source area by rows numbered 1 through 12 from north to south. As illustrated by this graph, total estimated biomass reflects survival rate (Figure 4) in the NM-6 clone (rows 1-3, 7-9). However, the DN-34 clone, while experiencing similar survivability, portrays one-third the biomass. Nearly identical differences appear when considering the data as average estimated biomass per surviving tree.

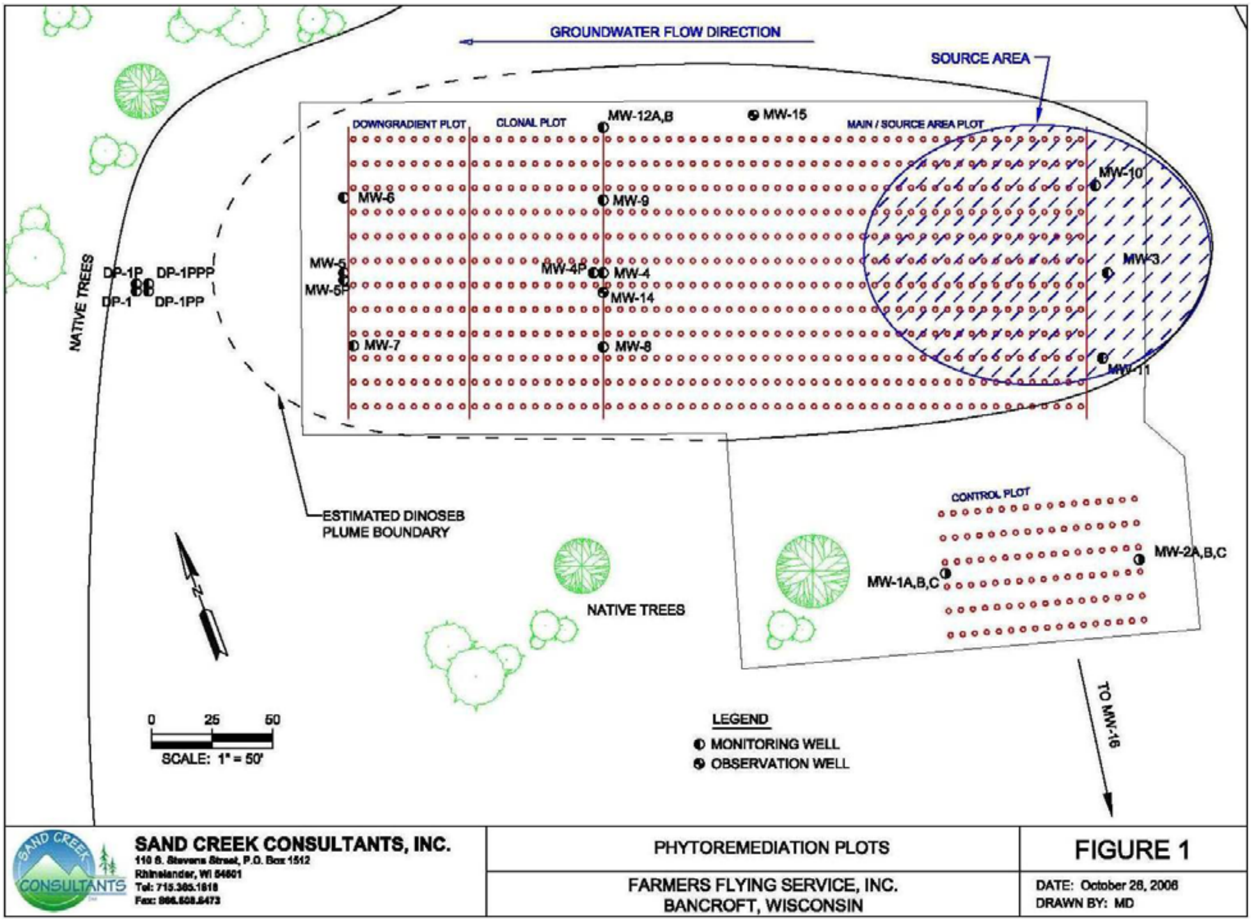

Figure 1. Site map with monitoring well locations.

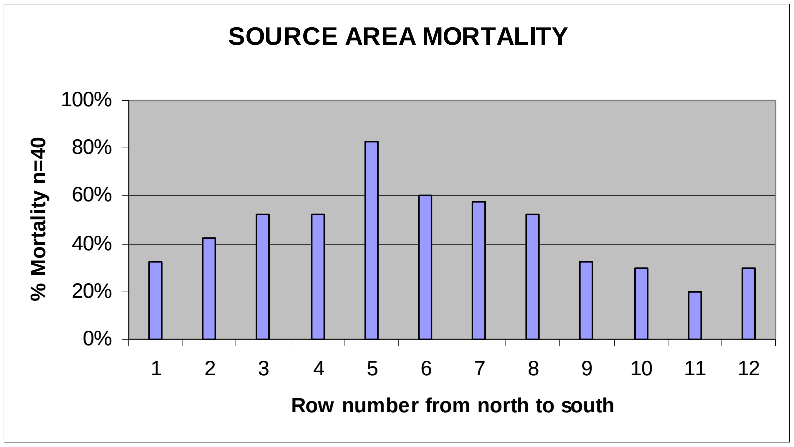

Figure 2. Source area mortality across rows

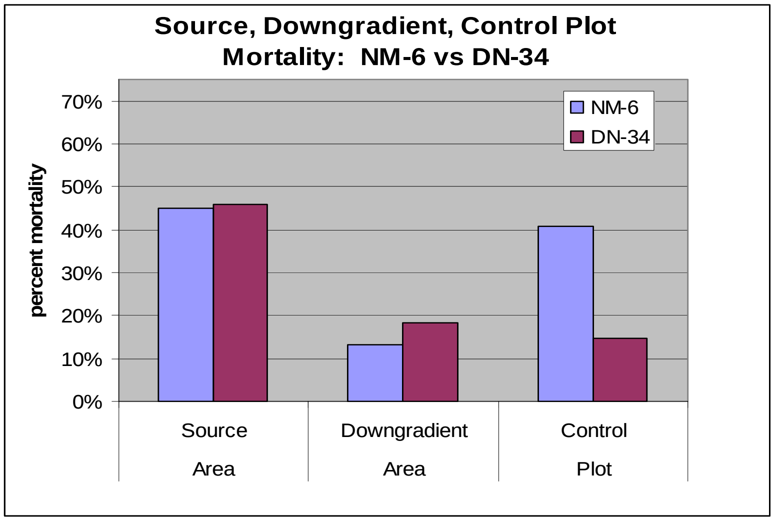

Figure 3. Downgradient, source and control plot mortality of DN-34 and NM-6 clones.

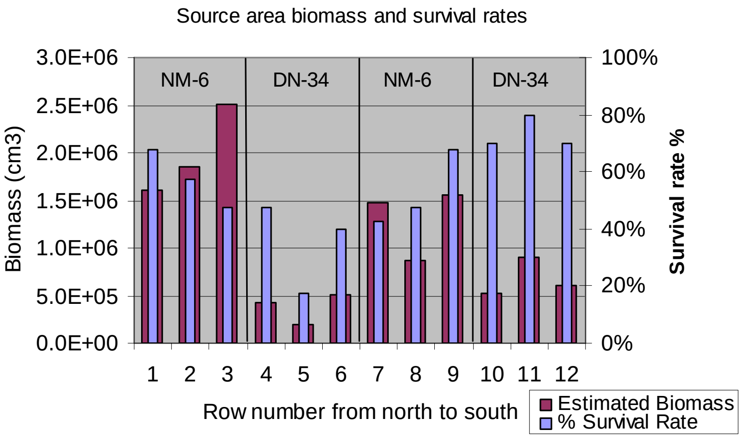

Figure 4. Estimated biomass production and survival rates in source area by row designation.

Groundwater Chemistry Results

Monitoring well locations are shown on Figure 1 and dinoseb concentrations in groundwater are summarized in Table 1. Six-year trends are also displayed in Figures 5 through 7. Dinoseb concentrations varied considerably in some wells during the four sampling rounds. Variability is expected, especially in very shallow wells subject to influence from infiltrating precipitation carrying dinoseb from contaminated soils to the water table. In addition, disturbance of contaminated soils associated with removal of buried containers probably resulted in increased concentrations of dissolved contaminants or "slugs" of dissolved dinoseb being carried past monitoring wells. It is likely that chemical handling and disposal practices along with cleanup efforts resulted in heterogeneous distribution of dinoseb in the subsoil. Dinoseb has an estimated octanol/soil organic carbon partition coefficient of 1250 (Michigan Dept. of Environmental Quality) which puts it in a category of highly sorbed. This estimation is dependant upon soil characteristics and somewhat dependant upon contaminant concentration. The high K_{oc} may serve to explain some of the great variation in dinoseb concentrations throughout the season. Monitoring well concentrations may vary depending upon large rainfall events that flush dinoseb from soil and into the saturated zone.

Table 1. Groundwater Chemistry Summary

	Monitoring Well	Oct. 04	May 05	Oct. 05	May 06	6-year avg.[1]
CONTROL PLOT	MW-1ABC	<5.0	<5.0	<5.0	<5.0	<5.0
	MW-2ABC	<5.0	<5.0	<5.0	<5.0	<5.0
UPGRADIENT	MW-3	589	126	57	41	400
	MW-10	511	655	1409	2967	1071
	MW-11	76	364	31	99	1314
MID-PLOT	MW-4AB	1498	2717	2004	996	671
	MW-4P 12' bgs	<5.0	18.7	10.3	16.4	8.0
	MW-8	<5.0	<5.0	<5.0	<5.0	29
	MW-9ABC	23.1	6.8	309	205	178
	MW-12AB	<5.0	2.1	9.5	3.5	8.6
DOWNGRADIENT	MW-5ABC	31.3	42.1	15.9	111.0	117
	MW-5P 17' bgs	<5.0	11.5	<5.0	<5.0	<5.0
	MW-6	<5.0	<5.0	56	180	122
	MW-7	<5.0	<5.0	22.5	53.4	20
DOWNGRADIENT (OFF SITE)	DP-1	<5.0	<5.0	no water	<5.0	16.8
	DP-1P 17' bgs	<5.0	<5.0	<5.0	<5.0	372
	DP-1PP 22' bgs	<5.0	<5.0	<5.0	<5.0	<5.0
	DP-1PPP 25' bgs	<5.0	<5.0	<5.0	<5.0	<5.0

All values as parts per billion (ug/L).

Samples taken from wells with "ABC" designation were taken at water table.

1. Averages of values <5.0 µg/L were calculated as 2.5 µg/L - (1/2 of the detection limit)

Contaminant concentration trends for a 6-year period are displayed in Figures 2 through 4. The upgradient wells display spikes suggesting slugs of dinoseb being released from the source area soil, probably associated with large rainfall events. Mid-site wells MW-4 and MW-9 display similar spikes, while MW-8 has consistently been below detection limits since October 2004. Downgradient wells (MW-5, 6, and 7) appear to be trending upwards with the last three samples increasing in dinoseb concentration. This is probably related to a slug of dinoseb migrating from the source area. Significantly, no dinoseb has been detected in downgradient off site wells for the past two years, suggesting that dinoseb has been immobilized within the plantation area.

Groundwater Elevation Data

Hydrogeologic response as groundwater elevation was monitored using AquaRods (Sequoia Scientific, Inc.) placed in observation wells MW-14, MW-15, and MW-16. Data has been collected seasonally since August 2001. Groundwater elevations were normalized for ease of comparison between wells; i.e., beginning AquaRod elevations were subtracted from subsequent readings making zero the starting point for the recorded period. Readings were also normalized when data loggers were swapped between wells, and after data were downloaded. Normalized groundwater fluctuations for summer seasons of 2004, 2005 and 2006 are shown on Figures 8 through 10 as are daily totals for rainfall events. The water table fluctuated 807 mm, 334 mm and 774 mm during the 2004, 2005 and 2006 data collection periods, respectively. Quick rises in water table elevations corresponded to large rainfall events.

In August 2002 water table elevation data for MW-14 indicated a possible diurnal groundwater elevation fluctuation of up to 8 mm (Figure 11). These fluctuations were not observed in the other monitoring wells in successive years. This is believed to be the result of rapidly fluctuating water table elevations due to extensive regional pumping combined with rainfall events. Since August 2002 the water table has not had more than one recorded day where the water table was not rising or falling quickly. The water table was observed to drop in steps as the water dropped due to pumping, with the steepest steps occurring during the day and flattening at night. However, this might not have been caused by the trees, although the background well (MW-16) did not show the same step function.

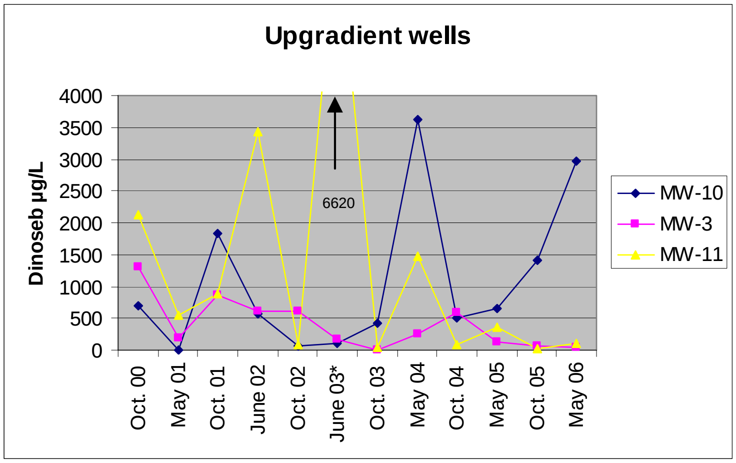

Figure 5. Dinoseb concentrations in upgradient wells for a 6-year period.

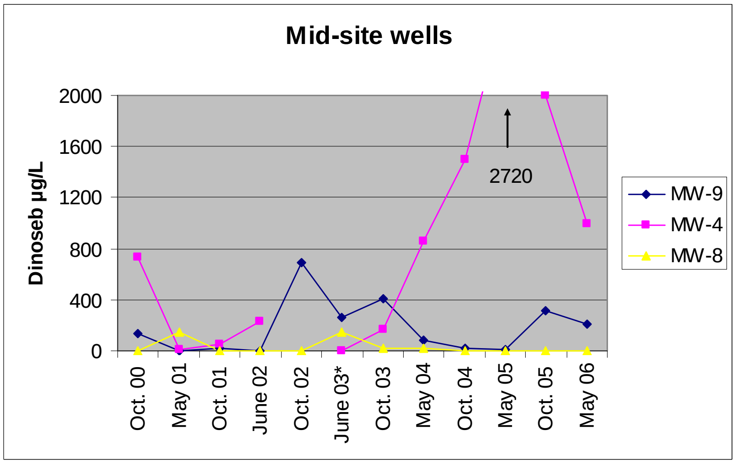

Figure 6. Dinoseb concentrations in mid-site wells for a 6-year period.

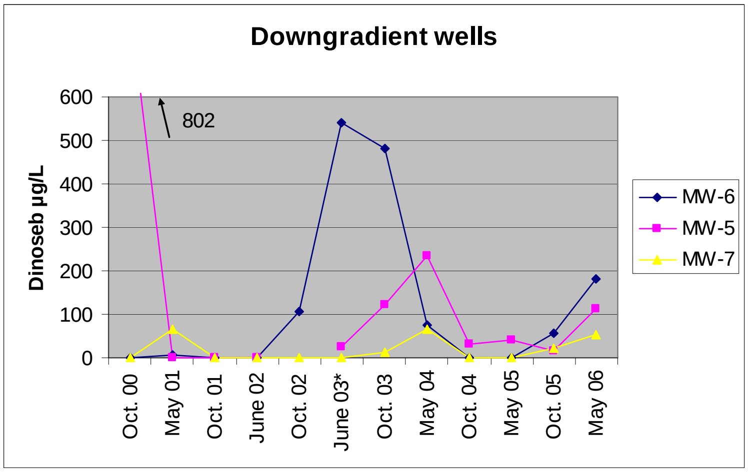

Figure 7. Dinoseb concentrations in downgradient well for a 6-year period.

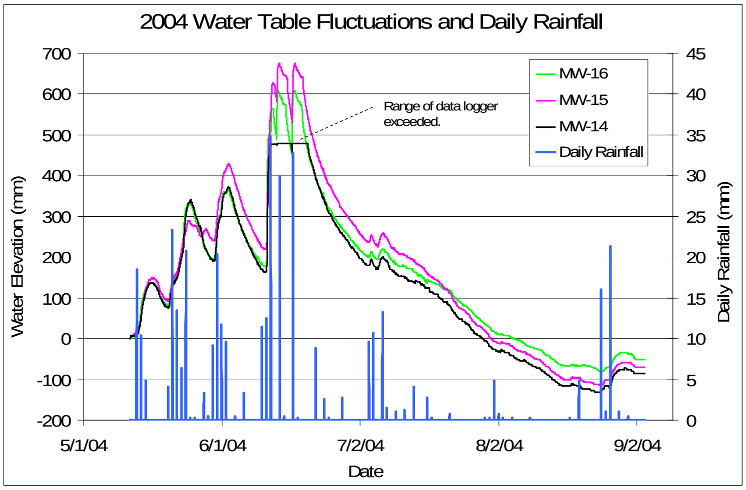

Figure 8. 2004 water table fluctuations and daily rainfall.

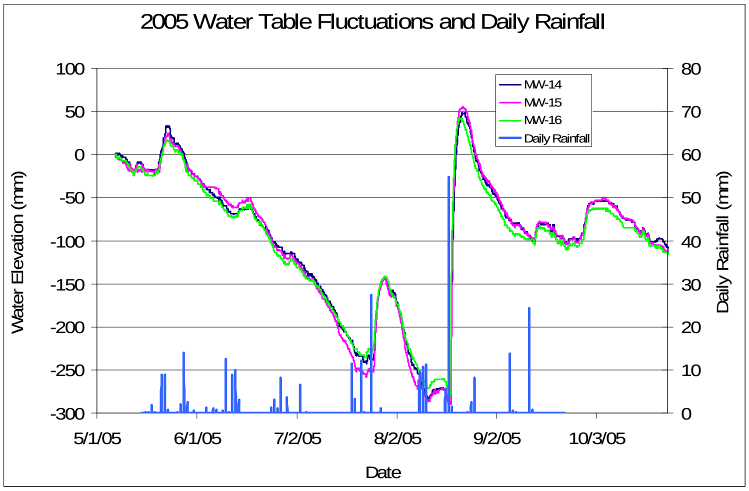

Figure 9. 2005 Water table fluctuations and daily rainfall.

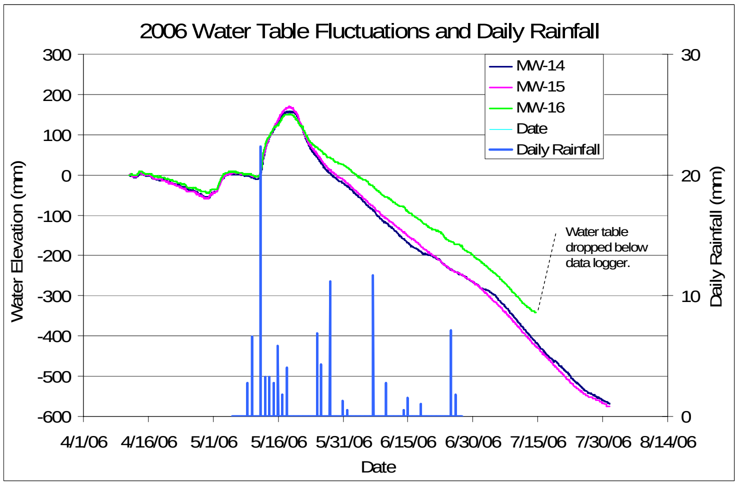

Figure 10. 2006 Water table fluctuations and daily rainfall.

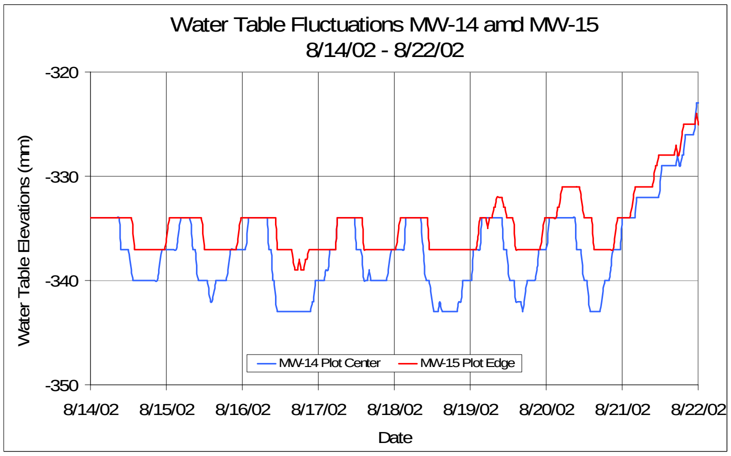

Figure 11. 2002 diurnal water table fluctuations due to influence from trees.

CONCLUSIONS AND RECOMMENDATIONS

There were no significant differences in mortality between the NM-6 and DN-34 hybrid poplars within the source area, however, the NM-6 clone produce 3 times more biomass than the DN-34. There were significant differences between the mortality rates from the source area and the downgradient area. This may be due to toxins in the soil and/or groundwater, or disturbance of the soil from the excavation of buried containers that stripped the topsoil of its water holding capacity and nutrients.

Large variations in dinoseb concentrations were observed in most monitoring wells. The cause for this variability is likely associated with the chemical properties of dinoseb and with seasonal and event-based fluctuations in water elevations and precipitation infiltration rates. Any apparent trends in downgradient monitoring wells must be viewed with caution as other trends have been reversed in other wells on frequent occasion.

Despite high hydraulic conductivity, the groundwater velocity at the site is quite low due to the low groundwater gradient. This low velocity will reduce mass migration rates of contaminants out of the treatment area and possibly lead to increased degradation of contaminants as the trees mature.

Research has shown (9) that a phytoremediation site planted with eastern cottonwoods (*Populus deltoides*) provided enough dissolved organic carbon to a shallow (<3m) aquifer to lower dissolved oxygen concentrations, consequently providing conditions for in situ reductive dechlorination of trichloroethene. Dinoseb is known to degrade readily in anoxic conditions. An evaluation of oxygen in the saturated and unsaturated zones should be conducted to determine whether the lack of oxygen is leading to degradation of dinoseb. Conceptually, it may be possible that the tree roots "chase" the falling water table in the summer, then die back and decompose when water levels rebound. Does this decomposition deplete oxygen levels enough to initiate conditions favorable to the breakdown of dinoseb?

Rapidly dropping water table elevations due to regional pumping compromised our ability to evaluate diurnal water table fluctuations. An aquifer unexposed to dramatic drawdown might lead to a more conclusive observation of poplar transpiration having a direct affect on daily water table elevations.

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(4) Burken, J.G. and Schnoor, J.L. 1998. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. Environmental Science and Technology. Vol 32, No. 21 pp. 3379-3385.

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(6) Alpha Terra Science. 1999. Site investigation and remedial action options report for pesticide impacted soils at Farmers Flying Service, Inc. Bancroft, WI. DACTP file reference #88405071101.

(7) DeVita, W.M., Dawson, M. 2002. Effectiveness of Phytoremediation and Hydrologic Response at an Agricultural Chemical Facility in Bancroft, WI – Phase I. Report issued to Wisconsin Department of Agriculture, Trade and Consumer Protection.

(8) DeVita, W.M., Dawson, M. 2004. Monitoring the Effectiveness of Phytoremediation and Hydrogeologic Response at an Agricultural Chemical Facility. Report issued to Wisconsin Water Resources Institute – University of Wisconsin.

(9) Eberts, S.M. et al. 2005. Long-term changes in ground water chemistry at a phytoremediation demonstration site. Ground Water. Vol 43, No. 2, pp.178-186.

Groundwater sustainability in a humid climate: Groundwater pumping, groundwater consumption, and land use change.

Basic Information

Title:	Groundwater sustainability in a humid climate: Groundwater pumping, groundwater consumption, and land use change.
Project Number:	2004WI82G
Start Date:	9/1/2004
End Date:	12/31/2006
Funding Source:	104G
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	Water Use, Groundwater, Management and Planning
Descriptors:	
Principal Investigators:	Madeline Beth Gotkowitz, Charles P Dunning, David John Hart

Publication

1. Gotkowitz, M. 2006. Sustainable Pumping From Regional Aquifers: Quantifying Water Use. GSA National Meeting. Philadelphia. Abstracts with Programs Vol. 38, No. 7.

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Jim Hurley
Submitted: 6/19/2007

Project Title

WR04R009: Groundwater Sustainability in a Humid Climate: Groundwater Pumping, Groundwater Consumption and Land Use Change

Project Investigators

Madeline Gotkowitz, Wisconsin Geological and Natural History Survey

Progress Statement

We completed all planned data collection and analysis. Findings include:
1. Municipal wells supply 75% of the groundwater pumped in Waukesha County, where about 30% of the land is in suburban and urban development.
2. In Sauk County, where 8% of the land is similarly developed, municipal systems supply only 25% of the groundwater used in the County.
3. Growth in municipal water use over the last 75 years is highly correlated to population growth in both study areas.
4. Rates of pumping from non-municipal wells in both counties reflect historical trends in agricultural irrigation.
5. The population of Waukesha County is four times greater than Sauk County, but we estimate that total groundwater use in Waukesha County is only 20% greater than in Sauk County. This suggests that while urbanization accompanied by a reduction in irrigated agriculture reduces overall water use, it concentrates pumping within a smaller geographic region (that is, within municipal well fields).
6. We have compiled some suggestions for tracking water use that will reduce uncertainty in current estimates of groudnwater withdrawals in these settings.

We are writing the final project report and preparing a manuscript for a peer-reviewed journal.

Impacts

Description	We completed compilation of pumping records and compared these to population growth and land use change in the study areas. These provide the basis for recommendations for water use tracking in Wisconsin that will be presented in the final project report.

Interactions

Description	Hart and Gotkowitz discussed project findings with Daniel Feinstein and Cheryl Buchwald of the USGS Wisconsin Water Science Center. We discussed use of the Wisconsin high capacity well database to estimate pumping rates for the USGS's Southeast Wisconsin groundwater modeling effort.

	Alternatives to this data set include agriculture statistics compiled by the Wisconsin Agricultural Statistics Service and housing estimates compiled from U.S. Bureau of the Census data. In addition to this discussion of results, we provided Feinstein and Buchwald with the project database.
Event Date	5/4/2007

Presentations & Public Appearances

Title	Evaluating Groundwater Use in Southern Wisconsin
Presenter(s)	Rozumalski, Laura L., Madeline B. Gotkowitz, David J. Hart, Charles P. Dunning, Kenneth W. Potter
Presentation Type	Poster session
Event Name	Wisconsin Section of American Water Resources Association
Event Location	Elkhart Lake Wisconsin
Event Date	3/2/2006
Target Audience	Scientific audience
Audience Size	150
Description	

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Title	SUSTAINABLE PUMPING FROM REGIONAL AQUIFERS: QUANTIFYING WATER USE
Presenter(s)	Gotkowitz
Presentation Type	Professional meeting
Event Name	GSA National Meeting
Event Location	Philadelphia
Event Date	10/23/2006
Target Audience	Scientific audience
Audience Size	100
Description	GSA Abstracts with Programs Vol. 38, No. 7.

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Title	Estimating groundwater use in urban and rural areas of Wisconsin
Presenter(s)	Gotkowitz
Presentation Type	Professional meeting
Event Name	Wisconsin Section American Water Resources Assocaition
Event Location	Wisconsin Dells, Wisconsin
Event Date	3/2/2007
Target Audience	Scientific audience
Audience Size	75
Description	Our study of pumping rates in representative urban (Waukesha County) and rural (Sauk County) areas of Wisconsin illustrates the impact of withdrawals to the water budgets of regional aquifers. Although pumping rates can be measured more accurately than hydrogeologic parameters such as recharge and permeability, Wisconsin has no requirement to meter or report non-municipal groundwater withdrawals. This results in significant uncertainty about total withdrawals from the state's regional aquifers. Groundwater flow models are well-suited to evaluate sustainable use of

groundwater resources, but uncertainty in pumping rates increases uncertainty in model calibration and simulation of aquifer response to pumping.

On the basis of well records and land use information, we estimate that municipal wells supply 75% of the groundwater pumped in Waukesha County, where about 30% of the land is in suburban and urban development. In Sauk County, where 8% of the land is similarly developed, municipal systems supply only 25% of the groundwater used in the County. Growth in municipal water use over the last 75 years is highly correlated to population growth in both study areas. Rates of pumping from non-municipal wells in both counties reflect historical trends in agricultural irrigation. Currently, the population of Waukesha County is four times greater than Sauk County, but we estimate that total groundwater use in Waukesha County is only 20% greater than in Sauk County. This suggests that while urbanization accompanied by a reduction in irrigated agriculture reduces overall water use, it concentrates pumping within a smaller geographic region. We found that relatively simple improvements in tracking water use will reduce uncertainty in current pumping rates and improve our understanding of the impacts of groundwater withdrawals.

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Title	GROUNDWATER PUMPING IN URBAN AND RURAL AREAS OF WISCONSIN
Presenter(s)	Gotkowitz
Presentation Type	Government briefing
Event Name	Wisconsin Groundwater Coordinating Council
Event Location	Madison, Wisconsin
Event Date	5/25/2007
Target Audience	State government agency
Audience Size	8
Description	Presented project results to administrators from Wisconsin Departments of Natural Resources, Dept. of Agriculture, Trade and Consumer Protection, Department of Transportation, and Department of Health and Family Services.

Students & Post-Docs Supported

Student Name	Jonathon Carter
Campus	University of Wisconsin-Madison

Advisor Name	Mary Anderson
Advisor Campus	University of Wisconsin-Madison

Degree	Expected Masters
Graduation Month	December
Graduation Year	2007
Department	Geology and Geophysics
Program	Hydrogeology
Thesis Title	
Thesis Abstract	

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Student Name	Tara Root
Campus	University of Wisconsin-Madison

Advisor Name	Jean Bahr
Advisor Campus	University of Wisconsin-Madison

Degree	PhD
Graduation Month	August
Graduation Year	2005
Department	Geology and Geophysics
Program	Hydrogeology
Thesis Title	unrelated to current project
Thesis Abstract	unrelated to current project

Climate Signals in Groundwater and Surface Water System: Spectral Analysis of Hydrologic Processes

Basic Information

Title:	Climate Signals in Groundwater and Surface Water System: Spectral Analysis of Hydrologic Processes
Project Number:	2005WI005O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Hector Ramon Bravo

Publication

1. Namdar Ghanbari, R., H.R. Bravo, J.J. Magnuson, R.J. Hunt, D.T. Feinstein, W.G. Hyzer. 2007. Trend and oscillations in the ice cover duration of Lake Mendota, Wisconsin. 32nd Congress of IAHR, the International Association of hydraulic Engineering and Research
2. Namdar Ghanbari, R and HR Bravo. 2005. Identification of Groundwater Discharge and Recharge Sites through Temperature Time Series. Hydrological Science and Technology 21, 1-4.
3. Namdar Ghanbari, R, H.R. Bravo, J.J. Magnuson, A.A. Tsonis, R.J. Hunt, D.T. Feinstein, W.G. Hyzer and B.J. Benson. 2007. Coherence between large scale climate signals, local climate, and ice cover duration of Lake Mendota, Wisconsin. Journal of Hydrology. In Press.
4. Namdar Ghanbari, R. and H.R. Bravo. 2007. Coherence between large scale climate signals, regional climate, and Great Lakes water levels. Advances in Water Resources. In review.
5.

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Jim Hurley
Submitted: 6/20/2007

Project Title

WR05R005: Climate Signals in Groundwater and Surface Water System: Spectral Analysis of Hydrologic Processes

Project Investigators

Hector Bravo, University of Wisconsin-Milwaukee

Progress Statement

Work during the second year of the project included:
Spectral analyses revealed significant coherence between three levels of time series: large-scale signals, local or regional climate, and hydrologic time series. The first level of series analyzed includes the Southern Oscillation Index (SOI), Pacific decadal Oscillation (PDO), North Atlantic Oscillation (NAO), and Northern Pacific Index (NP). Series in the second level include precipitation, snowfall and snow depth, evaporation, and air temperature. The third level of time series includes groundwater level, Great Lakes levels, and ice duration cover in Lake Mendota, Wisconsin.
Physical reasoning helped to explain the direct effect of large-scale signals on hydrologic time series, and the effect transmitted through local or regional climate.

Work during the first year of the project included:
a) Significant effort in the gathering of time series of precipitation, streamflow, groundwater level, and lake levels for the State of Wisconsin, and the Trout Lake Basin in particular.
b) Graphical representation and preliminary analysis of the data, and selection of representative sites, with adequate record length, in the forested, unglaciated, and agricultural areas of the State.
c) Implementation and detailed testing of the methods of analysis, including non-parametric analysis of trends, Singular Spectrum Analysis (SSA), Multi Taper Method (MTM) of spectral analysis, and estimation of cross-covariance, coherency, and phase functions.
d) Application of the methods of analysis to different datasets and achievement of preliminary results.

Impacts

Description

The study demonstrates the effect of large-scale signals on local or regional climate and hydrologic time series. The findings are expected to raise awareness on the effects of climatic variability on water availability, which have been largely ignored so far.

The methods listed in item c) above were applied to analyze and quantify the links between climate variability signals and:
i) The ice cover duration in Lake Mendota, Wisconsin,
ii) Great Lakes water levels,

iii) Time series of precipitation, streamflow, groundwater level, and lake levels in three regions listed in item b above; this particular step in still underway.

A clear, quantitative picture is emerging of the links between climate variability signals and the different hydrologic time series.

Interactions

Description	Several meetings were held in Milwaukee and Madison with USGS researchers, including Randy Hunt, Charles Dunning and Daniel Feinstein, and John Magnuson from UW Madison. The meetings greatly helped in data selection, clarification of the methods, and analysis of results.
Event Date	

Journal Articles & Other Publications

Publication Type	Proceedings/Symposium
Title	Trend and oscillations in the ice cover duration of Lake Mendota, Wisconsin
Author(s)	Namdar Ghanbari, R., H.R. Bravo, J.J. Magnuson, R.J. Hunt, D.T. Feinstein, W.G. Hyzer
Publication/Publisher	32nd Congress of IAHR, the International Association of hydraulic Engineering and Research
Year Published	2007
Volume & Number	
Number of Pages	
Description	
Any Additional Citation Information	

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Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Identification of Groundwater Discharge and Recharge Sites through Temperature Time Series Analysis
Author(s)	Namdar Ghanbari, R. and HR Bravo
Publication/Publisher	Hydrological Science and Technology
Year Published	2005
Volume & Number	21, 1-4
Number of Pages	
Description	
Any Additional Citation Information	

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Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Coherence between large scale climate signals, local climate, and ice cover duration of Lake Mendota, Wisconsin
Author(s)	Namdar Ghanbari, R, H.R. Bravo, J.J. Magnuson, A.A. Tsonis, R.J. Hunt, D.T. Feinstein, W.G. Hyzer and B.J. Benson

Publication/Publisher	submitted to Journal of Hydrology
Year Published	2007
Volume & Number	
Number of Pages	
Description	
Any Additional Citation Information	

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Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Coherence between large scale climate signals, regional climate, and Great Lakes water levels
Author(s)	Namdar Ghanbari, R. and H.R. Bravo
Publication/Publisher	submitted to Advances in Water Resources
Year Published	2007
Volume & Number	
Number of Pages	
Description	
Any Additional Citation Information	

Partners

Name/Organization	Randall J. Hunt
Affiliation	US Geological Survey
Affiliation Type	Federal
Email	rjhunt@usgs.gov
Description	

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Name/Organization	John J. Magnuson
Affiliation	University of Wisconsin-Madison
Affiliation Type	Academic Institutions
Email	jjmagnus@wisc.edu
Description	

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Name/Organization	Anastasios A. Tsonis
Affiliation	University of Wisconsin-Milwaukee
Affiliation Type	Academic Institutions
Email	aatsonis@uwm.edu
Description	

Presentations & Public Appearances

Title	Trend and oscillations in the ice cover duration of Lake Mendota, Wisconsin
Presenter(s)	Hector R. Bravo
Presentation Type	Seminar
Event Name	CEE919 EFM/WRR Seminar
Event Location	University of Wisconsin-Madison
Event Date	12/7/2006
Target Audience	University students
Audience Size	20
Description	

Students & Post-Docs Supported

Student Name	Reza Namdar Ghanbari
Campus	University of Wisconsin-Milwaukee

Advisor Name	Hector Bravo
Advisor Campus	University of Wisconsin-Milwaukee

Degree	PhD
Graduation Month	August
Graduation Year	2007
Department	Civil Engineering and Mechanics
Program	Engineering
Thesis Title	Climate signals in groundwater and surface water systems: Spectral analysis of hydrologic processes
Thesis Abstract	

Grant No. 04HQGR0034 The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling The Transport, Fate and Cycling of Mercury in Watersheds and Air Sheds

Basic Information

Title:	Grant No. 04HQGR0034 The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling The Transport, Fate and Cycling of Mercury in Watersheds and Air Sheds
Project Number:	2005WI150S
Start Date:	11/15/2003
End Date:	11/30/2006
Funding Source:	Supplemental
Congressional District:	
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Jim Hurley

Publication

1. Gorski, P.R., DE. Armstrong, J.P. Hurley and M.M. Shafer. 2006. Speciation of aqueous methylmercury influences uptake by a freshwater alga (Selenastrum capricornutum). Environmental Toxicology and Contamination. 25 (2): 534-540.
2. Branfireun, B.A., D. P. Krabbenhoft, H. Hintelmann, R. J. Hunt, J. P. Hurley, and J.W.M. Rudd. 2005. The Transport And Speciation Of Atmospheric Mercury In A Boreal Forest Wetland: A Stable Mercury Isotope Approach. Water Resources Research, v. 41, W06016, oi:10.1029/2004WR003219, 2005.
3. Hall, B.D., H. Manolopoulos, J.P. Hurley, J. J. Schauer, V.L. St. Louis, D. Kenski, J. Graydon, C.L. Babiarz, L.B. Cleckner, and G.J. Keeler. 2005. Methyl and total mercury in precipitation in the Great Lakes region. Atmospheric Environment. 39(39):7557-7569.
4. Stoor, R.W., J.P. Hurley, C.L. Babiarz and D.E. Armstrong. 2006. Subsurface Sources of Methylmercury to Lake Superior from a Wetland-Forested Watershed. In Press. Science of the Total Environment.
5. Chadwick, S.P., C.L. Babiarz, J.P. Hurley and D.E. Armstrong. 2006. Influences of iron, manganese, and dissolved organic carbon on the hypolimnetic cycling of amended mercury. In Press. Science of the Total Environment.
6. Babiarz, C.L., J.P. Hurley, D.P. Krabbenhoft, T.R. Trinko, M. Tate, S.P. Chadwick and D.E. Armstrong. 2003. A hypolimnetic mass balance of mercury from a dimictic lake: results from the METAALICUS project. Journal de Physique IV. 107:83-86.
7. Reed Harris , Marc Amyot , Christopher Babiarz , Ken Beaty , Paul Blanchfield , R. A. (Drew) Bodaly , Brian Branfireun , Cynthia Gilmour , Jennifer Graydon , Andrew Heyes , Holger Hintelmann , James Hurley , Carol Kelly , David Krabbenhoft , Steve Lindberg , Robert Mason , Michael Paterson , Cheryl Podemski , Art Robinson , Ken Sandilands , George Southworth , Vincent St. Louis and Michael Tate. 2007. Whole-Ecosystem Study Shows Rapid Fish Mercury Response to Changes in Mercury Deposition. In review, Proc. Nat. Acad. Sci.

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Jim Hurley
Submitted: 6/8/2007

Project Title

WR03R010: The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling

Project Investigators

James Hurley, University of Wisconsin Sea Grant Institute

Progress Statement

Two abstracts were prepared for the Eighth International Conference on Mercury as a Global Pollutant and presented during the August 6-11th, 2006 event in Madison, Wisconsin. The papers highlighted our research emphasis on the transport of mercury from the uplands and wetlands to the study lake in the Experimental Lakes Area of Canada. During the winter of 2006-07 we completed a summary manuscript on the first three years of the METAALICUS project, and the paper has been submitted to the journal Proceedings of the National Academy of Sciences. In addition, this past winter we completed the analysis of all backlogged samples collected during the spring, summer and fall of 2006 and the data have been entered into our data base. In the spring of 2007, sampling and flow monitoring instrumentation was reinstalled at the field site and are presently operating.

Impacts

Description	The METAALICUS project has direct and important implications for policy makers and resource managers regarding mercury pollution of the environment. One of the central unknowns is how effective mercury pollution prevention measures may be in reducing contaminated aquatic food webs and exposure to wildlife and human. The METAALICUS project is specifically designed to help address these critical unknowns and is providing feed back to regulators and resource managers in the US and internationally.

Committees, Memberships & Panels

Group Name	National Mercury Monitoring Strategy Committee
Description	This committee has recently been formulated to begin discussion concerning the establishment of a National Mercury Monitoring Network. The kickoff meeting is scheduled for June 2007.
Start Date	6/20/2007
End Date	

Journal Articles & Other Publications

Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Whole-Ecosystem Study Shows Rapid Fish Mercury Response to Changes in Mercury Deposition
Author(s)	Reed Harris , Marc Amyot , Christopher Babiarz , Ken Beaty , Paul Blanchfield , R. A. (Drew) Bodaly , Brian Branfireun , Cynthia Gilmour , Jennifer Graydon , Andrew Heyes , Holger Hintelmann , James Hurley , Carol Kelly , David Krabbenhoft , Steve Lindberg , Robert Mason , Michael Paterson , Cheryl Podemski , Art Robinson , Ken Sandilands , George Southworth , Vincent St. Louis , Michael Tate
Publication/Publisher	Proceedings of the National Academy of Sciences
Year Published	2007
Volume & Number	submitted
Number of Pages	
Description	Mercury contamination of fisheries, from centuries of industrial atmospheric emissions, negatively impacts humans and wildlife worldwide. The response of fish mercury concentrations to changes in mercury deposition has been difficult to establish, though, because sediments/soils contain large pools of historical contamination, and many factors in addition to deposition affect fish mercury concentrations. To directly test the response of fish contamination to changing mercury deposition, we conducted a whole-ecosystem, multi-year experiment in which the mercury load to a boreal headwater lake and its watershed was increased using enriched stable mercury isotopes. The use of stable isotopes allowed us to follow new mercury deposition separately from stored pools, and to examine bioaccumulation of mercury deposited to different parts of the watershed. Fish mercury concentrations responded rapidly to changes in mercury deposition over the first three years of study. Essentially all of the increase in fish mercury concentrations was derived from mercury deposited directly to the lake surface. In contrast, <1 % of the mercury isotope deposited to the watershed was exported to the lake. Equilibrium was not reached within three years. Lake mercury isotope concentrations were still rising in lake biota, and watershed mercury isotope concentrations were increasing slowly in runoff. Therefore, we predict that mercury emissions reductions will yield rapid (years) reductions in fish mercury concentrations, and concomitant reductions in risk. However, a full response will be delayed by watershed retention of mercury. The rate of response will vary among lakes depending on the relative surface areas of water and watershed.
Any Additional Citation Information	

Presentations & Public Appearances

Title	An In Situ Mercury Isotope Injection Experiment to Assess Cycling and Transport of Mercury in Streams
Presenter(s)	Michael T. Tate
Presentation Type	Professional meeting
Event Name	Eighth International Conference on Mercury as a Global Pollutant.
Event Location	Madison, Wisconsin
Event Date	8/8/2006
Target Audience	Scientific audience
Audience Size	1100
Description	The METAALICUS project has shown that watershed nputs of mercury (Hg) dominate the mass flux to lakes and wetlands, substantially exceeding direct deposition. However, we know comparably little about the details of Hg cycling within streams. The purpose of this study was to determine how the speciation of Hg may control downstream transport and partitioning. In August 2005, a series of four daily, in-stream, injections were carried out at the Experimental Lakes Area (site of the METAALICUS project) in northwestern Ontario, using four different Hg stable-isotope tracers. We conducted the

experiment during base flow conditions to minimize the possible effects of changing stream flow on the successive isotope injections. A potassium bromide injection was conducted one day prior to the Hg injections to determine transport characteristics of the stream. Monitoring for field parameters and collection of water and sediment samples was conducted at four stations (10m, 17m, 37m, 51m) downstream from the injection point for at least 105 minutes. The volume injected was very small percentage of the stream discharge (<4%) over any one of the tests. The first Hg injection contained two isotopic tracers: 201Hg and Me199Hg that were diluted into a concentrated solution of humic acid from a nearby stream. The next two injections contained 202Hg in a concentrate of humic acid from the Florida Everglades and 200Hg diluted into a HCl matrix. The bromide tracer showed break through times at the 10m, 37m, and 51m sampling locations were 2, 14 and 19 minutes, respectfully. The measured mass balance for the bromide was close to 100%, suggesting any loss to downward water seepage is expected to be minimal. The effect of varying the complexation of the injected Hg isotopes had a dramatic effect on transport efficiency. The breakthrough time at the 37m monitoring site for the 200HgCl complex was twice that of the Everglades humic acid-202Hg complexes. After 90 minutes at the 51m sampling location all of the humic acid-Hg complexes had passed, whereas the chloride-Hg complexes were still early on the rising limb of the breakthrough curve.

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Title	Mercury Mass Fluxes from the Lake 658 Watershed
Presenter(s)	David P. Krabbenhoft
Presentation Type	Professional meeting
Event Name	Eighth International Conference on Mercury as a Global Pollutant
Event Location	Madison, Wisconsin
Event Date	8/9/2006
Target Audience	Scientific audience
Audience Size	1100
Description	One of the greatest areas of uncertainty for making reliable predictions of the environmental response to changes in atmospheric mercury (Hg) deposition is quantifying the flux of Hg from terrestrial systems to downstream aquatic ecosystems. This is especially problematic for settings where terrestrial inputs may dominate the Hg mass balance. In these cases, is may be difficult to estimate the overall magnitude and timing of change to mass fluxes for aquatic ecosystems. The METAALICUS project, a whole-ecosystem Hg loading experiment located at the Experimental Lakes Area (ELA), northwestern Ontario, Canada. This project offers several potential insights into some of these response questions due to the unique nature of the study. Starting in the spring of 2001, the METAALICUS team has been dosing the entire Lake 658 watershed with about 20 ug/m2/y (about 4-5 times the current ambient load). However, the applied Hg is in the form of enriched stable isotopes that can be analytically distinguished from previously existing, or currently depositing Hg. Thus, measuring the net accumulation rate of the applied isotope in the various terrestrial compartments provides a unique opportunity to better estimate Hg clearing times. With this information in hand, improved predictive capability of response times of Lake 658 (and other similar lakes) can be achieved. Net accumulation of the applied isotope is reflected in the steadily increasing isotope concentration in terrestrial soils with each year of application (2001-2004). However, although the isotope application rate is greatly above ambient deposition, the total accumulation in the upland soils is comprises only about a quarter of the application rate. The remaining isotope mass is primarily accounted for by reemission from soils and plants, and canopy interception and storage. Likewise, the concentration and overall flux rate of the isotope in runoff has increased about linearly with each year of application, but runoff mass fluxes

are small compared to the isotope application rate (about 1-3 percent). The overall goal of this aspect of the METAALICUS project is to gain a better understanding of the processes controlling Hg mass fluxes from uplands, and the expected change due to altering atmospheric loading rates. Simple numerical box models will be presented that estimate clearing rates for the isotope applied to the Lake 658 watershed.

Validation of transport of VOCs from Composite Liners

Basic Information

Title:	Validation of transport of VOCs from Composite Liners
Project Number:	2005WI154O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Engineering
Focus Category:	Solute Transport, Geochemical Processes, None
Descriptors:	remediation; groundwater treatment
Principal Investigators:	Tuncer B. Edil, Craig H Benson

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Tuncer Edil
Submitted: 5/24/2007

Project Title

WR05R008: Validation of Transport of VOCs from Composite Liners

Project Investigators

Craig Benson, University of Wisconsin-Madison
Christopher Carlsen, Wisconsin Department of Natural Resources
Tuncer Edil, University of Wisconsin-Madison

Progress Statement

Tasks Completed

Target Compound Selection
Five volatile organic compounds (VOCs) were selected among frequently detected VOCs in Wisconsin Landfills, considering classes, melting points, boiling points, gas chromatographic retention times and contrasts of density, solubility, molecular diameter, and aqueous diffusion coefficient. Selected VOCs are Methylenechloride, Trichloroethylene, Chlorobenzene, Toluene, and Methyl Tertiary Butyl Ether.

VOC Analytical Method Development
Gas chromatograph (GC) will be used with sample direct extraction/injection method for VOC analysis. When conducting diffusion tests with columns and tanks, the amount of sample extraction is critical and should be minimized not to affect the diffusion. The detection method also should be simple minimizing loses of VOCs. After careful evaluation, sample direct extraction/injection method was selected over SPME (Solid Phase Micro-Extraction) method because of the simplicity and the leakage of SPME sampler during sampling. The effect of sample extraction was evaluated using HYDRUS-2D transport code, and the results have shown that the concentration differences were less than 1 % except at the bottom (2.9 %) for 5 µl of pore fluid extraction per sampling port a week for a year. Therefore, extracting less than 5 µl every 2 weeks is adopted and considered not to seriously affect the VOC diffusive transport.

Selection and Characterization of Liner Soil
Kamm clay, which is used in Dane county sanitary landfill, was used for the compacted clay layer material in the experiments. It has been obtained and characterized.

Column Development
Test columns simulating geomembrane-compacted clay composite liner system have been designed and manufactured to detect the VOC concentrations using sampling ports in the clay layer to monitor the VOC breakthrough. To prevent side-wall leakage from the geomembrane, a geomembrane chamber was developed. All the column parts were tested to be leak free and hydraulic conductivity tests of the clay liner are being conducted.

Batch Test
Batch tests are 80% completed with five VOCs and the selected liner soil. The method was developed to use 1:1 soil-liquid ratio to reflect the field condition. Batch tests are conducted in different concentrations with multi-solutes and single-solutes. Partition characteristics of the selected VOCs will be assessed through batch isotherms.

Impacts

Description

Recent research by the PIs indicates that VOCs are showing up in lysimeters earlier than theory would suggest and at higher concentrations. Several factors may be responsible for these unexpected observations (e.g., uncertainty in rate of advection, uncertainty in the degradation rate, uncertainty in sorption processes, unknown transformation processes occurring within the liner, migration of landfill gas, etc.), but the scatter in the field data is too large to identify those mechanisms controlling the rate of VOC migration. Thus, the capability of current transport models to accurately predict VOC transport through composite liners is not known. The validity of these models must be tested if reliable evaluations of landfill impacts are to be made, and the current models need to be adjusted if they have shortcomings. Such an evaluation can only be made if good quality data exist with minimal ambiguities. However, no carefully conducted physical experiments modeling composite liners have been conducted.

A two-stage study is proposed. The first stage consists of laboratory experiments to verify existing transport models for composite liners. Causes and mechanisms of VOC transport through composite liners will be assessed, and the models will be adapted if necessary. In the second stage, the verified transport model for composite liners will be coupled with a two-dimensional flow and contaminant transport model (HYDRUS-2D). The coupled models will be used to assess long-term impacts of VOCs on groundwater for typical site conditions and existing lining technologies. Changes to landfill design practices may also be suggested based on the findings of this assessment.

Arsenic Species (III,V) Distribution in Wisconsin Groundwaters: Field Measurements and Prediction Using Multivariate Analysis of Geochemical Data Prediction Using Multivariate Analysis of Geochemical Data

Basic Information

Title:	Arsenic Species (III,V) Distribution in Wisconsin Groundwaters: Field Measurements and Prediction Using Multivariate Analysis of Geochemical Data Prediction Using Multivariate Analysis of Geochemical Data
Project Number:	2005WI155O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Groundwater, Geochemical Processes, Water Quality
Descriptors:	arsenic speciation; analytical chemistry
Principal Investigators:	Martin Shafer, James Schauer

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Martin Shafer
Submitted: 6/13/2007

Project Title

WR05R001: Arsenic Species (III,V) Distribution in Wisconsin Groundwaters: Field Measurements and Prediction Using Multivariate Analysis of Geochemical Data Prediction Using Multivariate Analysis of Geochemical Data

Project Investigators

Kristie Ellickson, University of Wisconsin-Madison
James Schauer, University of Wisconsin-Madison
Martin Shafer, University of Wisconsin-Madison

Progress Statement

The primary objectives of this two year study are to:

1. Perform a meta-analysis on existing groundwater data for co-variation of geochemical analytes and test their association with total arsenic concentrations using multivariate methods. (Years 1 and 2).
2. To identify the most likely inorganic arsenic species (oxidation states III or V) for each identified principal component of the existing data based on known geochemical mechanisms for arsenic release. (Year 2).
3. To directly measure arsenic speciation and important geochemical parameters in 50 of the previously analyzed sites to test the predictions developed in objectives 1 and 2. These new data will be analyzed by factor analysis and arsenite and arsenate concentrations compared to previous predictions. (Year 2).

In year one, we have nearly completed objective 1, and have assembled all the sampling and analytical tools to complete objective 3. Field work for objective 3 will begin in late July or early August of 2006. A brief summary of our accomplishments follows.

Basic geochemical and arsenic data from the following systems/studies has been assembled into a large Access database. This effort likely represents the largest of its type to date.

1. Oakland County Michigan. 37 samples. [Ground-Water Quality Atlas of Oakland County, MI. Water-Resources Investigation Report 00-4120]
2. Mahomet Aquifer Illinois; Champaign and Tazwell counties. 144 samples. [Illinois Department of Natural Resources, WMRC Report RR-107, May 2004].
3. Idaho – Washington County. 75 samples. [Ground water Quality Technical Report No. 6. Idaho Division of Environmental Quality, September 1995].
4. Minnesota Pollution Control Authority. 954 samples.
5. New Jersey. 170 samples. [Ambient Ground Water Quality in the Newark Basin, New Jersey. By M.S. Serfes, Digital compilation by G.C. Herman and M.S. Serfes, N.J. Geol. Survey Digital Geodata Series DGS96-3].

6. Ohio. 72 samples. [WDR-OH-AR-02.2. 2003 USGS Water Data Report OH-3-2].
7. Ohio. 21 samples. [Miami, OH].
8. New England Coastal Basin. 804 samples. [USGS Water Resources Investigations Report 99-4162]. 1999.
9. Wisconsin. 2648 samples. [Department of Natural Resources, Municipal and Private Wells].
10. Ontario, Canada. 430 samples.

We have over 5355 sample records in the database as of June 2006. The geology covers several aquifers across the Midwest, with a range of deposit types as well (Precambrian, Cambrian, Ordovician, Cretaceous, Devonian, and mixed Quaternary).

In addition to the arsenic data (speciated in a few studies), we have incorporated the following supporting geochemical data from each sample (Note: the degree of comprehensiveness of the geochemical data varies among the studies).

1. Well depth
2. Temperature
3. pH
4. Specific Conductance
5. Dissolved Oxygen
6. Dissolved Solids
7. Hardness/Alkalinity
8. Carbonate/Bicarbonate
9. Sulfate
10. Phosphate
11. Chloride
12. Bromide
13. Fluoride
14. Calcium
15. Magnesium
16. Potassium
17. Silica
18. Nitrogen Species (ammonia, nitrate, nitrite)
19. Dissolved Organic Carbon
20. Trace metals [Al, Sb, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Sr, U, V, Zn.

Factor analysis is in progress and is expected to be complete by mid-late July. The unbalanced and imperfect nature of the various datasets has complicated application of certain statistical approaches, so we have in specific cases segregated the database to improve data matrix completeness.

We have prepared 75 field sampling kits that will provide a very comprehensive analytical characterization of the chosen wells.

1. Arsenic speciation/separation will be carried out on site using an As(V) specific solid phase sorbent placed in miniature columns.
2. Fe(II) using on-site ferrozine complexation
3. Nitrogen species (nitrate, nitrite, ammonia) by discrete analyzers
4. Silica by discrete analyzer
5. Sulfide using both ISE (in SAOB buffer) and HPLC-Molybdenum blue approaches
6. Chloride, Sulfate, Nitrate by Ion Chromatography
7. Elemental Analysis by High Resolution ICP-MS (30 elements)
8. DOC by high temperature combustion
9. Oxygen isotopes (18O/16O) by isotope ratio mass spectrometry
10. Temperature, pH, Specific Conductance, Redox Potential, Dissolved Oxygen by multiparameter sonde

Assembly of the large well database was completed in late 2006 with the addition of data from (a) USGS NAWQA wells (including monitoring and homeowner wells) and (b) additional public sector wells in WI from WI DNR records.

Even after segregating the larger database into sub-sets of wells with similar data completeness, it still proved quite difficult to generate stable and robust factor models. Further complicating this statistical analysis was the need, because of extant data quality/quantity issues, to run multiple models to cover the desired range of site geochemistries. Ultimately we believe that the models we ran will be field testable in the context of this small study. However, to further ensure that the sampling program was structured to be able to definitively address key questions related to the coupling of aquifer geochemistry to arsenic speciation, we developed an alternate sampling matrix. This matrix was developed around nearly universally available well concentrations of calcium, iron, sulfate, and total arsenic. A four-by-four matrix of sites with quartiles of Ca and Fe as axes was constructed. Over 150 well/sites were placed within the 16 cells, with gradients of sulfate and total arsenic represented within each cell. With this approach, we will be able to use statistically robust methods (cell-cell comparisions, strict ANOVA, regression analysis) to test the influence of aquifer geochemical indicators on arsenic speciation.

Field sampling of this matrix is progressing well, with expected completion in June. For most matrix cells we have been able to aquire data for 4-5 wells.

The sampling/analytical program is generating data for the following Arsenic Species:
(a) Total Arsenic (filtered + particulate; III + V)
(b) Particulate Arsenic (III + V) [i.e > 0.4 micron]
(c) Filterable (dissolved) Arsenic (III + V) [i.e. < 0.4 micron]
(d) Filterable (dissolved) Arsenic III
(e) Filterable (dissolved) Arsenic V

All of the analytes listed above (analyte groups 1-10 above) are currently being measured, with the exception of 4 (Silica by discrete analyzer), where instead we are determining total Si by HR-ICP-MS.

The well sampling program has been very successful in capturing the desired concentration range of each geochemical variable, and thereby validating the primary and secondary matrix sampling constructs. For example: calcium over the range of 5 to >200 mg/L; iron over the range of 0.001 to >20 mg/L; sulfate over the range of below detection to >250 mg/L; pH over the range of 5.5 to 8.5; dissolved oxygen over the range of below detection to nearly saturated; sulfide over the range of below detection to >100 ppb; and total arsenic from 0.25 to over 85 ppb.

Impacts

Description	The release mechanism for arsenic in ground water is a critical factor for understanding and predicting levels of arsenic species in ground/drinking water. Therefore this effort should be of major interest to environmental chemists and environmental health scientists. These results will be useful to regulators for health-based decision making and prioritization of monitoring efforts. This work may also provide a tool to use extant basic geochemical data where arsenic concentrations are not available or are suspect. Since we can interpret the data with relation to total arsenic as well as arsenite concentrations, our approach should be a useful tool for predicting mechanisms driving total arsenic mobilization as well as mechanisms leading to the mobilization of the most toxic form of arsenic.
Description	Our well sampling program incorporates a large set of private (homeowner) water supplies. These interactions are increasing awareness among the public of issues surrounding groundwater arsenic and providing visibility to research programs at the UW-Madison. Also, importantly, we are providing

the homeowner participants a "free" comprehensive report on constituents/contaminants in their well water, along with appropriate reference ranges and interpretation.

Description	In developing/providing a very comprehensive geochemical database/analysis (cations and anions) of each of the study systems we are documenting the full suite and range of groundwater geochemistries that Arsenic removal/treatment strategies will encounter. This information should ultimately help regulators and technology providers select/develop more robust treatment systems.

Description	We are reporting concentrations for nearly 40 elements in the groundwaters, many of which are rarely if ever measured. In providing data for these elements, many of which are classed as potentially toxic, we are establishing critical "baseline" data that follow-up studies can benchmark.

Interactions

Description	We have worked closely with the USGS Wisconsin Water Science Center in Middleton WI, in particular Dr David Saad (Hydrologist), in well/site selection. Dr Saad has provided us access to a series of NAWQA wells (including domestic, public supply, and monitoring) that , we either have or are in the process of sampling. In doing so, we are synergistically supporting the research/monitoring of both programs.
Event Date	4/1/2007

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Description	Dr Kelly Warner of the USGS Illinois Water Science Center allowed us access to NAWQA wells sited within the glacial and cambrian-ordovician aquifers of Northern IL and Southern WI.
Event Date	5/1/2007

Partners

Name/Organization	David Johnson
Affiliation	Wisconsin Department of Natural Resources
Affiliation Type	Local & State
Email	
Description	

Students & Post-Docs Supported

Student Name	Kristie Ellickson
Campus	University of Wisconsin-Madison

Advisor Name	Martin Shafer
Advisor Campus	University of Wisconsin-Madison

Degree	Post Doc
Graduation Month	

Graduation Year	
Department	State Laboratory of Hygiene
Program	American Public Health Laboratory Fellowship
Thesis Title	
Thesis Abstract	

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Student Name	Jackson Helmer
Campus	University of Wisconsin-Madison

Advisor Name	Martin Shafer
Advisor Campus	University of Wisconsin-Madison

Degree	Other
Graduation Month	
Graduation Year	
Department	
Program	Undergraduate Student
Thesis Title	
Thesis Abstract	

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Student Name	Sara Kerr
Campus	University of Wisconsin-Madison

Advisor Name	David Armstrong
Advisor Campus	University of Wisconsin-Madison

Degree	PhD
Graduation Month	June
Graduation Year	2007
Department	Civil & Environmental Engineering
Program	Environmental Chemistry & Technology
Thesis Title	Trace Metal Cycling in a Northern Wisconsin Watershed
Thesis Abstract	

Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer

Basic Information

Title:	Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer
Project Number:	2005WI158O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Geochemical Processes, Toxic Substances, Non Point Pollution
Descriptors:	pesticides; nitrate; unsaturated zone
Principal Investigators:	George J. Kraft, Bryant Browne

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Jim Hurley
Submitted: 5/16/2007

Project Title

WR05R003: Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer

Project Investigators

Bryant Brown, University of Wisconsin-Stevens Point
George Kraft, University of Wisconsin-Stevens Point

Progress Statement

- A project team of consisting of UW-Stevens Point water resources scientists, U-Platteville agricultural system scientists, Wisconsin Geological and Natural History, geologists and geophysicists, and Discovery Farm outreach staff has been assembled.

- A preliminary set of 9 boreholes, mostly financed by a grant that leverages this project, was installed to gain insight to the hydrogeology of the area.

- Two boreholes were installed to fulfill the objectives of this study.

- All boreholes have been geophysically logged.

- Piezometer material was evaluated for potential sources of analytical interferences. Piezometer design has been altered as a result.

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NEW:

- The total number of boreholes installed in the study area has been increased to 12, mostly financed by a grant that leverages this project.

- All boreholes have been geophysically logged, including with an "Optical Borehole Instrument" subsurface visualization device.

- One of these boreholes has been instrumented with a Flute-type multilevel sampler with 8 ports specifically to meet the objectives of this study.

- Remaining boreholes have been instrumented with 2-5 piezometers isolated at different depth intervals.

- The Flute sampler is currently conditioning to come into chemical equilibrium with the subsurface.

- A sampling is being planned of the Flute sampler for June 2007.

Impacts

Description	- A better understanding of the agrichemical pollutant load to the aquifer is resulting.

Other Project Support

Source	University of Wisconsin System - Consortium
Dollar Value	$40,000
Description	The research dollars of the Joint Solicitation project have leveraged UW-System Consortium funds
Start Date	7/1/2006
End Date	6/30/2008

Partners

Name/Organization	University of Wisconsin - Platteville
Affiliation	
Affiliation Type	Academic Institutions
Email	
Description	This research takes place on the UWP farm, and we are using their facilities to make inferences about groundwater quality in the larger landscape.

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Name/Organization	Wisconsin Geological and Natural History Survey
Affiliation	
Affiliation Type	Academic Institutions
Email	
Description	We are jointly exploring the hydrogeology of the study area.

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Name/Organization	UW-Discovery Farms
Affiliation	
Affiliation Type	Academic Institutions
Email	
Description	Together we are using the outcomes of the research to inform an agricultural audience about groundwater impacts of farming practices.

Transient Functioning of a Groundwater Wetland Complex, Allequash basin, Wisconsin

Basic Information

Title:	Transient Functioning of a Groundwater Wetland Complex, Allequash basin, Wisconsin
Project Number:	2005WI159O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Wetlands, Groundwater, Climatological Processes
Descriptors:	goundwater modeling; wetlands; riparian zone
Principal Investigators:	Mary Anderson

Publication

1. Lowry, C.S., M.P. Anderson, R.J. Hunt. 2006. Modeling groundwater flow and heat transport within a fen/stream complex. In: Proceedings of MODFLOW and More 2006: Managing ground water systems, IGWMC, Golden, Colo. 5 pp.
2. C. S. Lowry, J.F. Walker, R.J. Hunt, M.P. Anderson. 2007. Identifying spatial variability of groundwater discharge in a wetland stream using a distributed temperature sensor. Water Resource Research Information. In review.

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Mary Anderson
Submitted: 5/17/2007

Project Title

WR05R007: Transient Functioning of a Groundwater Wetland Complex, Allequash basin, Wisconsin

Project Investigators

Mary Anderson, University of Wisconsin-Madison

Progress Statement

We are investigating transient hydrologic processes in a wetland in northern Wisconsin (Vilas County). Two monitoring transects have been established across the wetland. In this reporting period, we continued monitoring broundwater heads and temperautres in the transects as well as streamflow. We also conducted two major field experiments, described below, and are completing work on on groundwater flow model of the system.

Distributed Temperature work
A one-kilometer long fiber-optic based distributed temperature sensor (DTS) was placed just below the stream/sediment interface in Allequash Creek, to measure variations in temperature. The difference in temperature between groundwater and surface water was used to identify gaining and losing reaches along the stream. Results show a pattern of focused zones of groundwater discharge within the streambed. The presence of important zones of focused groundwater discharge within the stream is a significant finding as the existing paradigm calls for diffuse flow. One possible explanation for focused zones of groundwater discharge is the presence of soil pipes within the peat. Discharge rates at these zones of focused discharge were measured using seepage-meterss. Seepage meter results showed two orders of magnitude more discharge as compared to non-focused discharge zones.

Geophysics
A large scale ground penetrating radar survey (GPR) was conducted within Allequash Wetland in order to determine the extent of the peat. Based on the results from the GPR survey we have identified subsurface features that appear to control the position of springs, ponds and stream discharge zones within the wetland. Springs, ponds and stream discharge zones line up with breaks in slope in the peat/sand and gravel interface. We believe that these breaks in slope cause a refraction of groundwater flow lines causing groundwater to discharge at the surface.

Modeling
A two-dimensional groundwater flow and heat transport modeling using the groundwater flow MODFLOW linked to MT3DMS (modified for heat transport)l was calibrated with head and temperature measurements collected at three sets of nested piezometers in a north-south transect (Transect 1). The field data were collected using both discrete and continuous sampling methods. The parameter estimation code PEST was used to calibrate the model and determine sensitivity to input parameters. Simulating both groundwater flow and heat transport helped constrain parameters that are difficult to determine, such as hydraulic conductivity of peat. Results based on the 2D model are currently being used to build a 3D coupled groundwater flow and heat transport model using the code SEAWAT. The new 3D model takes into account temperature dependent changes in

viscosity and density of groundwater, which have been shown to change flowpaths within the wetland.

Impacts

Description	--Our use of Ground Penetrating Radar to delineate the vertical extent of peat in the wetland has yielded significant results in that we were able to identify structures that appear to control groundwater discharge to the wetland.
Description	Measurments beneath the streambed using a distributed temperature sensor helped identify important zones of focused groundwater discharge to the streambed, showing that the current paradigm of diffuse groundwater discharge to a stream does not apply here.

Awards, Honors & Recognition

Title	Best student paper award
Event Year	2007
Recipient	Chris Lowry
Presented By	Wisconsin Ground Water Association
Description	Cash prize to the best student paper (oral) presented at the annual conference of the WGWA.

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Title	Best student paper award
Event Year	2007
Recipient	Chris Lowry
Presented By	Wisconsin AWRA
Description	Best student paper award (oral) given at the annual conference of the WI AWRA.

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Title	Morgridge Distinguished Graduate Fellowship
Event Year	2007
Recipient	Chris Lowry
Presented By	Dept of Geology & Geophysics, UW-Madison
Description	9 month fellowship which includes a half-time RA appointment, a cash research award, and full tuition. Given for the period Sept 2007-May 2008

Interactions

Description	We have interated with a research group in Germany who have developed a heat transport code called SHEMAT.
Event Date	

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Description	We have interacted with the Limnology Lab and Prof. Emily Stanley.
Event Date	

Journal Articles & Other Publications

Publication Type	Other
Title	Modeling groundwater flow and heat transport within a fen/stream complex
Author(s)	Lowry, C.S., M.P. Anderson, R.J. Hunt
Publication/Publisher	MODFLOW and More 2006: Managing ground water systems, IGWMC, Golden, CO
Year Published	2006
Volume & Number	
Number of Pages	5
Description	Proceedings volume. Paper presented at an international conference in May 2006
Any Additional Citation Information	

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Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Identifying spatial variability of groundwater discharge in a wetland stream using a distributed temperature sensor.
Author(s)	C. S. Lowry, J.F. Walker, R.J. Hunt, M.P. Anderson
Publication/Publisher	Water Resource Research
Year Published	In Review
Volume & Number	
Number of Pages	
Description	
Any Additional Citation Information	

Other Project Support

Source	USGS
Dollar Value	$100,000
Description	The USGS provides logistical support and transportation to and from the site.
Start Date	
End Date	

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Source	LTER/Trout Lake Lab
Dollar Value	$1,000

Description	logistical support at the field site and free housing
Start Date	6/1/2006
End Date	8/31/2008

Partners

Name/Organization	Randy Hunt & John Walker
Affiliation	U.S. Geological Survey
Affiliation Type	Federal
Email	
Description	We work closely with the USGS- Middleton, WI office on all aspects of this project. They provide logistical support for field, lab and modeling work and some additional funding as well as field eqipment and free consultation.

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Name/Organization	Long Term Ecological Research Project (LTER)
Affiliation	UW-Madison
Affiliation Type	Academic Institutions
Email	
Description	We are working at the LTER site in Northern Wisconsin which is administered by the UW-Madison through its NSF sporspored research project at Trout Lake. Housing is provided free of charge at the Trout Lake Station. Some field eqipment is also provided.

Presentations & Public Appearances

Title	Modeling Groundwater Flow and Heat Transport within a Fen/Stream complex.
Presenter(s)	Lowry, C., M.P. Anderson, and R.J. Hunt
Presentation Type	Poster session
Event Name	MODFLOW2006
Event Location	Golden, Colorado
Event Date	6/23/2006
Target Audience	Scientific audience
Audience Size	400
Description	

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Title	Evidence for Focused Groundwater/Surface water Interaction Using a Distributed Temperature Sensor
Presenter(s)	Lowry, C.S., Walker, J.F., Hunt, R.J., and Anderson, M.P.
Presentation Type	Professional meeting
Event Name	Wisconsin Section of the American Water Resources Association,
Event Location	Wisconsin Dells
Event Date	3/1/2007

Target Audience	Mixed
Audience Size	100
Description	

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Title	Geophysical and temperature characterization of groundwater/surface water interactions in a peat-dominated wetland
Presenter(s)	Lowry, C.S., Walker, J.F., Hunt, R.J., Fratta, D., and Anderson, M.P.
Presentation Type	Professional meeting
Event Name	Wisconsin Ground Water Association,
Event Location	Wisconsin Dells
Event Date	2/23/2007
Target Audience	Mixed
Audience Size	200
Description	

Students & Post-Docs Supported

Student Name	Christopher Lowry
Campus	University of Wisconsin-Madison

Advisor Name	Mary Anderson
Advisor Campus	University of Wisconsin-Madison

Degree	PhD
Graduation Month	June
Graduation Year	2008
Department	Geology & Geophysics
Program	Geology
Thesis Title	Transient groundwater hydrology in a wetland (working title)
Thesis Abstract	not yet available

Evaluation of On-Site Wastewater Treatment as a Source of Antibiotic Resistance Genes in Groundwater

Basic Information

Title:	Evaluation of On-Site Wastewater Treatment as a Source of Antibiotic Resistance Genes in Groundwater
Project Number:	2005WI161O
Start Date:	7/1/2005
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Biological Sciences
Focus Category:	Toxic Substances, Solute Transport, None
Descriptors:	microbiology; antibiotics; on-site treatment
Principal Investigators:	Trina McMahon

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Katherine McMahon
Submitted: 6/18/2007

Project Title

WR05R006: Evaluation of On-Site Wastewater Treatment as a Source of Antibiotic Resistance Genes in Groundwater

Project Investigators

Katherine McMahon, University of Wisconsin-Madison

Progress Statement

We have collected samples from three groundwater monitoring wells, two water supply wells, and two septic tanks at our study site (a subdivision near Sun Prairie, WI). We have analyzed them for the presence of ten tetracycline resistance genes using a qualitative PCR assay that provides presence/absence information. We are currently performing quantitative PCR assays to determine the absolute abundance of three different resistance genes.

Monitoring wells that were presumably previously impacted by agricultural activity, but that are not currently impacted by septic tank effluent, contained several resistance gene types. Septic tanks contained more different types. We observed some differences in the number and types of genes detected, across our sampling events.

Impacts

Description	Our results suggest that some types of tetracycline resistance were already present in groundwater at this site and therefore may reduce the level of concern about resistance proliferation from septic tank effluent.

Students & Post-Docs Supported

Student Name	Erin Seyfried
Campus	University of Wisconsin-Madison
Advisor Name	Katherine McMahon
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month	August
Graduation Year	2007
Department	

	Civil and Environmental Engineering
Program	Environmental Engineering
Thesis Title	TBD
Thesis Abstract	

Foundry Slag for Treating Arsenic in Ground Water and Drinking Water

Basic Information

Title:	Foundry Slag for Treating Arsenic in Ground Water and Drinking Water
Project Number:	2005WI90B
Start Date:	7/1/2004
End Date:	6/30/2006
Funding Source:	104B
Congressional District:	2
Research Category:	Engineering
Focus Category:	Groundwater, Treatment, Water Quality
Descriptors:	
Principal Investigators:	Craig H Benson

Publication

1. Metz, S. and Benson, C. (2007), Iron Foundry Slags as Permeable Reactive Barriers Materials for Removing Arsenic from Groundwater, Proceedings, GeoDenver, American Society of Civil Engineers, in press.

IRON FOUNDRY SLAGS FOR REMOVING ARSENIC FROM WATER

by

Stacy E. Metz and Craig H. Benson
Geological Engineering
University of Wisconsin-Madison

Project Completion Report

WRI Project: 05-REM-02, WR04R008

Geo Engineering Report No. 06-23

October 22, 2006

Title: Iron Foundry Slags for Removing Arsenic from Water

Project ID: 05-REM-02, WR04R008

Investigators: Craig H. Benson, Professor, and Stacy E. Metz, Graduate Research Assistant, Geological Engineering, University of Wisconsin-Madison

Period of Contract: July 1, 2004 – February 28, 2006

Summary:

This paper describes findings from leach testing, total element analyses, and kinetic batch tests conducted to evaluate the feasibility of using iron foundry slag (an industrial byproduct of iron casting) as a reactive material in permeable reactive barriers used to remove arsenic (As) from groundwater. Tests were conducted on four slags from foundries in Wisconsin using solutions containing arsenite (As-III) and arsenate (As-V) having initial total As concentrations ranging from 100-2500 μg/L. Comparative tests were also conducted on zero valent iron (ZVI) and sand as a non-reactive control. Water leach testing and total elemental analyses suggested that leaching from slags is not appreciably different from ZVI, at least in the context of environmental regulations in Wisconsin. For the same liquid-to-solid ratio, As removal was slower with slag than ZVI. Arsenic removal rates also varied considerably from slag to slag, and did not depend on the quantity of iron in the slag. The removal rate typically decreased with increasing concentration, and was slower for As-III than As-V. Computations made using the rate coefficients measured in this study suggest that a common 1-m-thick PRB containing iron foundry slag could effectively treat groundwater contaminated with As-III or As-V at a concentration of 1000 μg/L, although other factors such as slag heterogeneity and competition with other species might influence effectiveness in a field setting.
Related Publications:

Related Publications:

Metz, S. and Benson, C. (2007), Iron Foundry Slags as Permeable Reactive Barriers Materials for Removing Arsenic from Groundwater, Proceedings, GeoDenver, American Society of Civil Engineers, in press.

Key Words: arsenic, groundwater, permeable reactive barrier, iron, slag, beneficial use

Funding: UWS

INTRODUCTION

Contamination of groundwater by arsenic (As) from natural and anthropogenic sources has become a significant issue because studies have shown that long-term ingestion of As via drinking water has serious impacts on health (Dhar et al. 1997, Mehang and Rahman 2003). The US Environmental Protection Agency (USEPA) also reports that As is the second most common contaminant of concern at Superfund sites (USEPA 2002). Natural sources of As in groundwater are also common, and in some cases are being aggravated by oxidation of bedrock in response to pumping of groundwater (Schreiber et al. 2000, Gotkowitz et al. 2004).

Contacting As-contaminated groundwater with zero-valent iron (ZVI) particles (e.g., using a permeable reactive barrier, or PRB, containing ZVI particles) has been shown to be an effective method for removing As from groundwater (Blowes et al. 2000, Su and Puls 2001, Nikolaidis et al. 2003, Leupin et al. 2005). However, world-demand for iron has driven up the cost and reduced the availability of ZVI. Consequently, there is interest in finding less costly, but effective, reactive materials that can be used to remove As from groundwater. Low-cost materials that improve sustainability, such as industrial byproducts, are particularly attractive (Lee and Benson 2004, Lee et al. 2004).

A recent case history by Wilkens et al. (2003) has shown that a PRB containing crushed steel slag (a byproduct of steel production) has been effective in removing As from groundwater at a site in Gary, Indiana, USA. Laboratory-experiments conducted with steel slags by McRae et al. (1999) and Ahn et al. (2003) have demonstrated similar effectiveness. Mechanisms thought to be responsible for As removal include sorption to metal oxides on the slag surface or precipitation of insoluble compounds (e.g. Ca-As compounds) (McRae et al. 1999, Ahn et al. 2003).

Iron foundry slag is a material similar to steel slag that is a byproduct of iron casting. Iron foundry slag is landfilled in large quantities by industrialized nations that produce cast iron products. Consequently, iron foundry slags can be obtained for little or no cost, and finding beneficial uses for iron slags improves sustainability. This paper describes findings from kinetic batch tests conducted to evaluate the feasibility of using iron foundry slags to remove As from groundwater. Tests were conducted on slags from four foundries in Wisconsin using solutions containing arsenite (As-III) and arsenate (As-V) having initial total As concentrations ranging between 100 and 2500 μg/L. Leach testing was also conducted to evaluate the potential for unintended impacts to groundwater.

MATERIALS

Control Materials

ZVI from Peerless Metal Powders, Inc. (Detroit, MI, USA) and a clean medium sand were used as control materials. The ZVI was used as a well-defined granular reactive material known to be effective in removing As from water (Su and Puls 2001). The sand was used as a non-reactive granular material. Physical properties of the ZVI are summarized in Table 1.

Table 1. Physical properties of ZVI and slags.

Material	USCS Classification	Specific Gravity	Surface Area (m^2/g)	Hydraulic Conductivity[a] (m/s)	% Iron[b]
ZVI	SP	6.85	0.96	2.4×10^{-3}	100
ARC	SW	2.73	0.098	8.0×10^{-4}	20
MAN	SW	2.50	0.10	1.5×10^{-3}	19
MTG	SP	3.11	0.15	2.4×10^{-4}	0.68
SHN	SW	3.04	0.089	1.6×10^{-3}	7.5

[a]measured following ASTM D 2434, [b]determined by X-ray fluorescence spectroscopy.

Slag

Iron foundry slags were collected from four foundries in Wisconsin noted as ARC, MAN, MTG, and SHN. The slags arrived unprocessed in large pieces ranging from 50 to 500 mm and were crushed using a mechanical crusher until they passed a US No. 4 sieve (4.75 mm). Some of the slags contained molten metal that could not be crushed. These pieces were excluded. Particle size distributions for the crushed slags and the ZVI are shown in Fig. 1. The slags have similar particle size distributions that have the convex shape characteristic of crushed materials. The slags are also coarser and more broadly graded than the ZVI.

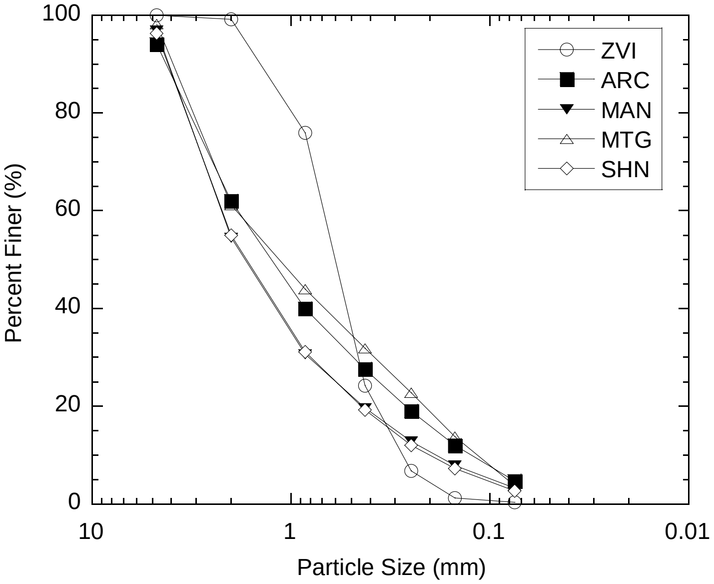

Fig. 1. Particle size distributions of slag and ZVI.

Physical properties of the slags are summarized in Table 1. The slags classify as poorly or well-graded sands in the Unified Soil Classification System (USCS) and have hydraulic conductivities on the order of 10^{-4} to 10^{-3} m/s. Two of the slags have specific gravities exceeding 3.0, which reflects the presence of heavier elements (e.g., metals) not typically found in abundance in soil minerals. Iron (Fe) content of the slags ranges from < 1% to 20%.

METHODS

Water Leach Testing and Total Elemental Analysis

Total elemental analyses (TEAs) and water leach testing (WLT) were conducted on each slag following USEPA Method 3050 (TEA) and ASTM D 3987 (WLT) as stipulated in the Wisconsin Administrative Code (WAC) for industrial byproducts used beneficially in lieu of landfilling (Wisconsin 2004). As required by the WAC, WLTs were conducted for aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), cyanide (CN^-), fluoride (F^-), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), sulfate (SO_4^{2-}), thallium (Tl), and zinc (Zn). TEAs were conducted for Sb, As, Ba, Be, Cr, Pb, and Tl.

Batch Kinetic Tests

Batch kinetic tests were conducted on each of the slags, the ZVI, and the sand. Solid (10.00 ± 0.02 g of slag, ZVI, or sand) was added to a 120 mL polyethylene bottle along with 100.0 ± 0.5 mL of deionized water. The bottle was then spiked with 0.1 to 0.2 mL of As stock solution to achieve a target As-III or As-V concentration of approximately 100, 500, 1000 or 2500 μg/L. The stock solutions were prepared with deionized water and reagent-grade $NaAsO_2$ (LabChem, Pittsburgh, PA, USA) or reagent-grade $Na_2HAsO_4•7H_20$ (J.T. Baker, Phillipsburg, NJ, USA). For each set of batch tests, at least two control samples were prepared without solids following the same method to determine the actual initial concentration.

After spiking, the bottles were immediately placed in a tumbler rotating at 30 rpm. Bottles were removed from the tumbler approximately 1 min before the designated end time and were mixed by hand during transfer from the tumbler to the bench. Samples to be collected within 2 min of spiking were mixed by hand for the duration of the experiment. At the designated end time, each sample was opened and filtered using a 0.2 μm syringe filter. A portion of the filtrate (50 mL) was collected, preserved with 0.5 mL of trace-metal grade nitric acid (Fisher Scientific, Toronto, Ontario, Canada), and refrigerated at 4.0 ºC prior to analysis. Another 25 mL was tested immediately for pH, redox potential (Eh), and electric conductivity.

Rate coefficients were determined by fitting first-order and second-order rate expressions to the batch test data using non-linear least squares regression implemented with the Solver package in Microsoft EXCEL. The first-order expression is:

$$C_t = C_0 \exp(-\lambda_1 t) \tag{1}$$

where C_t is the concentration at time t, C_0 is the initial concentration (average of concentrations from samples without solid) and λ_1 is the first order rate coefficient. The second-order expression is:

$$C_t = \frac{C_0}{1+\lambda_2 C_0 t} \tag{2}$$

where λ_2 is the second-order rate coefficient.

Analytical Methods

Metals analyses for the WLTs and the TEAs were conducted at the Wisconsin State Laboratory of Hygiene (Madison, WI). WLT samples were digested according to USEPA Method 3010 and then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) following USEPA Method 6020. Solutions from the TEAs were analyzed for metals by inductively coupled plasma-atomic emission spectrometry (ICP-AES) following USEPA Method 6010.

Analyses for CN^- and Hg were conducted by CT Laboratories (Baraboo, WI). Flow injection automated colorimetry with off-line distillation was used for the CN^- analyses following USEPA Method 9012A. Cold-vapor atomic adsorption was used for the Hg analyses following USEPA Method 7470.

Analyses for F^- and SO_4^{2-} were conducted in-house by high-performance liquid chromatography (HPLC) following USEPA Method 9056 with a modification for HPLC. Total As concentrations for the batch kinetic tests were determined in-house by ICP-AES following USEPA Method 6010. The arsenic detection limit was less than 6 μg/L.

RESULTS

Reuse Evaluation

Solid-phase concentrations from the TEAs are summarized in Table 2 along with maximum permissible concentrations (MPCs) stipulated in Section NR 538 of the WAC for beneficial use applications below the groundwater table. Concentrations exceeding MPCs are shown in bold. MPCs were exceeded for As, Be, and Cr for each of the slags as well as the ZVI. In fact, ZVI has some of the highest solid-phase concentrations for these elements. The MPC for Tl was also exceeded for MTG slag, but for none of the other slags or the ZVI.

Table 2. Solid-phase concentrations from total elemental analyses. Maximum concentrations stipulated in the Wisconsin Administrative Code for reuse applications below the groundwater table are shown in parentheses.

Reactive Material	Solid-Phase Concentration (mg/kg)						
	Sb (6.3)	As (0.042)	Ba (1100)	Be (0.014)	Cr (14.5)	Pb (50)	Tl (1.5)
ZVI	<2.0	**11**	20	**5.5**	**530**	41	<1.5
ARC	<2.0	**11**	20	**0.6**	**110**	5.5	<1.5
MAN	<2.0	**1.1**	28	**0.7**	**77**	3.4	<1.5
MTG	<2.0	**<0.8**	750	**9.0**	**28**	0.3	**7.4**
SHN	<2.0	**3.2**	320	**3.6**	**150**	3.2	<1.5

Note: "< X.Y" indicates that concentration is below the detection limit (X.Y mg/kg).

For the WLTs, only Mn was had a concentration above the MPC (25 μg/L) and only for one slag (ARC – 99 μg/L). The other 18 contaminants of concern were always below MPCs (Al<1500 μg/L, As<5 μg/L, Ba<400 μg/L, Be<0.4 μg/L, Cd<0.5 μg/L, Cr<10 μg/L, Cu<130 μg/L, CN^-<40 μg/L, F^-<800 μg/L, Fe<150 μg/L, Pb<1.5 μg/L, Hg<0.2 μg/L, Ni<20 μg/L, Se<10 μg/L, Sb<1.2 μg/L, SO_4^{2-} <125,000 μg/L, Tl<0.4 μg/L, and Zn<2500 μg/L).

The similarity of the findings for the iron foundry slags and ZVI suggests that slags used in PRBs should pose no greater risk for unintended groundwater contamination than ZVI, at least in the context of the criteria stipulated in the WAC. The higher liquid-phase Mn concentration for ARC slag is believed to be insignificant, as the Mn criterion is based on aesthetics rather than toxicity. The solid-phase Tl concentration for MTG slag is also believed to be insignificant because the solid-phase MPC was exceeded modestly and the liquid-phase Tl concentration from the WLT on MTG slag was below the detection limit (0.4 μg/L). However, more detailed study on the leaching behavior of slags is needed before a definitive conclusion can be made regarding the risks of unintended groundwater impacts. A study on the leaching properties of iron foundry slags currently is being conducted by the authors.

Slag Type and Reaction Order

Total As concentrations are shown as a function of time in Fig. 2 for batch tests conducted with a 100 μg/L As-V solution and the four slags. Comparative data are also shown for ZVI and for sand (non-reactive control). Trends obtained from other test series were similar to those shown in Fig. 3 regardless of As speciation or initial As concentration.

The solid lines shown in Fig. 3 correspond to fits of the first-order rate expression (Eq. 1). In general, similar fits were obtained using the first-order and second-order (Eq. 2) expressions, even though the mean square error typically was slightly higher for first-order fits compared to second-order fits (with only four exceptions, the difference between the mean absolute errors for the two fits was within a factor of 2.2). Because the first-order expression is simpler and provided a reasonable fit, first-order rate coefficients are used herein.

As shown in Fig. 2, the removal rate was always lower for the slags than ZVI. Also, essentially no removal was obtained for the sand, as expected. Slower removal was expected for the slags relative to ZVI, even if the intrinsic reactivity of the materials was the same, because the coarser slags have lower surface area than ZVI for the same amount of mass. The curves in Fig. 2 also show that the removal rate for the slags does not depend on the Fe content. For example, MAN slag, which had the second highest Fe content of the four slags that were tested, had the lowest rate of removal. In contrast, the highest rate of removal was obtained for the MTG slag, which has the lowest Fe content. This may indicate that different mechanisms are responsible for removal of As using ZVI and slag. Ahn et al. (2003) suggest that precipitation of relatively insoluble Ca-As compounds may be responsible for As removal using crushed steel slags. A similar mechanism may be occurring for iron foundry slags, which have appreciable Ca content due to the limestone or dolomite that is added as a fluxing agent to the molten iron.

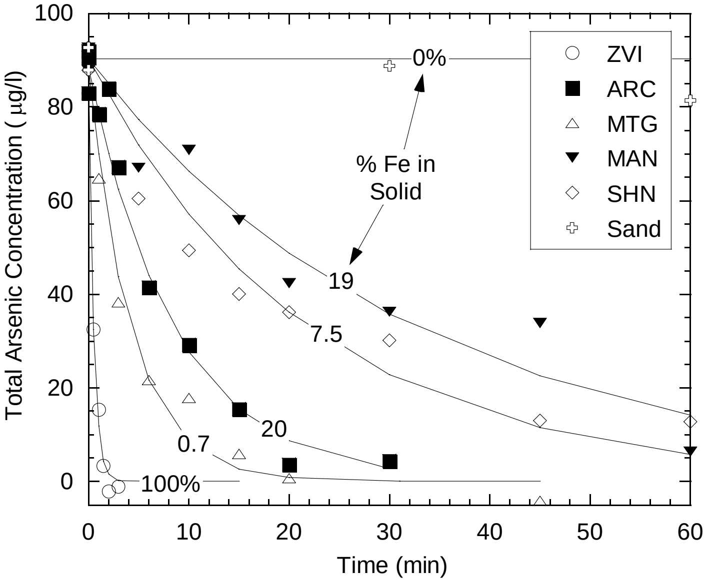

Fig. 2. Total arsenic removal for batch tests conducted with 100 µg/L As-V solution using slag, ZVI, or sand as the reactive material.

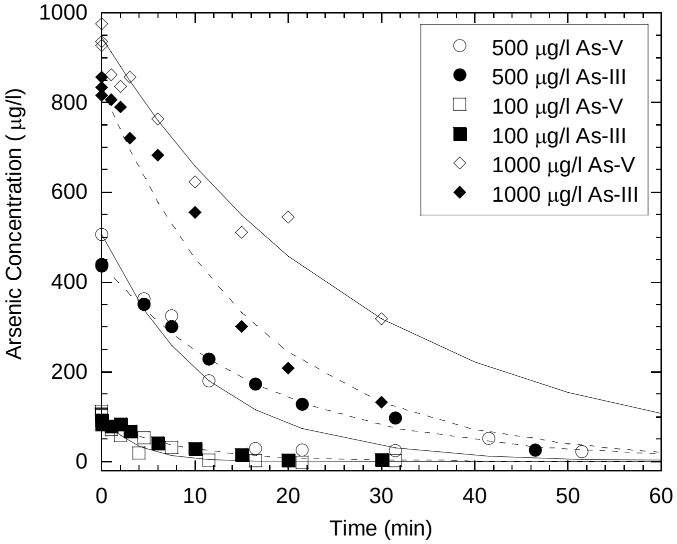

Fig. 3. As-III and As-V removal as a function of time using ARC slag for target initial concentrations of 100, 500, and 1000 µg/L. Solid lines are fits for As-V and dashed lines are fits for As-III.

Initial Concentration and Speciation

The effect of As speciation and concentration is illustrated in Fig. 3 for ARC slag. The rate of removal is slightly faster for As-V than As-III for initial concentrations of 100 and 500 µg/L, whereas As-III is removed faster than As-V at 1000 µg/L. The rate of removal also appears to be affected by concentration, with slower removal at higher concentration for both As-III and As-V.

The effect of initial concentration on As-V removal for all tests is shown in Fig. 4 in terms of normalized removal rate coefficients. The rate coefficient corresponding to an initial concentration of 100 μg/L was used for normalization for each slag. The removal rate coefficient decreases with increasing concentration for each slag, indicating slower removal as the concentration increases (Fig. 4). The effect of initial concentration on the rate coefficient is more significant for slags that are more reactive. For example, the rate coefficient for MTG slag, which is the most reactive (Fig. 2), is very sensitive to initial concentration, whereas the rate coefficient for the least reactive MAN slag is much less sensitive to concentration. The dependence on concentration also suggests that the removal reaction is not truly first order with respect to arsenic concentration. The removal reaction probably also depends on the availability of reactive materials (Fe, Ca, etc.) in the slag.

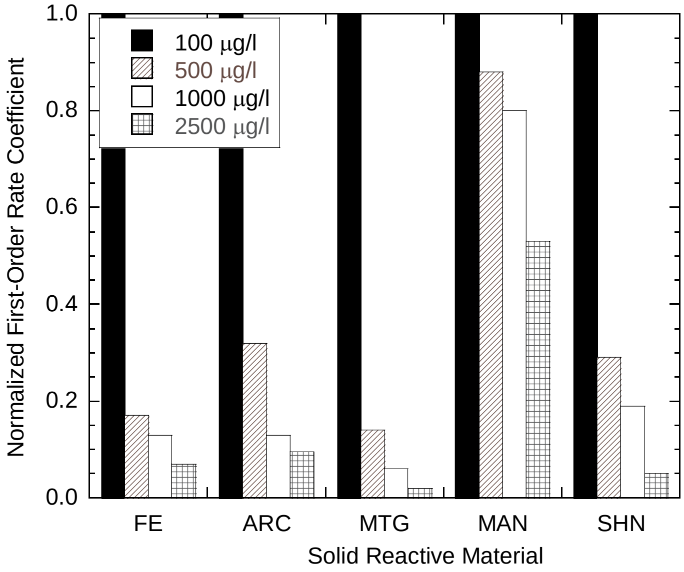

Fig. 4. Normalized As-V removal rate coefficients for initial concentrations of 100, 500, 1000, and 2500 μg/L.

The general effect of speciation is shown in Fig. 5, which shows first-order rate coefficients for As-III (λ_{III}) vs. those for As-V (λ_V) for tests conducted under similar conditions (e.g., the same slag and target initial concentration). In general, the rate coefficients are lower for As-III compared to As-V, with the difference between the rate coefficients increasing as the rate coefficients increase. There are some exceptions to this trend for lower rate coefficients. Whether these exceptions are real deviations is unclear, as they may also be due to heterogeneity in the slag samples or differences in initial concentration used in the batch test (initial As-III concentrations tended to be at least 10% lower than the initial As-V concentrations).

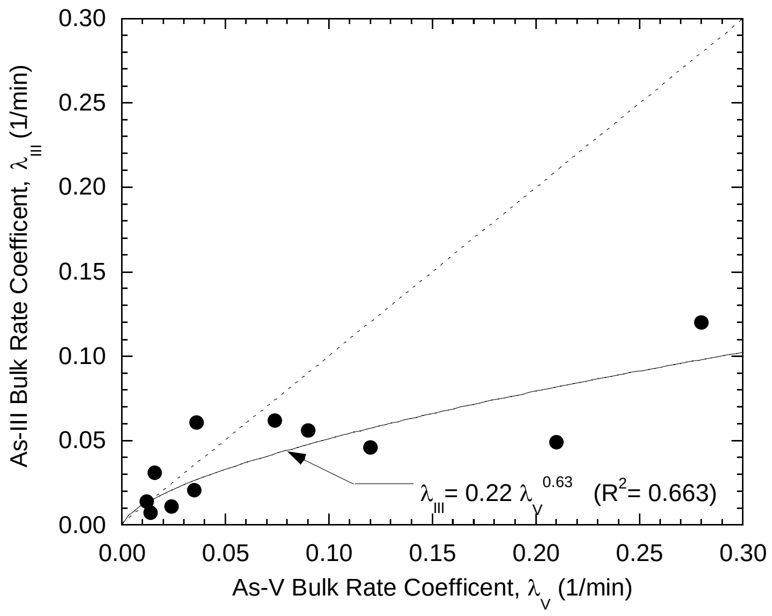

Fig. 5. Rate coefficients for As-III vs. those for As-V for tests conducted under similar conditions (target initial concentration and type of slag).

PRACTICAL IMPLICATIONS

Required thicknesses of PRBs containing iron slag for a typical field scenario were estimated using the data from the batch tests. Computations were made using the steady-state solution in Lee and Benson (2004) without dispersion. The seepage velocity was assumed to be 1 m/d and the influent concentration was assumed to be 1000 μg/L. The PRB was required to reduce the effluent concentration to 10 μg/L.

Rate coefficients obtained from the batch tests were adjusted to the liquid-to-solid ratio expected in an actual PRB assuming that the reactivity could be scaled by the surface area of the reactive material as described in Lee and Benson (2004). The porosities used in these computations were based on porosities achieved in column tests where slag was placed in lifts and gently tapped to simulate the procedure that might occur in the field. Rate coefficients obtained from batch tests with As-III solutions were used in the analysis to represent conditions where the removal rate is slower. The required PRB thicknesses are summarized in Table 3 along with the input parameters used in the analysis. In all cases, the required thickness is very small (< 7 mm) and is much less than the typical thickness of the reactive zone in PRBs (≈ 1 m).

An important consideration when using slag as a PRB material is the potential effects of heterogeneity. Unlike manufactured materials, slag is an industrial byproduct and the properties vary as manufacturing operations change. Even in a given lot of slag, the properties can vary from particle to particle. This is illustrated in the scanning electron micrographs (SEMs) shown in Fig. 6, which correspond to two particles from a single sample of slag used in this study. Despite coming from the same sample, the slags have very different surface properties, and therefore may have different reactivity. These heterogeneities may also be responsible for the greater scatter in the data obtained with slags relative to ZVI (e.g., see Figs. 2 and 3).

Table 3. Required thickness of PRB to reduce As-III concentration from 1000 μg/L to 10 μg/L for a seepage velocity of 1 m/d.

Material	Batch Rate Coefficient (1/min)	Porosity	Field Rate Coefficient (1/min)	Required PRB Thickness (mm)
ZVI	0.89	0.63	36	0.089
ARC	0.062	0.35	3.1	1.0
MAN	0.014	0.41	0.50	6.5
MTG	0.062	0.35	3.6	0.88
SHN	0.011	0.41	0.46	6.9

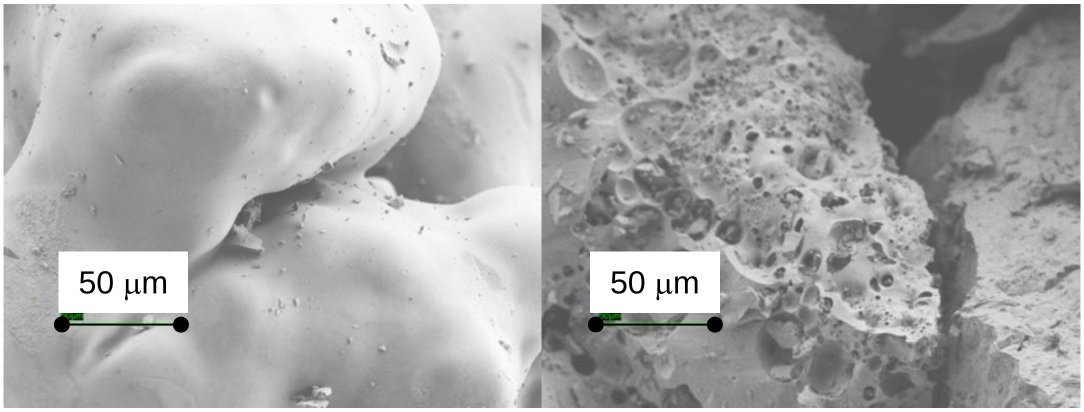

Fig. 6. SEMs of two particles of slag from the same sample.

SUMMARY AND RECOMMENDATIONS

The findings of this study suggest that slags from iron foundries may be effective low-cost reactive media for PRBs used to remove arsenic from groundwater. Iron foundry slags may not be as reactive as conventional ZVI, but do have sufficient reactivity so that PRBs having a reactive zone of typical thickness (< 1 m) could be constructed to effectively remove arsenic. However, the reactivity of the iron slags was evaluated under a limited set of idealized conditions, and more study is needed to demonstrate the generality of the findings. For example, column testing is needed to verify that the reactivity observed in the batch tests is realized under flow-through conditions at lower liquid-to-solid ratios. Additional factors that may be important in the field also need to be studied, such as the effects of other dissolved ions, pH, and dissolved oxygen content on the removal efficiency. The importance of slag heterogeneity, longevity of the reactivity, and the mechanisms controlling removal also need to be evaluated. Research on these issues is currently being undertaken by the authors.

ACKNOWLEDGEMENTS

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Occurrence of Estrogenic Endocrine Disruptors in Groundwater

Basic Information

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Project Number:	2005WI91B
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End Date:	2/28/2007
Funding Source:	104B
Congressional District:	2
Research Category:	Water Quality
Focus Category:	Water Quality, Toxic Substances, Methods
Descriptors:	
Principal Investigators:	William C. Sonzogni

Publication

Occurrence of Estrogenic Endocrine Disruptors in Groundwater

TABLE OF CONTENTS

LIST OF FIGURES AND TABLES

Project Summary

Occurrence of Estrogenic Endocrine Disruptors in Groundwater

Project ID: WR04R004

Wisconsin State Laboratory of Hygiene Investigators:
William Sonzogni PhD, Director
Jocelyn Hemming, PhD, Assistant Scientist
Miel Barman, Environmental Toxicologist
Steve Geis, Chemist Supervisor

July 1, 2004-June 30, 2006

Project Summary

Background:

Concern has emerged about a group of trace organic compounds identified in the aquatic environment which might affect reproduction and development of wildlife species and humans due to endocrine disruption (Colborn et al., 1996; Roefer et al., 2000). Studies in recent years have documented a high occurrence of these endocrine disrupting compounds (EDCs) in aquatic ecosystems which may have serious implications for groundwater quality (e.g., Kolpin et al., 2002). As the hydraulic demand on groundwater supplies increases, resulting in greater groundwater draw downs, the potential for EDC contaminated surface water input to groundwater increases, especially in areas where high capacity wells are located near surface waters. An additional route for entrance of EDCs into groundwater is through the leaching of septic system effluents. Areas such as non-sewered subdivisions may have an increased susceptibility to contamination of the groundwater by EDCs.

Compounds with endocrine disrupting activity include both anthropogenic chemicals produced industrially (such as surface active agents, pesticides, polychlorinated biphenyls (PCBs), plasticizers, food additives, birth control pills, herbal supplements and cosmetics) and natural occurring compounds (such as sex steroids, plant-produced estrogens and heavy metals) (National Research Council, 1999). EDCs are used in large quantities by consumers and industry. Domestic and industrial wastewater and agricultural run-off are recognized as the major sources of EDCs. Due to their physical-chemical properties and partial resistance to biotransformation, EDCs have been detected not only in wastewater effluents, but also at low concentrations in surface and groundwaters used as a source for water supply, and at very low concentrations in tap water samples (Stumpf et al., 1996; Ternes, 1999; Baronti et al., 2000).

Objectives:

1. To test high capacity municipal water supply wells located near surface waters impacted by industrial and municipal effluents will be tested for estrogenic EDCs.
2. To sample wells constructed to monitor groundwater close to non-conventional small scale on site waste disposal systems will be tested.
3. The breast cancer cell line (MCF-7) assay (E-screen) will be used to evaluate groundwater samples and septic samples for estrogenic activity.

Methods:

High capacity wells that may be impacted by nearby surface waters were selected from five Wisconsin communities. Associated drinking water and WDNR personnel were enlisted to perform sample collection. Each well and associated surface water were sampled four times per year to evaluate seasonal variability. A total of 21 samples were collected from traditional and non-conventional septic systems throughout Southeast Wisconsin. Soil pore water and groundwater samples were collected from lysimeters and monitoring wells installed beneath and adjacent to two of these systems.

Water samples were passed through a C_{18} solid phase extraction disk (Empore^{TM}). Compounds were eluted from the disks and concentrated to 1.5 ml. MCF-7 breast cancer cells were exposed to the extract. Cell proliferation was measured after five days of exposure using the SRB colorimetric protein assay.

Results and Discussion:

All surface waters contained some levels of estrogenic EDC activity. Water from high capacity wells did not contain any measurable estrogenic EDC activity. Estrogenic activity was detected in 20 of 21 septic effluent samples, although concentrations were markedly reduced in systems utilizing either sand filtration or aerobic pretreatment as compared to traditional systems. Although low levels of activity have been detected in soil water directly beneath one septic system, no estrogenic activity was found in groundwaters in this study.

Conclusions/Implications/Recommendations:

There appears to be no infiltration of estrogenic endocrine disrupting chemicals from the surface waters into the associated ground waters. Advanced pretreatment technologies (aerobic, sand filtration) appear to be quite effective at removing estrogenic compounds from septic effluent. Additional removal of EDCs occurs in unsaturated soils beneath septic leach fields; no EDCs were detected in groundwater beneath two systems without advanced pretreatment.

Related Publications:

Publication in progress: A manuscript based on the results from the septic effluents is in preparation in collaboration with Jeff Wilcox and will be submitted to the Journal of Environmental Quality.

Key Words:
Endocrine disruptors, high capacity wells, septic, non-sewered subdivisions, E-Screen.

Funding:
University of Wisconsin System portion of the Wisconsin Groundwater Research Program through the Water Resources Institute.

INTRODUCTION

During the past decade, concern has emerged about a group of trace organic compounds identified in the aquatic environment which might affect reproduction and development of wildlife species and humans due to endocrine disruption (Colborn et al., 1996; Roefer et al., 2000). Studies in recent years documented a high occurrence of these endocrine disrupting compounds (EDCs) in aquatic ecosystems which may have serious implications for groundwater quality (e.g., Kolpin et al., 2002). As the hydraulic demand on groundwater supplies increases, resulting in greater groundwater draw downs, the potential for EDC contaminated surface water input to groundwater increases, especially in areas where high capacity wells are located near surface waters. An additional route for entrance of EDCs into groundwater is through the leaching of septic system effluents. Areas such as non-sewered subdivisions may have an increased susceptibility to contamination of the groundwater by EDCs. The proliferation of non-conventional small scale on site waste disposal systems in rural areas may also result in the entrance of EDCs to groundwater. It is expected that such non-conventional systems will usually be installed in vulnerable groundwater settings, such as areas of shallow bedrock or high water tables, where conventional on-site septic systems would not be allowed.

Compounds with endocrine disrupting activity include both anthropogenic chemicals produced industrially (such as surface active agents, pesticides, polychlorinated biphenyls (PCBs), plasticizers, food additives, birth control pills, herbal supplements and cosmetics) and natural occurring compounds (such as sex steroids, plant-produced estrogens and heavy metals) (National Research Council, 1999). EDCs are used in large quantities by consumers and industry. Domestic and industrial wastewater and agricultural run-off are recognized as the major sources of EDCs. Due to their physical-chemical properties and partial resistance to biotransformation, EDCs have been detected not only in wastewater effluents, but also at low concentrations in surface and groundwaters used as a source for water supply, and at very low concentrations in tap water samples (Stumpf et al., 1996; Ternes, 1999; Baronti et al., 2000).

The objectives for this project were:

1. To test high capacity municipal water supply wells located near surface waters impacted by industrial and municipal effluents for estrogenic EDCs.
2. To sample wells constructed to monitor groundwater close to non-conventional small scale on site waste disposal systems as allowed by recently enacted Comm 83 rules for construction of septic systems and/or wells which already are suspected of having septic influences.
3. We used the breast cancer cell line (MCF-7) assay (E-screen) to evaluate >60 groundwater samples for estrogenic activity (breast cancer cells grow in the presence of estrogen or compounds that mimic estrogen).

High capacity wells expected either through modeling or direct empirical evidence to be impacted by nearby surface waters were chosen in consultation with DNR and USGS hydrologists. Drinking water personnel from selected communities were enlisted to perform sample collection. Each facility and associated surface water was sampled four times per year to evaluate seasonal variability. We sampled wells from five Wisconsin communities that utilize high capacity wells for their drinking water. Septic samples were collected from a housing subdivision that utilized unique septic systems. Approximately 31 samples were collected, either from monitoring wells or from cooperative homeowners.

Water samples were passed through a C_{18} solid phase extraction disk (Empore^{TM}). Compounds were then eluted from the disks and concentrated to 1.5 ml. MCF-7 breast cancer cells were then exposed to the extract. Cell proliferation was measured after five days of exposure using the SRB colorimetric protein assay. The WSLH has successfully developed the E-screen assay for use on water samples, and find it to be a highly effective and sensitive tool for detecting estrogenically active substances.

PROCEDURES AND METHODS

High capacity wells were sampled from five different Wisconsin municipalities along with their nearby surface water. All surface water samples were taken upstream from the well sites. Specific information on each sampling site can be found in Appendix B. Well water from two of the municipalities was further treated before distribution to the public. These post-treatment plant waters were also collected and tested. Each municipality was sampled four times to assess seasonal variation. A total of 80 well samples, 12 post treatment drinking waters, and 24 surface waters were collected and assayed for endocrine disruption activity. Collections of these waters occurred in November and December 2004, February and March 2005, May and June 2005, and August and September 2005.

Also, 21 septic-effluent samples were collected at 15 different residences in southeastern Wisconsin between April 2005 and February 2006. The types of septic systems included six aerobic treatment units, seven sand filters, and eight without any secondary pretreatment (Wisconsin Mound). Samples were collected before and after pretreatment from six of the systems using sand filtration. Aerobic treatment units and single-pass sand filters are used routinely in Wisconsin and elsewhere when site conditions are not considered suitable—due to shallow bedrock, high seasonal saturation, or limited infiltration capacity—for traditional systems. All samples were collected using peristaltic pumps and new Teflon tubing. In addition, soil-water and groundwater samples were collected beneath and immediately adjacent to two septic systems that utilize Wisconsin Mound distribution using previously-installed lysimeters and monitoring wells.

Water from the high capacity wells, nearby surface waters and septic systems was collected in 1 liter amber glass bottles. Samples were shipped overnight on ice to the laboratory. Samples (volumes of 1-2L) were extracted through a C_{18} disk, which was then eluted with solvents to capture the estrogenic chemicals. The extraction solvents were transferred into ethanol for a final volume of 1.5 ml. The extraction method was evaluated continually throughout the study using blanks, spikes, and duplicates. To ensure that the sampling method was not adding activity, sampling blanks were run using Type I water. Method and matrix spikes using 17β-estradiol were analyzed to ensure the extraction method was recovering the suspected EDCs. Interferences due to sample constituents, especially organic matter, were evaluated using matrix spikes. Duplicates were used to evaluate the consistency of the extraction procedures and assay.

All extracts were tested using the *in vitro* breast cancer cell proliferation assay known as the E-Screen. This assay utilizes the MCF-7 breast cancer cell line. The breast cancer cells proliferate in response to the presence of estrogen or chemicals that mimic estrogen. MCF-7 cells were grown in Dulbecco's Modified Eagle's Medium with 5% fetal calf serum at 37°C and 6.5% CO_2 and were sub-cultured every 7 days. To begin the assay, MCF-7 cells were trypsinized, counted with flow cytometry and plated into 24-well tissue culture plates at approximately 25,000 cells per well. Twenty-four hours after seeding, the media was removed and experimental media was added. The experimental media was Dulbecco's Modification of Eagles Medium without phenol red. The 5% fetal bovine serum used in this media is stripped of steroids with a charcoal dextran (CD) stripping procedure (referred to as CD-media). For plates containing the standards, the MCF-7 cells were exposed to 15 concentrations of estradiol ranging from 1×10^{-13} to 1×10^{-8} M. All treatments were done in quadruplicate and three plates were used to obtain a complete standard curve. Four control wells (CD-media only) were included on each plate. For plates on which samples were assayed, 0.1 ml of the water extract (in ethanol) was added to 9.9 ml of CD-media. A 50% dilution series was then made for a total of 5 concentrations. Each concentration was applied to four wells. In one of those wells, 1×10^{-9} M estradiol was added as a positive control. Again, each plate contained 4 control wells. After five days, cell proliferation was measured by the SRB protein assay: Cells were fixed with 10% tricholoracetic acid, rinsed and allowed to dry. The SRB dye was added to each well, followed by a rinse with 1% glacial acetic acid and allowed to dry. The dye was resuspended with 10mM Tris buffer at pH 10.5. The samples were read at 515 nM with a Molecular Devices microplate reader. To determine the estradiol equivalents (Eeq) of the samples, the standard curve was fit with a 4-parameter logistic equation, calculated by the Softmax PRO v. 2.6 analytical software package for the microplate reader. Estradiol equivalents for each sample was calculated by inserting the absorbance readings from the sample into the equation derived from the standard curve. Negative and positive wells were evaluated to ensure that the assay is running correctly. Low growth in the positive control wells may indicate the presence of substances that impede the normal growth of the cells. The limit of detection (LOD) was determined to be 0.02 ng/L Eeq and the limit of quantification (LOQ) was 0.04 ng/L Eeq.

RESULTS AND DISCUSSION

Two high capacity wells from five different municipalities were sampled four separate times. Well water from two of the municipalities was further treated before distribution to the public. These post-treatment plant waters were also collected and tested. Nearby surface water samples were also collected. Eighty well samples, twelve post treatment samples and twenty-four surface water samples were collected (Figures 1 through 5). Septic sampling occurred three times, with a total of 21 septic-effluent, four monitoring-well, and six soil-lysimeter samples being collected. Quality assurance samples include five matrix spikes, four travel blanks, three duplicates, two lab water blanks and two lab water spikes. In all, 121 samples have been analyzed for this study. The first round of high capacity well sampling had five of the six surface waters showing estrogenic activity which ranged from 0.05-0.09 ng/L with the sixth site having no estrogenic activity, while all of the well samples showed no estrogenic activity. The second round of sampling, for the high capacity wells had all six of the surface waters exhibiting estrogenic activity at an elevated rate from the first sampling. This activity ranged from 0.04-0.91 ng/L. The well waters from this round of sampling indicated activity levels that ranged from no detect (< 0.02 ng/L) to less than the LOQ (< 0.04 ng/L). The third round of sampling for the high capacity wells had all six surface waters with estrogenic activity ranging from 0.05-0.24 ng/L, while all of the well samples were below LOD. The fourth round of sampling for the high capacity wells had all six surface waters showing estrogenic activity which ranged from 0.07-0.66 ng/L. One of the sites showed estrogenic activity in both their well waters and post treatment waters. These activity levels ranged from <LOQ to 0.05 ng/L. The rest of the well waters did not exhibit estrogenicity. The levels of activity found in these samples are at or near the level of quantification (0.04 ng/L) and may be a result of sampling error or variation in the assay. Seasonality may have played a role in the increase in estrogenic endocrine disruptor activity in the second round of sampling. This round of sampling occurred during February and March, which follows a long period of cold temperatures. Biological activity of surface waters may lower as the temperature decreases. This phenomenon would explain the higher activity level if bacterial degradation of chemicals was happening at a slower rate.

Estrogenic activity in the 21 septic effluent samples ranged from <LOQ to 192.5 ng/L (Figure 6). The highest estrogenic activity (192.5 ng/L) was detected in a malfunctioning aerobic treatment unit. Excluding this data point, activity in samples collected following sand filtration and aerobic activity ranged from 0.058-3.81 ng/L (mean=0.76 ng/L) and 0.07-6.06 ng/L (mean=1.6 ng/L), respectively. Activity in eight samples with no advanced pretreatment—including the samples collected prior to sand filtration—ranged from 11.6-50.0 ng/L with a mean of 23.7 ng/L. These results indicate that concentrations of estrogenically-active substances can be significantly reduced in septic systems utilizing advanced pretreatment. As a comparison, a national survey of eight municipal wastewater treatment plants in which the E-screen was used to evaluate removal during secondary treatment indicated estrogenic activity ranging from 17 to 95 ng/L Eeq after primary treatment and 0.62 to 7.9 ng/L Eeq after secondary treatment (Drewes et al., 2005). Thus, removal appears fairly similar between municipal treatment and systems with advanced pretreatment.

Of the two systems that were instrumented with soil lysimeters and monitoring wells, one system showed effluent activity at 25.50 ng/L while the corresponding soil-water samples had no activity. The second system had an activity level of 19.57 ng/L in the effluent while activity in the three soil-water samples ranged from 0.28-0.38 ng/L. No estrogenic activity was detected in any of the groundwater samples.

Figure 1

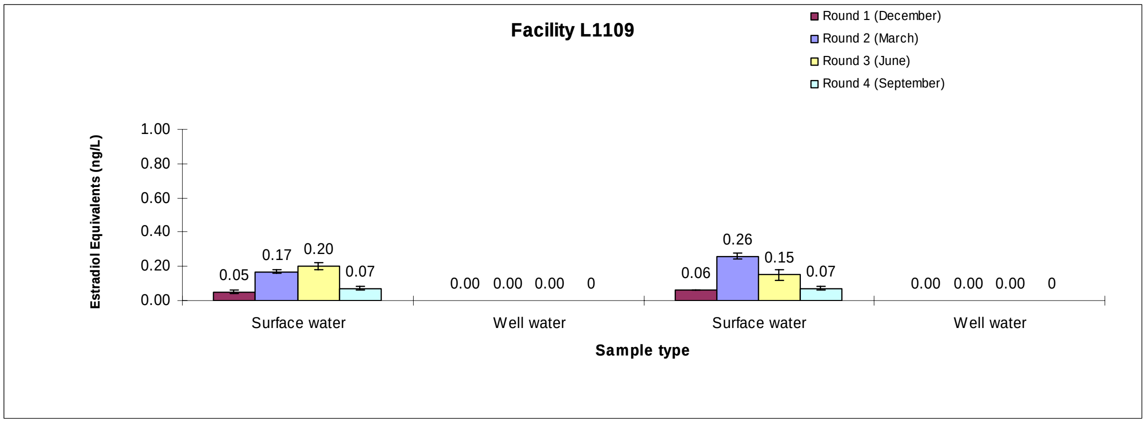


Figure 2

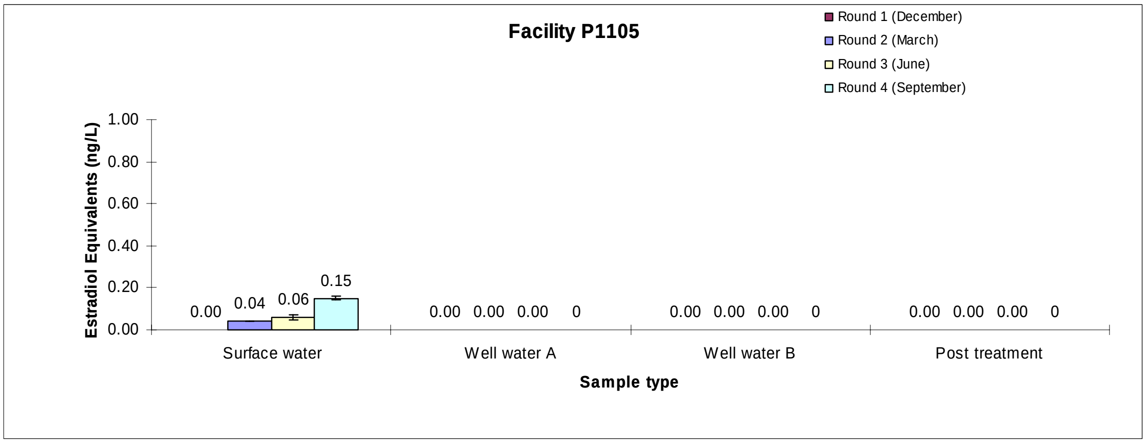


Figure 3

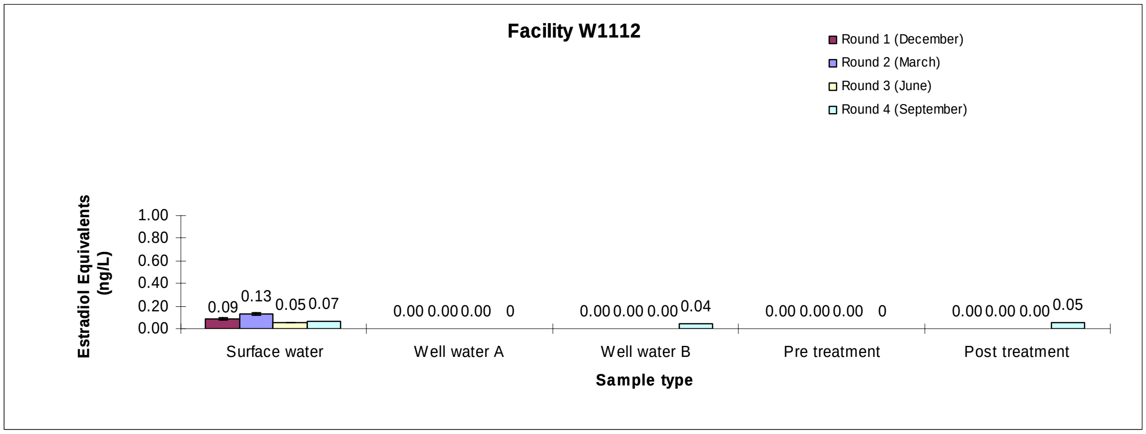


Figure 4

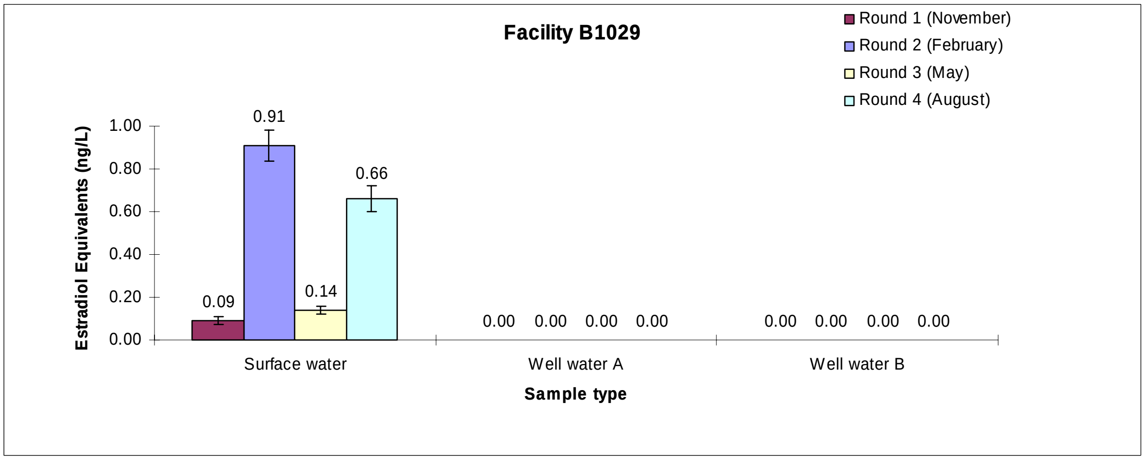


Figure 5

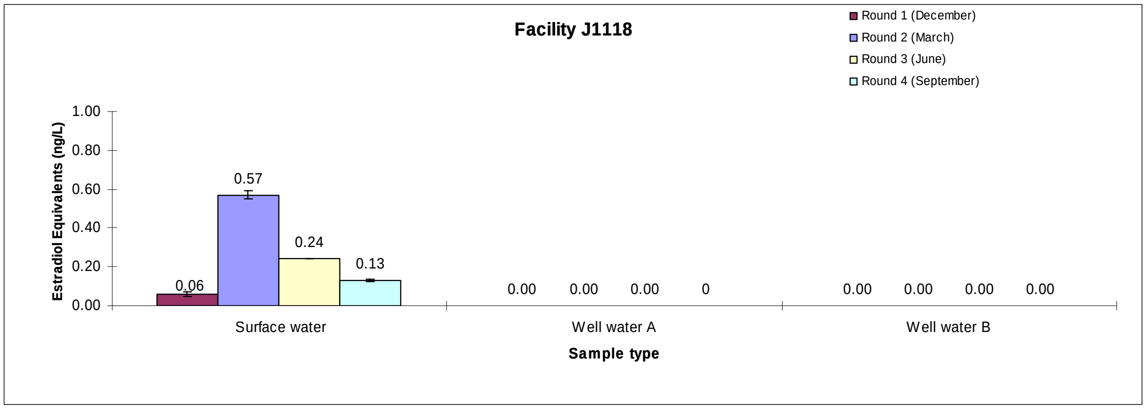
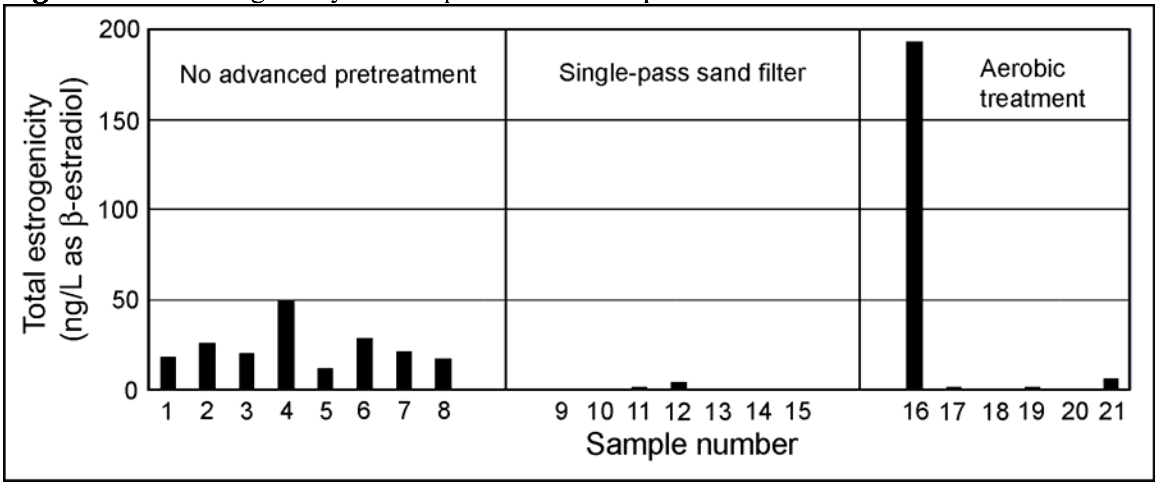


Figure 6 Total estrogenicity in 21 septic-effluent samples



Note that sample 16 was collected from a system that was not functioning properly.

Table 1 QC Sample Results

	QC sample		QC sample		QC sample		QC sample		QC sample
Sampling Round	**Lab Blank**	**Sampling Round**	**Travel Blank**	**Sampling Round**	**Lab Spike % Recovery**	**Sampling Round**	**Matrix Spike % recovery**	**Sampling Round**	**Duplicate % recovery**
1st	**ND**	**1st**	**ND**	**2nd**	**95**	**2nd**	**85**	**2nd**	**104**
1st	**ND**	**2nd**	**ND**	**3rd**	**88**	**2nd**	**81**	**3rd**	**127**
2nd	**ND**	**3rd**	**ND**			**3rd**	**77**	**4th**	**71**
3rd	**ND**	**4th**	**ND**			**4th**	**85**		

CONCLUSIONS AND RECOMMENDATIONS

With the exception of one sample, all the surface waters tested in this study exhibited estrogenic activity although this activity was at very low levels (all < 1 ng/L Eeq). When samples from high capacity wells that had the potential to be contaminated by the surface waters were tested, the vast majority of samples were below the detection limits of the assay. Therefore there is no evidence that the surface water is infiltrating into the groundwater. With respect to the pretreatment of septic effluent, both sand filtration and properly functioning aerobic treatment resulted in markedly reduced estrogenic activity in the samples relative to septic effluents with no pretreatment. However, estrogenic activity was reduced from untreated septic effluent in the soil column. Samples collected with a lysimeter indicated greater than 98% removal and removal below detection levels in samples collected from the monitoring wells.

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Ternes, T. A., Stumpf, M., Mueller, J., Haberer, K., Wilken, R.-D., and Servos, M. (1999), Behavior and occurrence of estrogens in municipal sewage treatment plants – I. Investigations in Germany, Canada and Brazil. *The Science of the Total Environment* **225**, 81-90.

APPENDIX A: AWARDS, PUBLICATIONS, REPORTS, PATENTS AND PRESENTATIONS

Presentation:

Wilcox, J.D., J.M. Bahr, C.J. Hedman, and K.R. Bradbury, 2006, Investigation of source concentrations and transport of hormones and pharmaceuticals beneath on-site wastewater treatment systems: GSA Annual Meeting Abstracts with Programs, vol. 38.

Barman, M., Sonzogni, W., Hemming, J., Geis, S. 2005, Occurrence of Estrogenic Endocrine Disruptors in Groundwater. Midwest Regional Society of Environmental Toxicology and Chemistry. Platform presentation April 2005, Madison WI.

Publication in progress:

A manuscript based on the results from the septic effluents is in preparation in collaboration with Jeff Wilcox and will be submitted to the Journal of Environmental Quality.

APPENDIX B:

Table 2 Well Information

Facility Code										
	1029 A	**1029 B**	**1105 A**	**1105 B**	**1109 A**	**1109 B**	**1112 A**	**1112 B**	**1118 A**	**1118 B**
Well distance from surface water (ft)	NA	NA	2640	3960	400	1800	900	100	50	800
Well depth (ft)	NA	NA	110	118	100	93	100	150	100	105
Municipal discharges	NA	NA	0	0	15	12	16	16	19	19
Industrial discharges	NA	NA	0	0	2	3	14	14	3	3
NA = information not provided by municipality										

Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil

Basic Information

Title:	Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil
Project Number:	2006WI135B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Hydrology, Groundwater, Models
Descriptors:	None
Principal Investigators:	Birl Lowery, John Norman

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Jim Hurley
Submitted: 6/20/2007

Project Title

WR05R002: Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil

Project Investigators

Brian Lepore, University of Wisconsin-Madison
Birl Lowery, University of Wisconsin-Madison
John Norman, University of Wisconsin-Madison

Progress Statement

An infiltration model based on the concept of Poiseuille equation has been developed for flow in a slit between soil structural units (peds), and Darcy's law was applied for flow from the slits into peds. The model allows for both saturated and unsaturated flow and is designed to be parameterized using relatively easily obtained field observations of soil structure. Initial parameterization was done using experimental field data acquired during the summers of 2005 and 2006 as part of the experimental aspects of this project. Water content and drainage data obtained from 1996 to 1999 at the same research site will be used for validation.

This model will be used as an infiltration module in the Precision Agriculture-Landscape Modeling System (PALMS) developed at the University of Wisconsin-Madison in support of the Wisconsin Buffer Initiative (WBI).

The experimental method developments and data and the infiltration model are expected to lead to three manuscripts for publication in peer reviewed journals. One manuscript has been submitted to the Soil Science Society of America Journal and one is in the final stage before submittal, while the third is still in its initial stages. All three manuscripts along with other material will compose the PhD thesis of Brian Lepore, who should complete his defense in summer, 2007.

Impacts

Description	The computer modeling simulation will improve the understanding of the types of landscapes and weather events which lead to increased rapid infiltration and drainage of rain water and dramatic groundwater contamination. The modeling studies will allow us to begin studying the impacts of different management decisions on risks of groundwater contamination.

Students & Post-Docs Supported

Student Name	Brian Lepore
Campus	University of Wisconsin-Madison

Advisor Name	Birl Lowery
Advisor Campus	University of Wisconsin-Madison

Degree	PhD
Graduation Month	
Graduation Year	2007
Department	Soil Science
Program	Soil Science
Thesis Title	
Thesis Abstract	

.....

Student Name	Unknown Undergrad 1
Campus	University of Wisconsin-Madison

Advisor Name	
Advisor Campus	University of Wisconsin-Madison

Degree	Other
Graduation Month	
Graduation Year	
Department	
Program	
Thesis Title	
Thesis Abstract	

.....

Student Name	Unknown Undergrad 2
Campus	University of Wisconsin-Madison

Advisor Name	
Advisor Campus	University of Wisconsin-Madison

Degree	Other
Graduation Month	
Graduation Year	
Department	
Program	
Thesis Title	
Thesis Abstract	

Assessing the Ecological Status and Vulnerability of Springs in Wisconsin

Basic Information

Title:	Assessing the Ecological Status and Vulnerability of Springs in Wisconsin
Project Number:	2006WI136B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	WI 1st; 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Ecology, Groundwater, Hydrology
Descriptors:	None
Principal Investigators:	Susan Swanson, Kenneth R Bradbury, David John Hart, David Zaber

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Susan Swanson
Submitted: 6/8/2007

Project Title

WR05R004: Assessing the Ecological Status and Vulnerability of Springs in Wisconsin

Project Investigators

Kenneth Bradbury, Wisconsin Geological and Natural History Survey
David J. Hart, Wisconsin Geological and Natural History Survey
Susan Swanson, Beloit College
David Zaber, University of Wisconsin-Madison

Progress Statement

The need for a clear understanding of the physical and ecological status of springs in Wisconsin provides the overall motivation for this project. The topic is relevant because the State has taken steps to protect springs that result “in a current of flowing water with flows of a minimum of one cubic foot per second at least 80 percent of the time” (2003 Wisconsin Act 310, p.2), and the Wisconsin Department of Natural Resources (WDNR) is charged with evaluating impacts to these springs that may result from groundwater pumping by high-capacity wells. We hope to provide a mechanism to evaluate impacts and provide feedback to the question of whether springs covered under Act 310 are sufficient to protect the range of Wisconsin’s spring resources.

The project includes cataloging historical and existing spring resources in Iowa and Waukesha Counties using a geographic information system (GIS) and characterizing a subset of springs in the two counties using a comprehensive springs classification system in development by Springer et al. (in prep.). This information will be used to develop typical hydrogeological conceptual models and associated descriptions of typical ecological characteristics of springs in each region.

Spring Surveys
Property owners for 271 of 406 historical springs in Iowa County were identified. We confirmed that approximately 185 of these springs persist in some form today. Conversations with property owners and observations in the field suggest that many other springs were not historically mapped, but do exist in Iowa County. Of the 185 springs for which locations were confirmed and access granted, a total of 24 springs were surveyed for the full suite of hydrological, physicochemical, and ecological characteristics included in the Springer et al (in prep.) classification system. These springs were selected on the basis of their proximity to major stratigraphic contacts; their elevation, slope, and aspect; and their geographic position within Iowa County. Only five of the springs are located on public lands. Most of these surveys were conducted in June 2006, and they were completed by early July 2006.

Property owners for 186 of 265 historical springs in Waukesha County were identified. Up to 65 of these springs may persist in some form today; however, actual confirmation of spring locations proved to be much more difficult in Waukesha County. Conversations with property owners and observations in the field suggest that many of the properties that historically contained springs have been developed for residential or commercial purposes. Ponds have also been created on at least six of the properties that once contained distinct springs. A total of 20 springs in Waukesha County were surveyed for the full suite of hydrological, physicochemical, and ecological characteristics included in the Springer et al (in prep.) These springs were largely selected on the basis of property access permission and, to some degree, the geologic setting and geographic distribution within the county. For example, half of the springs surveyed in Waukesha County are located on public lands. Spring surveys were conducted in July and August 2006.

We also completed an entire year of monitoring at three additional springs in Iowa County. Two of the springs are located in northern Iowa County, one near Highland and the other near Otter Creek. The other spring was monitored as part of a complementary geological study being conducted by the Wisconsin Geological and Natural History Survey; it is located in Governor Dodge State Park. The springs occur at different stratigraphic positions, elevations, and aspects. They also vary in terms of their level of disturbance. The springs were sampled on a bimonthly basis for the full suite of hydrological, physicochemical, and ecological characteristics included in the Springer et al (in prep.) classification system. Flow was measured on a monthly basis. Monitoring events took place in 2006 on Jan. 31st/Feb. 1st (full suite), Feb. 22nd (flow), March 9th (full suite), April 22nd (flow), May 24th (full suite), June 13th (flow), July 6th (full suite), August 16th (flow), September 24th (full suite), October 25th (flow), November 19th (full suite), and December 30th (flow), and on January 15th in 2007 (flow).

Progress continues on the analysis of physiochemical and biological data collected during during the spring surveys. This information is being used to develop typical hydrogeological conceptual models and associated descriptions of typical ecological characteristics of springs in each region.

References:

Springer, A.E., Stevens, L.E., Anderson, D.E., Parnell, R.A., Kreamer, D.K., and Flora, S.P., in prep. A comprehensive springs classification system: integrating geomorphic, hydrogeochemical, and ecological criteria, in Stevens, L.E., and Meretsky, V.J., eds., Every last drop: ecology and conservation of springs ecosystems in North America: Tucson, AZ, University of Arizona Press.

Impacts

Description

- Application(s) – The springs database for Iowa and Waukesha Counties is currently being used to characterize the physical and ecological status of spring resources in each county. In the future, we hope that the database and approach will serve as a working model for environmental assessments of spring resources elsewhere in the State.

- Impacts – The spring surveys that were conducted in Iowa and Waukesha Counties in June and July, 2006 are the first attempts to survey spring resources in these regions since 1959. A total of 27 springs were surveyed in Iowa County, and a total of 20 springs were surveyed in Waukesha County.

- Benefits – The physical, biological, and sociocultural data that have collected will allow us to make assessments of the physical and ecological status of typical spring systems in each county. This is a critical first step in assessing vulnerability to groundwater pumping because it provides baseline conditions to which changes can be compared. To further address the issue of vulnerability, the data we collect will allow us to formulate viable hydrogeological conceptual models of the typical spring systems in each county, which may be useful for modeling studies if high-capacity wells are proposed in the future.

Awards, Honors & Recognition

Title	Geochemical and Flow Characteristics of Two Contact Springs in Iowa County, WI
Event Year	2007
Recipient	Brandon Bartkowiak
Presented By	American Water Resources Association - Wisconsin Section
Description	Outstanding Undergraduate Presentation Award at the AWRA-WI annual meeting.

Interactions

Description	A Spring Projects Coordination Group, coordinated by the WDNR, met on April 12, 2006 at the Southern District office of the WDNR. Several representatives from the WDNR also attended this meeting, which focused on providing updates on the four projects to the Groundwater Advisory Committee, which was created by 2003 WI Act 310 to make recommendations to the State Legislature regarding future groundwater management needs in Wisconsin.
Event Date	4/12/2006

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Description	On October 18, 2006, Sue Swanson presented preliminary results of the project to the Iowa County Board. The meeting was organized by the Wisconsin Geological and Natural History (WGNHS) to communicate the status of their ongoing geological investigation of Iowa County. We have been working closely with the WGNHS because the project complements their study.
Event Date	10/18/2006

Presentations & Public Appearances

Title	An Assessment of Spring Resources in Southern Wisconsin
Presenter(s)	Susan Swanson
Presentation Type	Government briefing
Event Name	Iowa County Board meeting
Event Location	Wisconsin Geological and Natural History Survey Core Repository, Mt. Horeb, Wisconsin
Event Date	10/18/2006
Target Audience	Other
Audience Size	20
Description	On October 18, 2006, Susan Swanson presented preliminary results of the project to the Iowa County Board. The meeting was organized by the Wisconsin Geological and Natural History (WGNHS) to communicate the status of their ongoing geological investigation of Iowa County. We have been working closely with the WGNHS because the project complements their study.

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Title	Assessing the ecological significance and vulnerability of springs in southern Wisconsin
Presenter(s)	Susan Swanson
Presentation Type	Professional meeting
Event Name	American Water Resources Association - Wisconsin Section Annual Meeting
Event Location	Wisconsin Dells, Wisconsin
Event Date	3/2/2007
Target Audience	Scientific audience
Audience Size	75
Description	Wisconsin's springs are generally poorly studied. However, recently conducted surveys reveal the range of geological and biological conditions associated with springs in Iowa and Waukesha Counties

and illustrate the utility of baseline information in assessing the ecological significance and vulnerability of spring systems in these regions. The two counties differ in their bedrock geology, surficial geology, and development pressures. In Iowa County, springs are associated with every major stratigraphic unit, but most commonly occur as contact springs that discharge from Ordovician Sinnipee Group rocks, near the upper contact of the Ordovician St. Peter Formation, or near the upper contact of the Cambrian sandstones. Most of the springs that were mapped by the Wisconsin Conservation Department in 1958 still persist, but many springs are impacted by agricultural practices. Spring waters can be distinguished on the basis of major ion geochemistry, and springs discharging from stratigraphically higher units tend to have lower and more variable flow.

Spring systems in Waukesha County have been compromised by urban and residential development; very few historically identified springs remain in pristine condition. Those that do remain are largely found on public lands, in or near wetlands associated with former glacial lakebeds. Major ion geochemistry is less variable among springs, and flow rates are generally low. Preliminary results show that the springs in both settings have a relatively low diversity of aquatic insects, although springs with close biogeographical relationships to receiving waters have more taxa present, including more insects.

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Title	Geochemical and Flow Characteristics of Two Contact Springs in Iowa County, WI
Presenter(s)	Brandon Bartkowiak, Susan Swanson
Presentation Type	Poster session
Event Name	American Water Resources Association - Wisconsin Section Annual Meeting
Event Location	Wisconsin Dells, Wisconsin
Event Date	3/1/2007
Target Audience	Scientific audience
Audience Size	75
Description	Two contact springs in Iowa County, Highland Big Spring and Otter Creek Big Spring, were monitored from January 2006 to January 2007 to better understand groundwater flow paths to the springs. The springs are representative of those in Iowa County and the entire Driftless Area in that they occur near major stratigraphic contacts. Highland Big Spring discharges near the contact of the Prairie du Chien Group with the St. Peter Formation. Otter Creek Big Spring discharges near the contact of the Jordan Formation with the Prairie du Chien Group. Discharge was measured monthly using a current meter or a cutthroat flume, and geochemical sampling occurred on a bi-monthly basis. Alkalinity, conductivity, temperature, dissolved oxygen and pH were measured in the field using a multiparameter sonde, and grab samples were analyzed for major ion concentrations and stable isotopes of oxygen and hydrogen. The average monthly discharge is 0.9 cfs at Highland Big Spring and 0.3 cfs at Otter Creek Big Spring. Flow is more variable at the Highland Big Spring. Major ion concentrations are similar, but calcium and magnesium concentrations are slightly higher at the Highland Big Spring. The differences in flow variability and geochemistry may be due to a more direct groundwater flow path to the Highland Big Spring.

Students & Post-Docs Supported

Student Name	Brandon Bartkowiak
Campus	Beloit College

Advisor Name	Susan Swanson
Advisor Campus	Beloit College

Degree	Undergraduate
Graduation Month	May
Graduation Year	2007
Department	Geology
Program	
Thesis Title	
Thesis Abstract	

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Student Name	Rebecca Carvin
Campus	University of Wisconsin-Madison

Advisor Name	
Advisor Campus	University of Wisconsin-Madison

Degree	Masters
Graduation Month	May
Graduation Year	2008
Department	Water Resources Management
Program	Institute for Environmental Studies
Thesis Title	
Thesis Abstract	

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Student Name	Natalie Hunt
Campus	University of Wisconsin-Madison

Advisor Name	
Advisor Campus	University of Wisconsin-Madison

Degree	Masters
Graduation Month	August
Graduation Year	2007
Department	Water Resources Management
Program	Institute for Environmental Studies
Thesis Title	
Thesis Abstract	

Identifying High-Infiltration and Groundwater Recharge Areas

Basic Information

Title:	Identifying High-Infiltration and Groundwater Recharge Areas
Project Number:	2006WI146G
Start Date:	9/1/2006
End Date:	8/31/2008
Funding Source:	104G
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Models, Groundwater, Water Quantity
Descriptors:	None
Principal Investigators:	Stephen J. Ventura, John Norman, Cynthia A. Stiles

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Jim Hurley
Submitted: 7/2/2007

Project Title

WR06R004: Identifying High-Infiltration and Groundwater Recharge Areas

Project Investigators

John Norman, University of Wisconsin-Madison
Cynthia Stiles, University of Wisconsin-Madison
Stephen Ventura, University of Wisconsin-Madison

Progress Statement

Our proposal described a plan to produce relative infiltration maps for Dane County, Wisconsin using a weighting-and-rating of several GIS data layers. For example a site with high soil permeability, deep bedrock, and a deep water table could be expected to have a high infiltration rate relative to a site with less permeable soils, shallow bedrock or a shallow water table. Instead of using a weighting-and-rating system, we have decided to develop pedotransfer functions (PTFs), which predict saturated hydraulic conductivity (Ksat) from other soil properties. This approach will allow us to make quantitative comparisons between predicted and measured Ksat values.

We have developed a detailed plan to follow this approach. We will be developing broad-scale pedotransfer functions using the Wisconsin records in the National Cooperative Soil Survey (NCSS) pedon database. These PTFs will allow us to estimate Ksat from basic soil properties (such as texture and bulk density) available for each soil mapping unit in the National Soil Information System (NASIS) database for Dane County. We will be testing these PTFs with locally-collected Ksat measurements. These data will be used to develop fine-scale pedotransfer functions that include topography and land use as predictors of Ksat (in addition to soil properties). The availability of high-resolution digital data sets for these properties (a 10m-resolution county Digital Elevation Model, for example) will allow us to predict Ksat at resolutions finer than the soil mapping unit.

An important research question is whether or not we will be able to collect enough local data to develop models that predict Ksat with greater accuracy than existing models/databases (such as the NASIS database, which includes estimated Ksat values for each soil mapping unit). Since Ksat can vary by orders of magnitude over short distances (due to the presence of macropores, for example), numerous measurements are required to determine a representative value for a given area. We will be testing a new type of infiltrometer in this study- a rectangular steel frame that is 1m long, 0.5 m wide and 0.3m deep. We anticipate that this large sample area will be sufficient to capture more of the fine-scale spatial variability of Ksat, as compared to a smaller instrument, such as the single-ring infiltrometer (10-inch diameter). This should reduce the number of replicates needed to characterize the Ksat of an area.

This summer we will be collecting an initial set of local Ksat measurements. We have selected a watershed that is representative of Dane County in terms of land area percentages in classes of both estimated Ksat and land use. This watershed was sampled intensively in 2004 and 2006 for another project. Complete profile descriptions and chemical analyses of surface soil samples were done for nearly 500 locations. A subset of these (60 points) was selected randomly, stratified into 9 classes (3 for estimated Ksat and 3 for land use). The number of points in each class is roughly proportional to the land area percentages for that class. For this stratification, Ksat estimates were made using the textural class and bulk density of the surface horizon for the corresponding soil mapping units in the NASIS database. A table of national averages for Ksat in each textural class of both high and low bulk density was used to estimate Ksat. Land uses categories were determined from a GIS data layer developed by the Dane County Regional Planning Commission in 2005.

Impacts

Description	Fieldwork for the project only began in May 2007, so results and impacts have not yet been generated. The test infiltrometer described above is a UW innovation. Thus far, it appears to be superior to traditional methods for measuring in-field infiltration. It was vetted with a multi-agency group of infiltration specialists at the recent national conference of the National Cooperative Soil Survey. This group thought it was a useful direction and may eventually incorporate it or similar idea in national soil testing standards.

Committees, Memberships & Panels

Group Name	Infiltration working group of the National Cooperative Soil Survey
Description	
Start Date	
End Date	

Partners

Name/Organization	Kevin Connors
Affiliation	Dane County Land and Water Resources Department
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Description	GIS Analyst

.....

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Description	Urban Conservation Engineer

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Name/Organization	Chuck Dunning
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Name/Organization	Randy Hunt
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Name/Organization	Don Fehrenbacher
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.....

Name/Organization	Carl Wacker
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Description	Assistant State Soil Scientist

Presentations & Public Appearances

Title	Identifying High Infiltration and Ground Water Recharge Areas in Dane County, Wisconsin - an Integrated Field/GIS Study.
Presenter(s)	Stiles, Cynthia A.
Presentation Type	Professional meeting
Event Name	National Cooperative Soil Survey Conference.
Event Location	Madison, WI.
Event Date	6/6/2007
Target Audience	Federal agency
Audience Size	150

Description

Students & Post-Docs Supported

Student Name	Kathleen Arrington
Campus	University of Wisconsin-Madison

Advisor Name	Steve Ventura
Advisor Campus	University of Wisconsin-Madison

Degree	PhD
Graduation Month	May
Graduation Year	2009
Department	Soil Science
Program	Soil Science
Thesis Title	Identifying High Infiltration Areas
Thesis Abstract	

Grant No. 07HQGR0025 Effectiveness of Engineered Covers: From Modeling to Performance Monitoring

Basic Information

Title:	Grant No. 07HQGR0025 Effectiveness of Engineered Covers: From Modeling to Performance Monitoring
Project Number:	2006WI179S
Start Date:	12/1/2006
End Date:	1/15/2009
Funding Source:	Supplemental
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Jim Hurley
Submitted: 6/23/2007

Project Title

WR06R005: Effectiveness of Engineered Covers: From Modeling to Performance Monitoring

Project Investigators

Craig Benson, University of Wisconsin-Madison

Progress Statement

We began the project in January 2007 after the contracting issues were resolved. Our efforts to date have focused primarily on Task 1 (Estimating Hydraulic and Transport Properties, ~ 95% of our effort to date), but have also included Task 2 (Effectiveness of Monitoring Programs, ~ 5% of our efforts). Data from five of the decommissioned ACAP sites (Altamont, Cedar Rapids, Sacramento, Apple Valley, and Albany) are being analyzed in conjunction with water balance data collected during performance monitoring. The purpose of this analysis is to provide quantitative estimates of hydraulic properties appropriate for modeling cover performance and to assess the effectiveness of monitoring methods. We plan to continue these efforts throughout 2007 with the data obtained from decommissioning activities associated with the ACAP sites in Monticello, Utah and Boardman, Oregon. We will also be integrating data collected from a full-scale waste containment facility (Seven Mile Creek Landfill in Wisconsin) into this effort. Data from this additional site will be available this summer.

Impacts

Description	This project is providing insights on the long-term performance of covers for waste containment.

Students & Post-Docs Supported

Student Name	Seunghak Lee
Campus	University of Wisconsin-Madison
Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison
Degree	Post Doc
Graduation Month	June
Graduation Year	2010
Department	
Program	

Thesis Title	
Thesis Abstract	

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Student Name	Joseph Scalia
Campus	University of Wisconsin-Madison

Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison

Degree	PhD
Graduation Month	May
Graduation Year	2010
Department	
Program	
Thesis Title	
Thesis Abstract	

Mercury Speciation along a Groundwater Flowpath

Basic Information

Title:	Mercury Speciation along a Groundwater Flowpath
Project Number:	2006WI180S
Start Date:	7/1/2004
End Date:	6/30/2006
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Geochemical Processes, Solute Transport, Toxic Substances
Descriptors:	groundwater, mercury, methylation
Principal Investigators:	David Armstrong, Christopher L. Babiarz

Publication

1. Chadwick, S.P., C.L. Babiarz, J.P. Hurley, D.E. Armstrong. 2006. Evaluation of the Role of Dissolved Organic Matter in the Speciation of Mercury and Methylmercury in a Lacustrine Watershed Using Diethylaminoethyl Resin. Abstracts, Conference on Mercury as a Global Pollutant, Madison, WI.
2. Kerr, S., J. Overdier, and M. Shafer. 2004. Hyporheic processes regulating trace element cycling under differing hydrologic and biogeochemical regimes. Abstract. Paper presented at the American Geophysical Union Fall 2004 meeting. San Francisco, December 13-17 2004.
3. Shafer, M., S. Kerr, J. Overdier, and D.E. Armstrong. 2005. Trace metal cycling within riparian wetland and hyporheic regions of a northern temperate stream catchment. Abstract Paper presented at the American Geophysical Union Fall 2005 meeting. San Francisco, December 5-8 2005.
4. Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005. Contrasts in trace metal cycling within oxic and anoxic flowpaths of a northern temperate stream catchment. Abstract American Society of Limnology & Oceanography 2005 Aquatic Sciences meeting. Salt Lake City, February 20-25.

Project Report

"Mercury Speciation Along A Groundwater Flowpath"
(05-CTP-01, WR04R001)

By

D.E. Armstrong, C.L. Babiarz, M.M. Shafer and S.C. Kerr
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Funded By

The State of Wisconsin Groundwater Research Program

through the

University of Wisconsin Water Resources Institute
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Madison, WI 53706

November, 2006

TABLE OF CONTENTS

LIST OF TABLES AND FIGURES

PROJECT SUMMARY

Title: **Mercury Speciation Along A Groundwater Flowpath**
Project I.D.: 05-CTP-01, WR04R001
Principal Investigators: D.E. Armstrong, Professor Emeritus, and C.L Babiarz, Assistant Scientist
Affiliated Investigators: M.M. Shafer, Associate Scientist; S.C. Kerr and S.P. Chadwick, Research Assistants
Department: Water Science & Engineering Laboratory and Environmental Chemistry & Technology Program, University of Wisconsin-Madison
Project Period: July 1, 2004 to June 30, 2006

Objectives: Our investigation focused on the cycling of mercury in wetlands within the Trout Lake Basin in Vilas County, Wisconsin. The three main objectives were:

1. To characterize the levels of total Hg and methyl mercury (MeHg) carried in stream waters flowing through the wetlands;
2. To characterize hyporheic zones within these wetlands regarding (a) concentrations of aqueous total Hg and MeHg, (b) factors influencing MeHg levels, and (c) the importance of hyporheic zones in controlling MeHg in stream waters;
3. To probe the forms of inorganic Hg(II) and MeHg in hyporheic zone waters and examine the implications of speciation on transport and on the bioavailability of Hg(II) for methylation.

Methods: This investigation was conducted in the Trout Lake Basin (Vilas County, WI). Our primary study sites were located near Allequash Creek and Stevenson Creek. We collected samples of ground water, hyporheic-zone pore waters, and surface stream waters. Seasonal measurements were made of total Hg, MeHg, and constituents or parameters related to biogeochemical processes, including Fe, S (total S and sulfide), dissolved organic carbon (DOC), NH_4 and pH. Speciation of inorganic Hg(II) and MeHg was investigated by experimental and modeling approaches. Modeling involved equilibrium calculations based on reported stability constants for the respective mercury complexes, pH, and measured concentrations of important ligands – especially dissolved organic matter (DOM), and sulfide. In addition, association of MeHg and Hg(II) with both DOM and sulfide was probed by an experimental technique involving measurements of retention by an anion exchange resin.

Results and Discussion: Concentrations of total Hg and MeHg in streams exhibited considerable temporal variation. Highest concentrations were observed from late winter through spring and early summer, reaching over 4 ng/L for total Hg and 0.2 ng/L for MeHg. Overall, the spring melt period contributed high concentrations, loadings, and proportions of MeHg in the wetland streams.

Production of MeHg was indicated by high concentrations of MeHg in hyporheic zones, where favorable conditions for production of MeHg were also observed. Decreasing concentrations of sulfate and increasing concentrations of sulfide with depth were indicative of both sulfate reduction and the activity of sulfate-reducing bacteria (believed to be largely responsible for methylation of inorganic Hg(II) in reducing environments). Surface waters were the main source of sulfate to drive sulfate reduction in hyporheic zones, as evidenced by the high concentrations of sulfate in stream waters as compared to ground waters. Elevated concentrations of DOM, contributing to microbial activity in hyporheic zones, were attributed to diagenesis of plant material. Relationships between MeHg and Fe indicated the importance of hyporheic zones as a source of both Fe and MeHg to stream waters.

Speciation modeling predicted that HgS^0 was the dominant species of Hg(II) in sufidic (hyporheic) waters, while HgDOM complexes should be dominant in the absence of sulfide. In contrast, both $MeHgS^0$ and MeHg-DOM complexes were predicted to be important in the presence of sulfide. However, experimental measurements indicated HgDOM complexes were predominant in both sulfidic and non-sulfidic waters. These results raise important questions about factors controlling the bioavailability of Hg(II) for methylation.

Conclusions/Implications/Recommendations: Hyporheic zones are important sites for MeHg production and transport to surface waters. High DOC concentrations combined with sulfate (introduced mainly from surface water) promote the activity of sulfate-reducing bacteria (SRB). Inorganic Hg(II), partly from groundwater, is converted to MeHg, apparently by SRB, and transported into surface waters. Speciation modeling indicates that HgS^0 is dominant in these sulfidic waters. HgS^0 should facilitate methylation because neutral species of Hg(II) are presumed to be more available for uptake by SRB. However, experimental data indicate Hg(II) is bound mainly by dissolved organic matter (DOM) in sulfidic waters, indicating bioavailability of Hg(II) to SRB may be impeded by binding to DOM. Further investigations should explore the factors and conditions controlling methylation rates in hyporheic zones to facilitate new practices in wetland management that might limit MeHg production.

Related Publications and Presentations:

Chadwick, S.P., C.L. Babiarz, J.P. Hurley, D.E. Armstrong. 2006. Evaluation of the Role of Dissolved Organic Matter in the Speciation of Mercury and Methylmercury in a Lacustrine Watershed Using Diethylaminoethyl Resin. Abstracts, Conference on Mercury as a Global Pollutant, Madison, WI.

Kerr, S., J. Overdier, and M. Shafer. 2004. Hyporheic processes regulating trace element cycling under differing hydrologic and biogeochemical regimes. Abstract. – Paper presented at the American Geophysical Union Fall 2004 meeting. San Francisco, December 13-17 2004.

Shafer, M., S. Kerr, J. Overdier, and D.E. Armstrong. 2005. Trace metal cycling within riparian wetland and hyporheic regions of a northern temperate stream catchment. Abstract – Paper presented at the American Geophysical Union Fall 2005 meeting. San Francisco, December 5-8 2005.

Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005. Contrasts in trace metal cycling within oxic and anoxic flowpaths of a northern temperate stream catchment. Abstract –American Society of Limnology & Oceanography 2005 Aquatic Sciences meeting. Salt Lake City, February 20-25.

Key Words: Mercury, methyl mercury, groundwater, hyporheic zones, stream waters.

Funding: UWS

INTRODUCTION

The accumulation of methyl mercury (MeHg), the most toxic form of Hg, in aquatic foodwebs is a major problem in freshwaters across the United States. Production of MeHg occurs through methylation of inorganic Hg(II) by bacteria in anoxic environments such as wetlands (Benoit et al., 1999; Hammerschmidt et al., 2004). Groundwater is partly responsible for movement of Hg(II) into these environments (Meyer, 2005; Stoor et al., 2006). Although information is emerging, the factors and mechanisms controlling MeHg production are not well understood. Our investigation was designed to provide information on the importance of hyporheic zones as a site for MeHg formation and transport into surface waters. We also investigated the forms of inorganic Hg(II) and MeHg in the hyporheic zones, and examined the influence of speciation on both Hg(II) bioavailability for methylation, and MeHg transport into surface waters and foodwebs.

Our investigation focused on the cycling of mercury in wetlands within the Trout Lake Basin in Vilas County, Wisconsin. The three main objectives were:

1. To characterize the levels of total Hg and MeHg carried in stream waters flowing through the wetlands;
2. To characterize hyporheic zones within these wetlands regarding (a) concentrations of aqueous total Hg and MeHg, (b) factors influencing MeHg levels, and (c) the importance of hyporheic zones in controlling MeHg in stream waters;
3. To probe the forms of inorganic Hg(II) and MeHg in hyporheic zone waters and examine the implications of speciation on transport and on the bioavailability of Hg(II) for methylation.

PROCEDURES AND METHODS

Study Sites: This investigation was conducted in the Trout Lake Basin (Vilas County, WI) to co-locate with the UW-Madison Long Term Ecosystem Research (LTER) program and the U.S. Geological Survey (USGS) Water, Energy, and Biogeochemical Budgets (WEBB) program. This investigation benefited from collaboration with scientists in each program and from the sampling infrastructure originally installed by the USGS.

Our primary study sites were two areas within the Allequash Creek watershed (Fig. 1). The *Upper Springs* are the headwaters for Allequash Creek and consists of several groundwater point discharges at the base of a dominating hillslope. The terrain is forested by a mixture of deciduous and coniferous species. The *Middle Wetland* is defined by a three-meter wide riparian zone located on both sides of the main channel. A culvert at the discharge of the wetland restricts and slows the flow of the creek in this area. The hillslopes are similar to those in the Upper Springs, although the steepness of the terrain is greater at the Middle Wetland.
Our secondary study sites were *North Creek* and *Stevenson Creek,* two sub-watersheds within the Trout Lake Basin. These areas are are generally lacking in relief, and are overgrown with tussocks sedge, leatherleaf, black spruce, sphagnum moss, and tag alders.

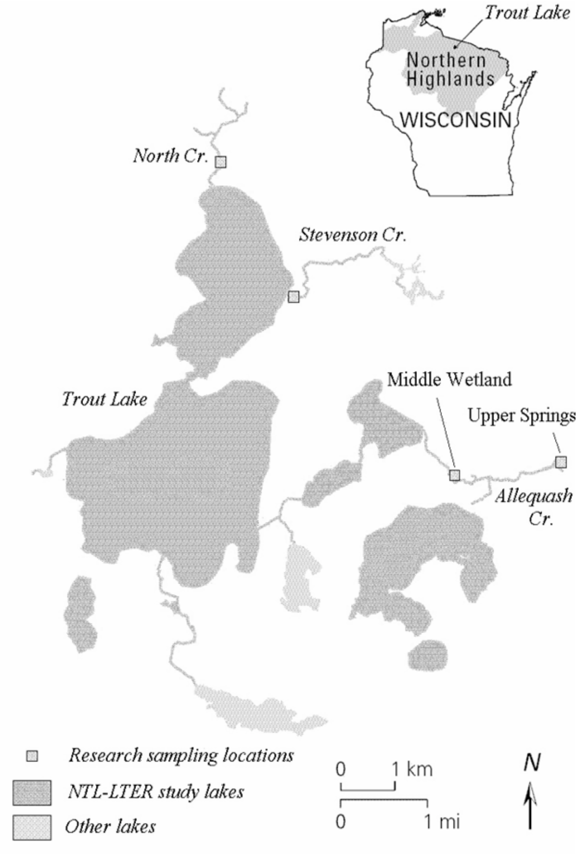

Figure 1: *Sampling locations within the greater Trout Lake Watershed in Vilas County, WI (From Meyer, 2005, as modified from USGS, 2000)*

Methods: Groundwater samples were collected from wells and piezometers, previously installed by the USGS WEBB project. Hyporheic pore-water samples were collected using a differential in-situ porewater sampler (DIPS) modeled after the MINIPOINT sampler of Duff et al. (1998). The sampler operated at 1.0 and 2.0 mL min^{-1} - a rate well below the observed discharge of upwelling waters at piezometers nests (~10.7 mL min^{-1}).

Surface waters were collected using a peristaltic pump to draw water through an all-Teflon sampling line and weight submerged under the water surface. Surface water samples obtained between March 2004 and November 2005 were collected by collaborators at the USGS in Middleton, WI and analyzed for total and methyl mercury in their laboratories.

At the UW Environmental Chemistry Program, total Hg and MeHg were analyzed using established procedures based on US EPA Methods 1630 and 1631 (Babiarz et al., 1998). Hyporheic waters were also analyzed for pH, Fe, S, sulfide, NH_4, and DOC.

Speciation of MeHg and inorganic Hg(II) was calculated based on the concentrations of important ligands (especially sulfide and DOC) and their binding constants using the equilibrium speciation code MINEQL+ (Schecher and McAvoy, 1998).

RESULTS AND DISCUSSION

Data Sets

Stream waters were collected monthly from Allequash Creek and Stevenson Creek from April 2004 through April 2005 and analyzed for total and filterable Hg and MeHg at the USGS Mercury Laboratory in Middleton, WI. Some of these data are summarized here. Other constituents, including dissolved organic carbon, were measured in our laboratories.

Hyporheic zone waters were collected from Allequash Creek and Stevenson Creek from March 2003 through June 2004 and analyzed for total Hg and MeHg in filtered samples at the UW-

Madison Mercury Laboratory. Some of these data are summarized here and are also reported by Meyer (2005) and Armstrong et al. (2005). This data set was extended by collecting additional hyporheic zone samples in July, August, and October 2005.

In conjunction with a concurrent research project (Shafer and Armstrong, 2003), samples from hyporheic zones and rivulets were collected by Sara Kerr and Martin Shafer (UW-Madison, Environmental Chemistry Program) from June 2004 through September 2005 for characterization of biogeochemical processes influencing trace metal levels and transport in the hyporheic zone (Kerr et al., 2004; Shafer et al., 2005a, b). Some of these data, including selected profiles of sulfate, sulfide, iron, and DOC, are included in this report.

Mercury in Stream Waters

Concentrations of THg and MeHg in streams exhibited considerable temporal variation as shown by the example from Allequash Creek (Fig. 2). In general, highest concentrations were observed in the late winter through spring and early summer, reaching over 4 ng/L for total Hg and 0.2 ng/L for MeHg. Similarly, the amounts of total Hg and MeHg carried by the stream were highest from January to May due to a combination of high concentrations and stream flow. The proportion of MeHg varied from approximately 5 to 45 %, with highest values occurring in the late winter-spring period. Overall, the spring melt contributed high concentrations, loadings, and proportions of MeHg in the wetland streams.

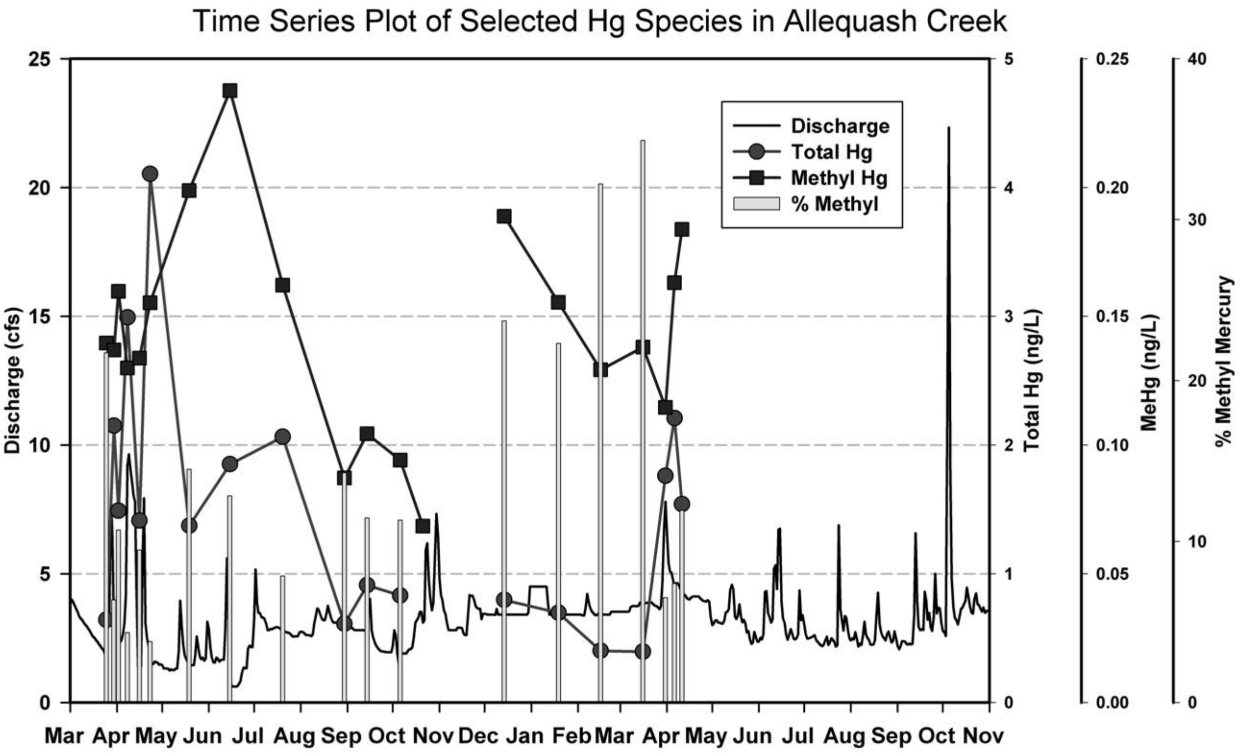

Figure 2. *Total and methyl mercury in Allequash Creek in 2005 (Shafer et al, 2005).*

Conditions in Hyporheic Zones

The wetland hyporheic zones showed favorable conditions for production of MeHg (see example in Fig 3). The decreasing concentrations of sulfate and increasing concentrations of sulfide with depth indicate sulfate reduction and the activity of sulfate-reducing bacteria. These bacteria are believed to be largely responsible for methylation of inorganic Hg(II) in reducing environments (Benoit et al., 1999; Hammerschmidt et al., 2004). Surface waters or recently infiltrated meteoric waters are the main source of sulfate to hyporheic zones, as evidenced by the high concentrations of sulfate (30 to 70 µM) in stream waters as compared to old ground waters (~ 1 µM). Even though groundwater flows upward (discharge) at the Allequash Creek site, mixing of ground water and surface water within the hyporheic zone is apparently sufficient to provide significant amounts of sulfate over the upper 15 cm. DOC concentrations in the hyporheic zones are higher than either surface water or ground water (Figure 3), indicating diagenesis of plant residues and/or peat. Profiles of NH_4 and Fe illustrate the influences of the hydrologic contrasts between the Allequash and Stevenson hyporheic zones (data not shown). At Stevenson (down flow), concentrations increased with depth, apparently reflecting production of NH_4 by organic matter diagensis and the enhancement of aqueous Fe by dissolution of Fe oxides. At the Allequash (up flow) site, concentrations exhibited subsurface maxima, apparently due to biogeochemical interactions influenced by the mixing of oxic surface water with oxygen-depleted ground water, producing a sub-oxic boundary created by bacterial oxidation of organic matter.

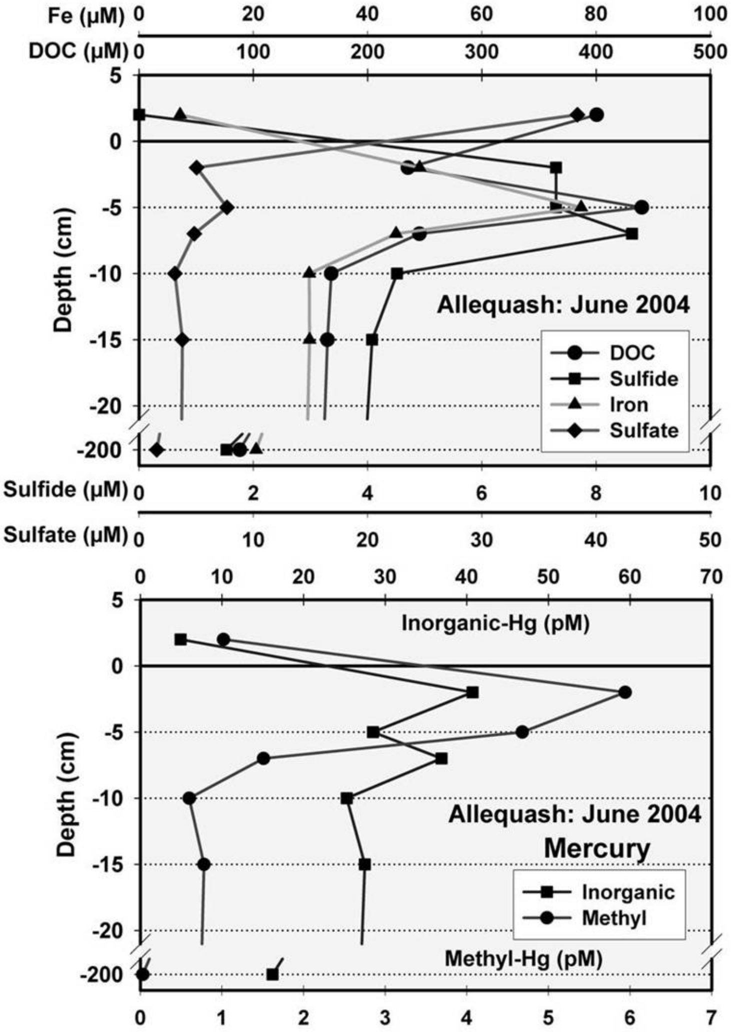

Figure 3. *Example profiles illustrating relation of total Hg and MeHg concentrations to biogeochemical processes in the hyporheic zone near Allequash Creek.*

Mercury in Ground Water and Hyporheic Zone Waters

Relatively high concentrations of MeHg were found in the hyporheic zones (Fig. 3, 4), indicating their importance for MeHg production. Concentrations varied considerably with site, depth, and time, likely reflecting differences in methylation – demethylation rates and partitioning between the aqueous and solid phases. MeHg concentrations peaked in the 0-5 cm zone of active sulfate reduction, as indicated by the declining sulfate and increasing sulfide concentration in this region (Fig. 3). Concentrations of MeHg in the hyporheic zones (0.2 to 1.2 ng/L) were higher than in either ground water (often < 0.03 ng/L, detection limit) or suface water (0.05 to 0.5 ng/L). This indicates that ground water discharge is not important as a direct source of MeHg to the hyporheic zone. Together, the data indicate that MeHg is largely produced within the hyporheic zone, and that the hyporheic zone is a source of MeHg to stream waters. In contrast, both ground waters and surface waters may be sources of Hg(II) to the hyporheic zone as shown by the overlapping concentrations observed in these waters. Concentration ranges observed were approximately 0.3 to 10, 0.5 to 6, and 1 to 10 ng/L for ground water, stream water, and hyporheic water, respectively.

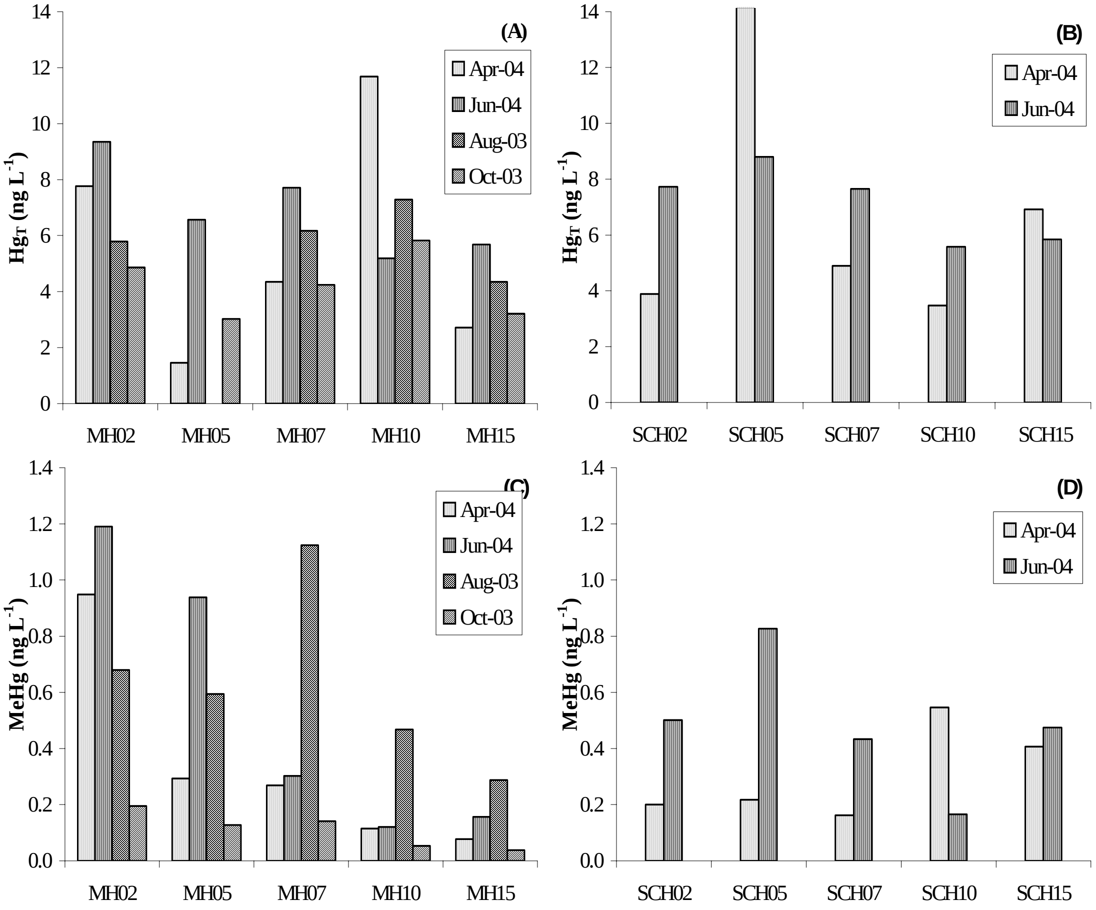

Figure 4: Concentrations of HgT and MeHg in hyporheic porewaters for Allequash Creek Middle Wetland (MH) and Stevenson Creek (SCH). The numbers on the x-axis are depth below the sediment surface (cm). (Meyer, 2005)

DOC likely plays a major role the transport of inorganic Hg(II) from ground water and surface water into the hyporheic zone where production of MeHg occurs. As observed in other systems, total Hg concentration was related to DOC (data not shown). Similarly, transport of MeHg from the hyporheic zone into surface waters is likely linked to transport of DOC. Evidence that the hyporheic zone is a source of MeHg to stream waters is observed in the relation of MeHg concentrations to Fe (Fig. 5). Concentrations of Fe are elevated in the anoxic hyporheic zone, apparently through reduction of solid-phase Fe(III) hydrous oxides. This leads to concurrent transport of Fe(II) and MeHg from the hyporheic zone into the stream.

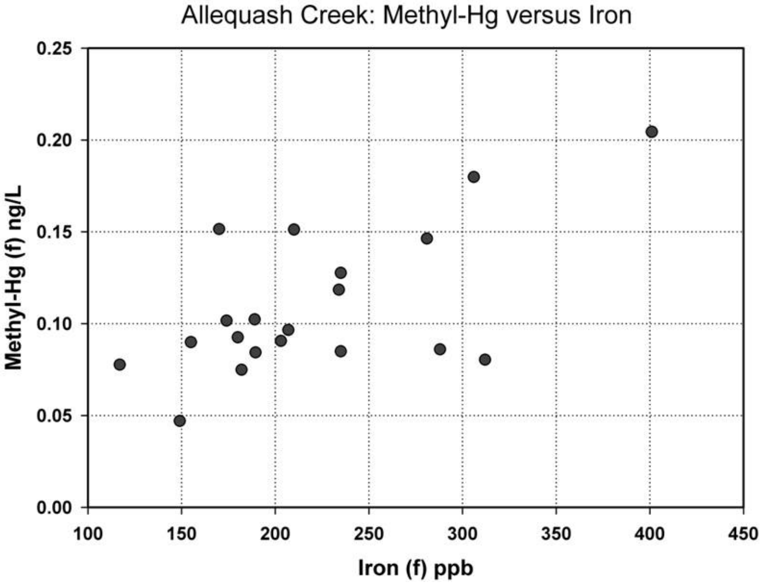

Figure 5. *Relation between MeHg and Fe indicates hyporheic zone is a source of MeHg to Allequash Creek (Shafer et al., 2005)*

Mercury Speciation

The production of MeHg is dependent in part on the bioavailability of Hg(II) to sulfate-reducing bacteria. The bioavailable species of Hg(II) is believed to be a neutral sulfide complex (Benoit et al., 1999). However, Hg(II) bound to DOC may not be bioavailable. Thus, bioavailability may be linked to concentrations of sulfide and DOC in the hyporheic zone. We investigated speciation through chemical modeling and experimental approaches. Modeling involved speciation calculations using reported binding constants and typical hyporheic zone conditions. These conditions included concentrations of sulfide, DOC, Fe(II), and pH as shown in Fig. 3. In addition, we used a anion exchange resin technique to experimentally probe the association of both Hg(II) and MeHg with sulfide and with DOM in anoxic waters comparable to those in hyporheic zones.

Speciation Modeling: Speciation calculations were performed using the chemical equilibrium modeling program MINEQL+ (Schecher and McAvoy, 1998). Modeling of the binding of Hg(II) by DOM was based on the best fit values for conditional equilibrium constants and a binding-site density of $5x10^{-9}$ sites per mg of DOC. Both the equilibrium constants and binding-site density were developed by Haitzer et al. (2003) in their investigation of seven DOM isolates. The equilibrium expressions obtained for deprotonation of the bidentate binding site and for association of Hg^{2+} with the fully deprotonated binding site are shown below. A log K for formation of the species HgS^0 was derived by Benoit et al. (1999).

$$H_2DOM \leftrightarrow HDOM^- + H^+ \quad \log K_1 = -6.3$$

$$HDOM^- \leftrightarrow DOM^{2-} + H^+ \quad \log K_2 = -10.3 \qquad Hg^{2+} + HS^- \leftrightarrow HgS^0 + H^+ \quad \log K = 26.5$$

$$Hg^{2+} + DOM^{2-} \leftrightarrow HgDOM \quad \log K = 28.7$$

Binding constants for the other Hg(II) sulfide species and for complexes with Cl^- and OH^- were used as reported in the MINEQL+ thermodynamic database. For equilibrium calculations, reactions with Hg^{2+} were converted to corresponding reactions with $Hg(OH)_2$, the Hg(II) "component" in MINEQL+ (see APPENDIX B for details).

MeHg complexation by sulfide was based on values from Stumm and Morgan (1996).

$$CH_3Hg^+ + S^{2=} \leftrightarrow CH_3HgS^- \quad \log K = 21.0$$

$$2CH_3Hg^+ + S^{2=} \leftrightarrow (CH_3Hg)_2S \quad \log K = 16.34$$

MeHg association with DOM was modeled based on the Amirbahman et al. (2002) investigation of binding of MeHg by humic acids. Values reported for the dominant DOM site, $RS(2)^-$, OH^-, and Cl^- are as follows:

$$MeHg^+ + H_2O \leftrightarrow MeHgOH + H^+ \quad \log K = -4.63$$

$$MeHg^+ + Cl^- \leftrightarrow MeHgCl \quad \log K = 5.22$$

$$H^+ + RS(2)^- \leftrightarrow RS(2)H \quad \log K = 7.0$$

$$MeHg^+ + RS(2)^- \leftrightarrow MeHg - RS(2) \quad \log K = 14.74$$

The corresponding equilibrium equations in MINEQL+ format using $MeHg^+$ as the component are shown in APPENDIX B:

Speciation Results: Modeling predicted dominance of Hg(II) sulfide complexes under "typical" hyporheic zone conditions (pH = 6.5, total S(-II) = 1 x10^{-6} M, Fe(II) = 1 x 10^{-4} M, Cl^- = 2 x 10^{-6} M, DOC = 6 mg/L; see Fig. 6). The dominant species was HgS^0 over pH range of 4 to 9 at this total sulfide concentration. Speciation is also influenced by the sulfide concentration. Dominance of the $HgHS_2^-$ negatively-charged species is important above total sulfide concentrations of 2 x 10^{-5} M, well above concentrations observed in hyporheic zone waters (see Appendix B, Fig. B-1). In the absence of sulfide, predicted speciation of Hg(II) is dominated by DOM, and the dominant species is HgDOM (Appendix B, Fig. B-2). The HgDOM species becomes dominant when the DOM site concentration exceeds 0.9 x 10^{-12} molar, i.e., when the DOM site concentration is about one-third of the total Hg(II) concentration. Thus, even though Hg(II) binds strongly to DOM, sulfide complexes will dominate even if concentrations of sulfide are low (i.e., when total sulfide concentration approaches the total Hg(II) concentration). Based on the formation equations used, modeling predicts that a DOM site concentration approximately 10^8 times higher than the HS^- concentration is required for equal concentrations of the HgDOM and HgS^0 species at pH = 6.5. When sulfide is absent, HgDOM complexes are predicted to dominate when the DOM site concentration approaches the total Hg(II) concentration (Fig. B-2).

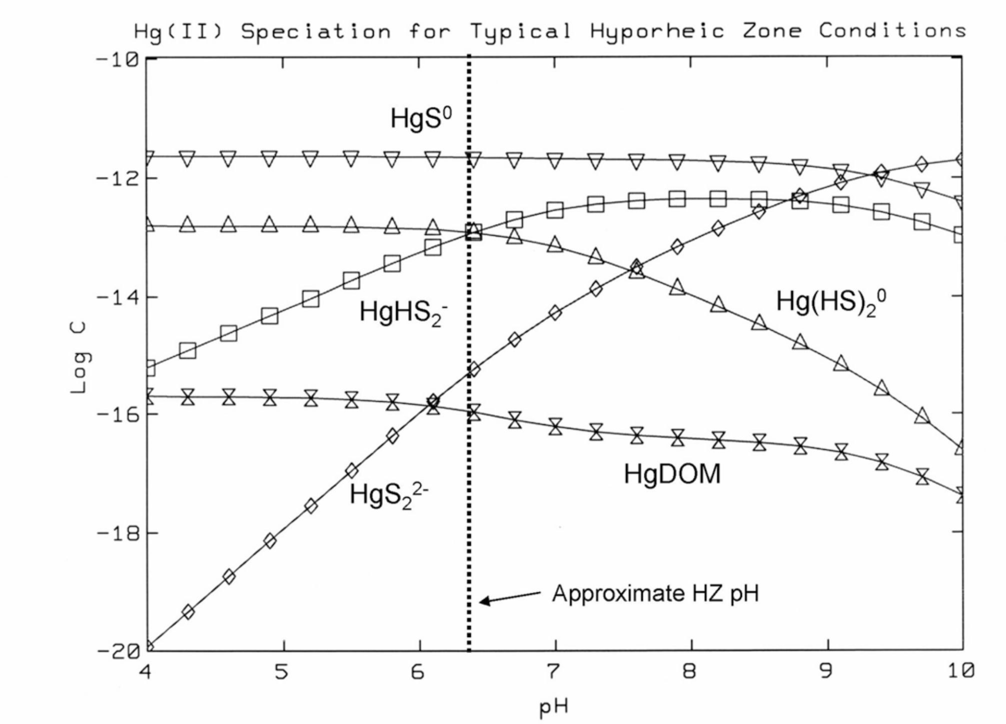

Figure 6. Modeled speciation of Hg(II) when S(-II) = 1E-6M and DOC = 6 mg/L, conditions typical of hyporheic zones.

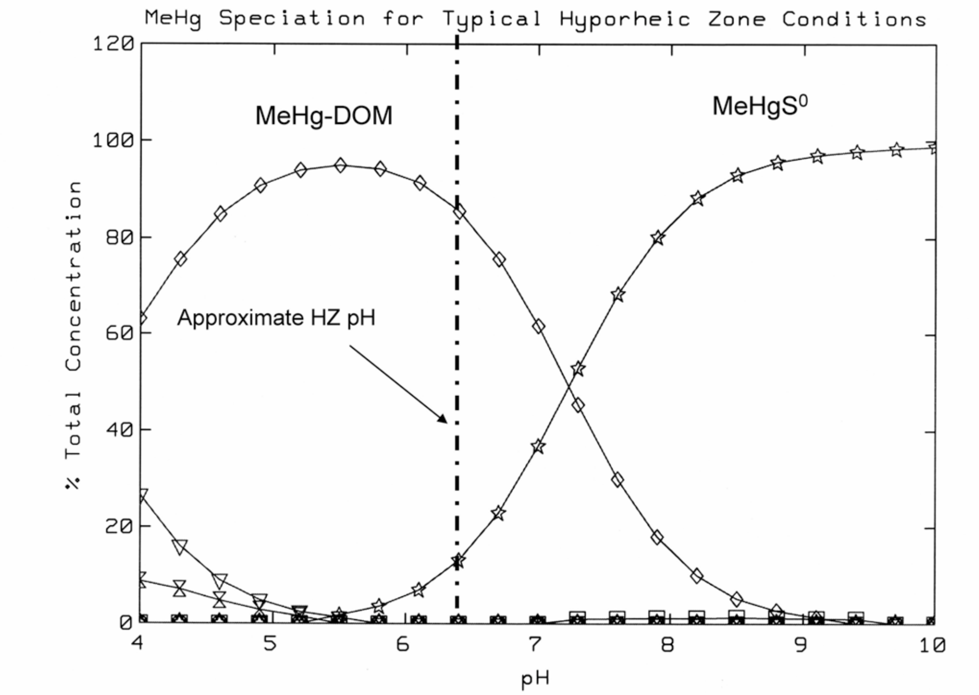

Figure 7. Modeled speciation of MeHg when total S(-II) = 1E-6 M and DOC = 6 mg/L

In contrast to Hg(II), DOM complexes of MeHg are predicted to be important in the presence of sulfide (Fig. 7.) For typical hyporheic zone conditions, the dominant species is a MeHg-DOM complex (designated MeHgRSb), but MeHgS still represents about 20% of the total aqueous MeHg. Species dominance is influenced by total S(-II) concentration. At pH = 6.5, sulfide and DOM complexes of MeHg are equally important at approximately 5 x 10^{-6} molar S(-II). At higher sulfide concentrations, MeHgS is the predicted dominant species (Appendix B, Fig. B-3).

While modeling indicated that neutral sulfide species of Hg(II) should be dominant in sulfidic pore waters, experimental measurements indicated DOM complexes of Hg(II) may be important in both oxic and anoxic waters (Table 1). We used a DEAE resin techniques to probe Hg speciation (Chadwick, 2006). The resin is expected to retain anionic species, including Hg(II) and MeHg complexed by DOM, while allowing neutral species to elute. The expected behavior of the resin was verified using synthetic solutions; anionic species were retained, and neutral species passed through the resin columns (Table 1). In oxic surface waters, the Hg was largely retained by the resin, consistent with binding of Hg to DOM. In anoxic waters the Hg was also retained by the resin, indicating Hg-DOM complexes remain dominant, even though modeling predicted dominance of neutral sulfide complexes of Hg(II). The smaller amounts of Hg that passed through the column could be either Hg(II) or MeHg bound in neutral sulfide complexes. The reasons for the apparent differences between modeled and measured speciation are uncertain, but modeled speciation is strongly influenced by the assumption of equilibrium and the accuracy of stability constants for Hg binding to sulfide.

Table 1. *Fractionation of Hg(II) and MeHg complexes based on net charge using a DEAE resin technique. Negative complexes are retained by the resin column; neutral complexes are eluted (from Chadwick, 2006). Equilibrium calculations indicate Hg(II) speciation should be dominated by neutral sulfide complexes in anoxic waters while experimental results indicate Hg(II) is dominated by negative (DOM) complexes in both oxic and anoxic waters. DL is the analytical detection limit.*

Description	Retained	Eluted
Synthetic Waters		
Neutral chloride complexes		
Hg(II)	< DL	> 95 %
MeHg	< DL	> 98 %
Neutral sulfide complexes of Hg(II)	< DL	> 94%
Anionic chloride complexes of Hg(II)	102 %	< DL
Natural Waters (Lake 658, West Basin; 8-18-03)		
Anoxic water; S(-II) = 8.3 nM	83 %	17 %
Anoxic water; S(-II) = 8.5 nM	80 %	20 %
Oxic water, 2 m	82 %	18 %
Oxic water, 5 m	85 %	15 %

CONCLUSIONS AND RECOMMENDATIONS

Hyporheic zones are important sites for MeHg production and transport to surface waters. High DOC concentrations combined with sulfate (introduced mainly from surface water) promote the activity of sulfate-reducing bacteria (SRB). Derived partly from groundwater, inorganic Hg(II) is converted to MeHg and transported into surface waters. Speciation modeling indicates that HgS^0 is dominant in these sulfidic waters, and that should facilitate methylation because neutral species of Hg(II) are presumed to be more available for uptake by SRB. However, experimental data indicates Hg(II) is bound mainly by dissolved organic matter (DOM), indicating bioavailability of Hg(II) to SRB may be impeded by binding to DOM. Further investigations should explore the factors and conditions controlling methylation rates in hyporheic zones so that practices that might limit MeHg production can be incorporated into wetland management.

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Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005a. Trace metal cycling within riparian wetland and hyporheic regions of a northern temperate stream catchment. Abstract – Paper presented at the American Geophysical Union Fall 2005 meeting. San Francisco, December 5-8 2005.

Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005b. Contrasts in trace metal cycling within oxic and anoxic flowpaths of a northern temperate stream catchment. Abstract –American Society of Limnology & Oceanography 2005 Aquatic Sciences meeting. Salt Lake City, February 20-25.

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APPENDIX A: Awards, Publications, Reports, Patents, and Presentations

Kerr, S., J. Overdier, and M. Shafer. 2004. Hyporheic processes regulating trace element cycling under differing hydrologic and biogeochemical regimes. Abstract – Paper presented at the American Geophysical Union Fall 2004 meeting. San Francisco, December 13-17 2004.

Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005a. Trace metal cycling within riparian wetland and hyporheic regions of a northern temperate stream catchment. Abstract – Paper presented at the American Geophysical Union Fall 2005 meeting. San Francisco, December 5-8 2005.

Shafer, M., S. Kerr, J. Overdier, and D. Armstrong. 2005b. Contrasts in trace metal cycling within oxic and anoxic flowpaths of a northern temperate stream catchment. Abstract –American Society of Limnology & Oceanography 2005 Aquatic Sciences meeting. Salt Lake City, February 20-25.

APPENDIX B: Supplemental Information

Speciation Calculations.

Speciation calculations were performed using the chemical equilibrium model MINEQL+ (Schecher and McAvoy, 1998). Modeling of the binding of Hg(II) by DOM was based on the best fit values for conditional equilibrium constants and binding site density ($5\text{x}10^{-9}$ sites per mg of DOC) developed by Haitzer et al. (2003) in their investigation of seven DOM isolates. The equilibrium expressions obtained for deprotonation of the bidentate binding site and for association of Hg^{2+} with the fully deprotonated binding site are as follows:

$$H_2DOM \leftrightarrow HDOM^- + H^+ \quad \log K_1 = -6.3$$
$$HDOM^- \leftrightarrow DOM^{2-} + H^+ \quad \log K_2 = -10.3$$
$$Hg^{2+} + DOM^{2-} \leftrightarrow HgDOM \quad \log K = 28.7$$

For equilibrium calculations, reactions with Hg^{2+} were converted to corresponding reactions with $Hg(OH)_2$, the Hg(II) “component” in MINEQL+, e.g.,

$$Hg^{2+} + DOM^{2-} \leftrightarrow HgDOM \quad \log K = 28.7$$
$$Hg(OH)_2 \leftrightarrow Hg^{2+} + 2OH^- \quad \log K = -21.2$$
$$2OH^- + 2H^+ \leftrightarrow 2H_2O \quad \log K = 28.0$$
$$\therefore Hg(OH)_2 + DOM^{2-} + 2H^+ \leftrightarrow HgDOM + 2H_2O \quad \log K = 35.5$$

A log K for formation of the species HgS^0 was derived by Benoit et al. (1999).

$$Hg^{2+} + HS^- \leftrightarrow HgS^0 + H^+ \quad \log K = 26.5$$

Binding constants for the other Hg(II) sulfide species and for complexes with Cl^- and OH^- were used as reported in the MINEQL+ thermodynamic data base. In MINEQL+ format, the following reactions were used for calculation of Hg(II) binding to DOM and S(-II):

$$[HDOM^-] = [H^+][DOM^{2-}] \cdot 10^{10.3}$$
$$[H_2DOM] = [H^+]^2[DOM] \cdot 10^{16.6}$$
$$[HgDOM] = [Hg(OH)_2][H_2O]^{-2}[H^+]^2[DOM^{2-}]$$
$$[H_2S_{(aq)}] = [H^+][HS^-] \cdot 10^{7.02}$$
$$[S^{2-}] = [H^+]^{-1}[HS^-] \cdot 10^{-17.3}$$
$$[Hg(HS)_2^0] = [H_2O]^{-2}[H^+]^2[Hg(OH)_2]^1[HS^-]^2 \cdot 10^{44.51}$$
$$[HgHS_2^-] = [H_2O]^{-2}[H^+]^1[Hg(OH)_2]^1[HS^-]^2 \cdot 10^{38.12}$$
$$[HgHS_2^{2-}] = [H_2O]^{-2}[H^+]^0[Hg(OH)_2]^1[HS^-]^2 \cdot 10^{29.41}$$
$$[HgS^0] = [H_2O]^{-2}[H^+]^1[Hg(OH)_2]^1[HS^-]^1 \cdot 10^{32.69}$$

Reactions of for complexation of MeHg with sulfide are reported by Stumm and Morgan (1996):

$$CH_3Hg^+ + S^{2=} \leftrightarrow CH_3HgS^- \quad \log K = 21.0$$
$$2CH_3Hg^+ + S^{2=} \leftrightarrow (CH_3Hg)_2S \quad \log K = 16.34$$

Amirbahman et al. (2002) investigated the binding of MeHg by humic acids. Through modeling of experimental data, they obtained three binding sites, designated RS(1)$^-$, RS(2)$^-$, and RS(3)$^-$. Reactions for formation of OH$^-$ and Cl$^-$ complexes for deprotonation of the DOM binding sites were modeled as:

$$MeHg^+ + H_2O \leftrightarrow MeHgOH + H^+ \quad \log K = -4.63$$
$$MeHg^+ + Cl^- \leftrightarrow MeHgCl \quad \log K = 5.22$$
$$H^+ + RS(1)^- \leftrightarrow RS(1)H \quad \log K = 4.0$$
$$H^+ + RS(2)^- \leftrightarrow RS(2)H \quad \log K = 7.0$$
$$H^+ + RS(3)^- \leftrightarrow RS(3)H \quad \log K = 10.0$$

Binding constants varied somewhat among the different humic acids investigated. For Suwanee River humic acids, the binding to the DOM sites was modeled as:

$$MeHg^+ + RS(1)^- \leftrightarrow MeHg - RS(1) \quad \log K = 10.39$$
$$MeHg^+ + RS(2)^- \leftrightarrow MeHg - RS(2) \quad \log K = 14.74$$
$$MeHg^+ + RS(3)^- \leftrightarrow MeHg - RS(3) \quad \log K = 14.84$$

Site densities (nmol/mg DOC) for this humic acid were estimated as 0.15, 0.24, and 1.44 for RS(1)$^-$. RS(2)$^-$, and RS(3)$^-$, respectively.

The corresponding equilibrium equations in MINEQL+ format using MeHg$^+$ as the component are:

$$[MeHgOH] = [MeHg^+][H_2O]^1[H^+]^{-1} \cdot 10^{-4.63}$$
$$[MeHgCl] = [MeHg^+][Cl^-] \cdot 10^{5.22}$$
$$[RSaH] = [H^+][RSa^-] \cdot 10^{4.0}$$
$$[RSbH] = [H^+][RSb^-] \cdot 10^{7.0}$$
$$[RScH] = [H^+][RSc^-] \cdot 10^{10.0}$$
$$[MeHg - RSa] = [MeHg^+][RSa^-] \cdot 10^{10.39}$$
$$[MeHg - RSb] = [MeHg^+][RSb^-] \cdot 10^{14.74}$$
$$[MeHg - RSc] = [MeHg^+][RSc^-] \cdot 10^{14.84}$$

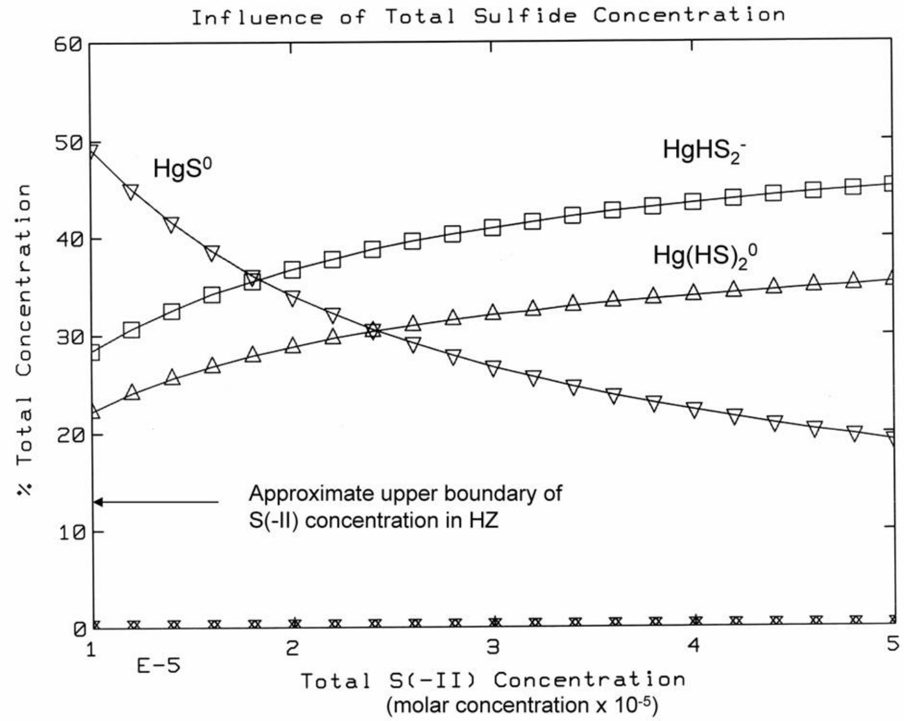


Figure B-1. Modeled influence of sulfide concentration on speciation of Hg(II); pH = 6.5 and DOC = 6 mg/L

2: Hg(HS)2 (△ 2: HgHS2-1 □ 2: HgS2-2 ◇ 2: DOMHg ⧖ 2: HgS(aq) ▽

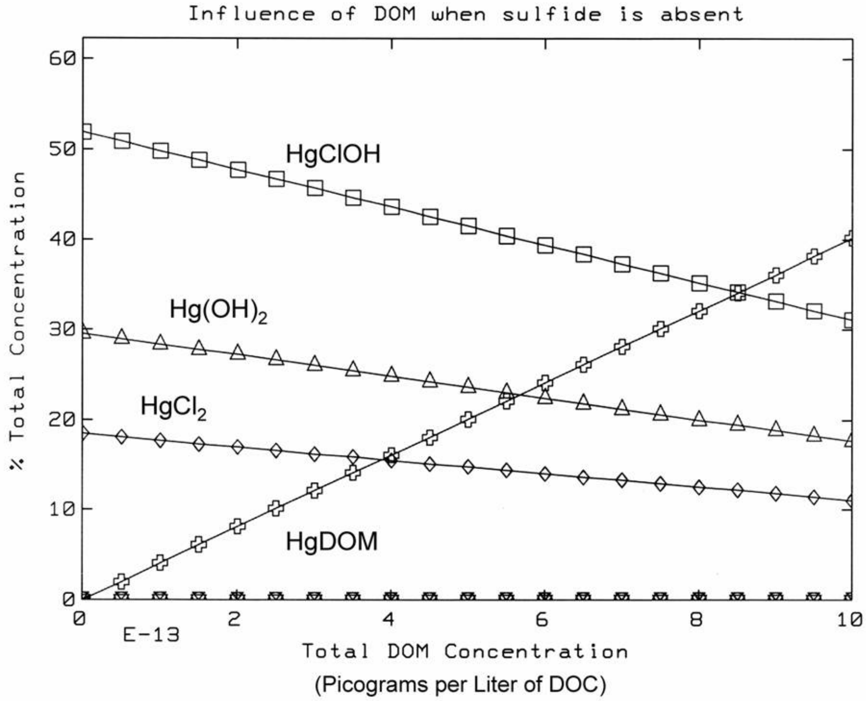
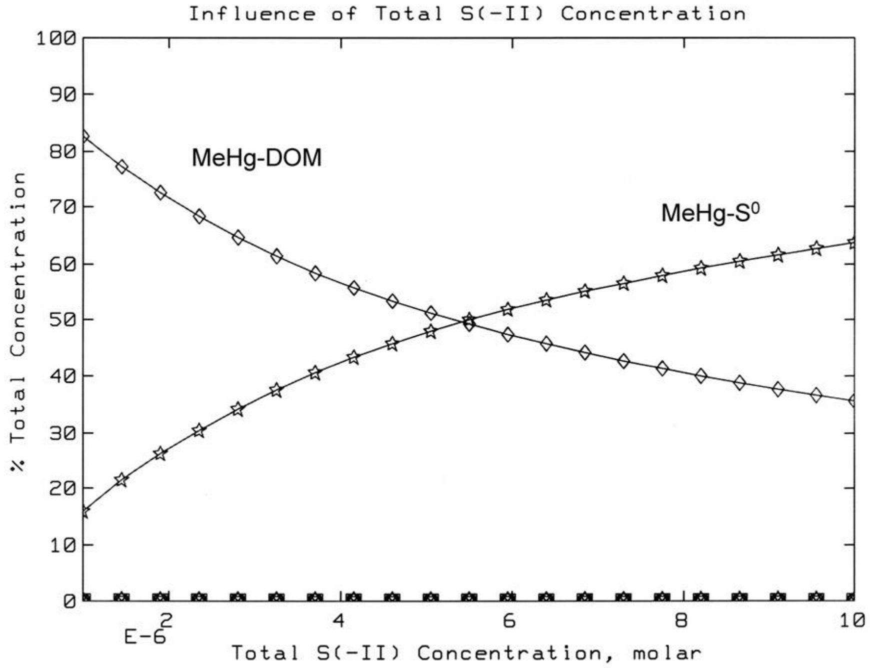


Figure B-2. Influence of DOM concentration on Hg(II) speciation when sulfide is absent and pH = 6.5

1: Hg(OH)2 △ 2: HgClOH (a □ 2: HgCl2 (aq ◇ 2: HgHCO3+ ⧖ 2: HgCO3 (aq ▽
2: HgOH+ ○ 2: DOMHg ✚



(molar concentration times 10^{-6})

Figure B-3. Influence of sulfide concentration on MeHg speciation at pH = 6.5

1: MeHg △ 2: MeHgRSc □ 2: MeHgRSb ◇ 2: MeHgRSa ⧖ 2: MeHgCl ▽
2: MeHgOH ○ 2: (MeHg)2S ✚ 2: MeHgS ☆

Application of LSQR to Calibration of a Regional MODFLOW Model: Trout Lake Basin, Wisconsin

Basic Information

Title:	Application of LSQR to Calibration of a Regional MODFLOW Model: Trout Lake Basin, Wisconsin
Project Number:	2006WI189O
Start Date:	7/1/2006
End Date:	6/30/2007
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Hydrogeochemistry, None
Descriptors:	groundwater, modeling
Principal Investigators:	Mary Anderson

Publication

1. Muffels, C., M. Tonkin, H. Zhang, M. Anderson, T. Clemo. 2006. Application of LSQR to Calibration of a MODFLOW Model: A Synthetic Study. In, Managing Ground-Water Systems, International Ground Water Modeling Center, Colorado School of Mines Golden, Colorado Pages 283-287

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Mary Anderson
Submitted: 5/24/2007

Project Title

WR06R003: Application of LSQR to Calibration of a Regional MODFLOW Model: Trout Lake Basin, Wisconsin

Project Investigators

Mary Anderson, University of Wisconsin-Madison
Haiijang Zhang, University of Wisconsin-Madison

Progress Statement

Our research addresses the need for new, improved calibration methods for predictive models. We focus on groundwater flow models and show how a technique known as LSQR, a matrix-equation solution technique, can be used to estimate parameters in a complex groundwater flow model of a system in northern Wisconsin. LSQR has been used to solve problems in geophysics; it is a powerful technique because it is able to solve inverse problems with many unknown parameters. In our research, LSQR was first used to solve a relatively simple synthetic linear groundwater model. Results from LSQR compared favorably with other inverse solutions.

An initial attempt to use LSQR (within PEST) with regularization to calibrate a complex groundwater flow model of a field situation, the Trout Lake basin in northern Wisconsin, was only partly successful. The calibration with LSQR successfully reduced the objective function but the resulting parameter set was unacceptable because many of the parameters were driven to their upper bounds. The Trout Lake model was restructured with more layers and a more explicit representation of the geology and explicit representation of low-lying wetland areas in an attempt to constrain parameters. LSQR is currently being used to calibrate the re-structured model and results will be compared with results from other inverse solution methods.

Impacts

Description	Based on our initial successful testing of LSQR to solve inverse problems for groundwater flow, Dr. John Doherty, the developer of the well known and widely used parameter estimation code PEST, incorporated the LSQR method as a solution option in PEST. PEST can be downloaded free of charge. Hence, by using PEST, LSQR can be used for parameter estimation in other predictive groundwater models in Wisconsin and elsewhere.

Interactions

Description	We are interacting with: 1. Dr. Randy Hunt, USGS, Middleton, WI 2. Dr. John Doherty of Watermark Numerical Computing, Brisbane, Australia;

	3. Mr. Matt Tonkin, S.S. Papdopulos and Associates; 4. Prof. Tom Clemo, Boise State University
Event Date	

Journal Articles & Other Publications

Publication Type	Proceedings/Symposium
Title	Application of LSQR to Calibration of a MODFLOW Model: A Synthetic Study
Author(s)	Muffels, C., M. Tonkin, H. Zhang, M. Anderson, T. Clemo
Publication/Publisher	International Ground Water Modeling Center, Colorado School of Mines Golden, Colorado
Year Published	2006
Volume & Number	MODFLOW and More 2006, Managing Ground-Water Syste
Number of Pages	283-287
Description	Proceedings volume
Any Additional Citation Information	

Presentations & Public Appearances

Title	LSQR and Tikhonov Regularization in the Calibration of a Complex MODFLOW Model
Presenter(s)	Muffels, C., J. Doherty, M. Anderson, R. Hunt, T. Clemo, M. Tonkin
Presentation Type	Poster session
Event Name	Geological Society of America Annual Meeting
Event Location	Pennsylvania Convention Center, Philadelphia PA
Event Date	10/24/2006
Target Audience	Mixed
Audience Size	200
Description	

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Title	Incorporating PROPACK into PEST to Estimate the Model Resolution Matrix for Large Groundwater Flow Models.
Presenter(s)	Muffels, C., H. Zhang, J. Doherty, R. Hunt, M. Anderson, M. Tonkin
Presentation Type	Poster session
Event Name	American Geophysical Union Fall Meeting
Event Location	San Francisco
Event Date	12/12/2006
Target Audience	Mixed
Audience Size	200
Description	

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Title	Regularized Inversion of a Groundwater Flow Model of the Trout Lake Basin.

Presenter(s)	Muffels, C., R. Hunt, J. Doherty, M. Anderson
Presentation Type	Professional meeting
Event Name	American Water Resources Association-Wisconsin Section
Event Location	Wisconsin Dells
Event Date	3/1/2007
Target Audience	Mixed
Audience Size	150
Description	oral presentation

Students & Post-Docs Supported

Student Name	Christopher Muffels
Campus	University of Wisconsin-Madison
Advisor Name	Mary Anderson
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month	December
Graduation Year	2007
Department	Geology & Geophysics
Program	MS
Thesis Title	Application of LSQR to Calibration of a Regional MODFLOW Model: Trout Lake Basin, Wisconsin
Thesis Abstract	not yet available

Multi-Parameter, Remote Groundwater Monitoring with Referencing Using Crossed Optical Fiber Fluorescent Sensor Arrays

Basic Information

Title:	Multi-Parameter, Remote Groundwater Monitoring with Referencing Using Crossed Optical Fiber Fluorescent Sensor Arrays
Project Number:	2006WI190O
Start Date:	7/1/2006
End Date:	6/30/2008
Funding Source:	Other
Congressional District:	
Research Category:	Water Quality
Focus Category:	Groundwater, None, None
Descriptors:	remote monitoring, groundwater, sensor
Principal Investigators:	Peter Geissinger

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Jim Hurley
Submitted: 6/20/2007

Project Title

WR06R001: Multi-Parameter, Remote Groundwater Monitoring with Referencing Using Crossed Optical Fiber Fluorescent Sensor Arrays

Project Investigators

Peter Geissinger, University of Wisconsin-Milwaukee

Progress Statement

During this grant period, we constructed separate optical fiber sensor systems for pH and oxygen sensing. Both sensor systems incorporate our crossed-fiber sensing configuration.

For pH sensing the dye fluorescein was used; its fluorescence intensity changes with pH. As the measurement is based on intensity changes, an intensity reference is needed to account for intensity fluctuations due source intensity fluctuations, etc. In our scheme, this is readily accomplished: using appropriate optical filters, we detected on one end of the detection fiber the fluorescence of the sensor dye, on the other end light scattered into the detection fiber at the sensor region. The scattered light constitutes a viable reference as long as the fluorescence intensity is much less than the scattered light intensity. This referencing procedure greatly improved the accuracy of the measurement; however, we noticed that after a period of inactivity (~days), the quality of measurement fluctuated. The reason was that after a (partial) drying of the swellable polyethylene glycol cladding, which was attached to the fibers at the sensor region, the geometry of the fiber-fiber junction changed slightly, which changes the coupling strength of the fibers and thereby the intensity of the captured fluorescence. While in a groundwater or streamwater application, the sensor is most likely to be submerged continuously, which should eliminate the problem, we embarked on an alternative approach, which was based on using a hydrophobic fiber cladding; in order to allow transport of aqueous analytes through this medium, it was engineered to contain nanoscale and microscale channels using a strategy called nano/microsphere templating. This procedure offers high control of the pore size which can be used for size occlusion of larger interfering particles in real-world environments. Also, a superporous material created by this technique effectively increases the rate of diffusion of the analyte to the sensing area thus greatly reducing the response time of the sensor. A fiber-fiber junction cast with the material is much for rigid, which is important for applications in harsh environments. Finally, this procedure allows the use of a hydrophobic resin for sensing in an aqueous environment since water is allowed to flow the pores. We created such fiber sensor junctions and recorded the pH response repeatedly: every time the expected pH response was obtained. Initial estimates indicate that a pH resolution of better than 0.1 pH units may be obtained – in a remote and real-time measurement.

In these measurements, the sensor dye was dissolved in the analyte flow stream; in the next grant period we will develop scheme to attached the sensor dyes permanently to the cladding material in the sensor junction.

Oxygen measurements are based on the fluorescence quenching of a ruthenium complex embedded in a photo-polymerized hydrogel matrix made from poly (ethylene glycol) diacrylate, which is covalently attached to the surface-modified fiber core. Due to the fact that the hydrogel matrix is highly cross-linked, swelling is less critical. As the oxygen measurement is intensity-based

measurement, again an intensity reference is needed. In this case, we use a second sensor region located a few mm from the first one; the reference region contains a second dye which possesses an oxygen independent fluorescence intensity. Alternatively, we can determine the fluorescence lifetime changes of the ruthenium upon change of oxygen concentration (remotely, in real-time and spatially resolved); measurement of this quantity is intensity independent.
In the first step of development of this sensor it was tested in a gas phase environment for sensitivity, repeatability and reproducibility. Results showed that the fluorescence intensity decreased upon exposure to oxygen gas, indicating that the ruthenium complex was responsive to the presence of the oxygen gas; the sensor response was found to be regenerable by flushing it with nitrogen gas.

This sensor was also tested in aqueous environment. Upon immersion in water, a color change of the water was observed immediately due to leaching of the dye. As there is a distribution of local environments, some sensor molecules are encapsulated in the host matrix to a lesser degree than others. Thus, the initial washing releases those sensor dyes that are contained in more open pores of the hydrogel. It was estimated from lost-mass measurements that the remaining concentration of sensor dyes in the hydrogel is 25% less than the initial dye concentration. It is likely that not all of the remaining dye molecules will contribute to the sensor signal due to tight encapsulation. Fluorescence intensity measurements using a fresh hydrogel sample (containing sensor and reference dyes) over a two-hour period (while the sensor is submerged in water with nitrogen bubbling through the liquid) showed an intensity drop of ~25%. Again, this is attributed to leaching of the sensor dye and not to photoinduced decomposition as the ruthenium complex exhibits good photostability. During the subsequent period of 70 minutes, the (referenced) signal dropped further, but only by 3%.

Finally, the dependence of the referenced signal was monitored under variation of the dissolved oxygen concentration, which ranged from 0% to 100% oxygen in an oxygen/nitrogen mixture. Due to the preceding loss of sensor dye, the signal/noise ratio is low in spite of averaging of 2000 pulses; note, however, that in our experiments we probe only the volume between the two fibers in a fiber-fiber sensor junction, and that the sensor dye concentration in the subnanomolar range. We are currently working on chemical attachment of the sensor dye to the hydrogel matrix by modifying both the hydrogel matrix and the sensor dye; this will be one important focus for the next project period.

It also was found that the photoluminescence intensity of oxygen varies with temperature (as does the pH response of the fluorescein dye use for the pH measurements). To account for the temperature dependence we are including temperature-sensitive luminophore Kiton Red (KR) in polymer nanospheres comprised of polyacrylonitrile, which is oxygen impermeable; this sensor will be used in yet another sensor region close to the primary one. This will allow for correcting for the temperature dependence of the oxygen sensor. Note that it is a virtue of our crossed-fiber sensing architecture that additional sensor regions are easily added for various referencing and correction purpose in close proximity to the sensor region providing the primary sensing function.

Impacts

Description

Applications:
The use of a hydrophobic polymer (with nano/microscale channels for analyte transport) as fiber cladding in the sensor regions adds considerable robustness to our sensor arrays, which is important for eventual deployment. It provides a rigid framework for the fiber-fiber junctions that form a sensor region.

Both oxygen and pH measurements were made more reliable using the intensity referencing process, which is readily accomplished in our sensor arrays; intensity referencing is essential for sensors that respond with fluorescence intensity changes to changes in the measured parameter. If an array of such sensors is deployed, each sensor with have its own intensity reference, allowing for reliable measurements at many locations.

Moreover, due to the use of pulsed laser systems, we are in position of also measuring changes of the fluorescence lifetimes at every sensor region; thus, fluorescence lifetimes may be used as sensor response. A fluorescence lifetime measurement does not depend on the intensity of the fluorescence, thus, fluctuation of pulse intensities are of no concern for the measurement; for such sensors referencing may be avoided, albeit at the cost of a more involved data analysis procedure.

Impact & Benefits:
Real-time monitoring of aqueous systems at many locations for various pollutants and for general parameters such as pH, pO2, temperature, etc. is essential for studying, for example, the source, transport and fate of pollutants.

Interactions

Description	Contact was established with Intelligent Optical Systems Corporation in Torrance, CA. I will visit the company in June 2007 to discuss common fields of interest.
Event Date	

Presentations & Public Appearances

Title	The "Lighter" Side of Remote Sensing: Distributed Optical Fiber Sensing using Fiber-Grid Arrays and Metal-Enhancement Effects
Presenter(s)	Peter Geissinger
Presentation Type	Seminar
Event Name	Department of Chemistry Colloquium
Event Location	University of Wisconsin-Whitewater
Event Date	3/23/2007
Target Audience	Scientific audience
Audience Size	15
Description	

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Title	The "Lighter" Side of Communication: Connecting the World with Optical Fibers
Presenter(s)	Peter Geissinger, Robert J. Olsson
Presentation Type	Seminar
Event Name	Science Bag Public Lecture Series
Event Location	University of Wisconsin-Milwaukee
Event Date	1/5/2007
Target Audience	Public
Audience Size	175
Description	Note: The lectures took place on 1/5/07; 1/12/07; 1/14/07; 1/19/07; 1/26/07. Attendance varied from 150 - 200 per event.

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Title	Optical Sensing of Dissolved Oxygen and Temperature in Aqueous Environments
Presenter(s)	M. Veronica Rigo, Robert J. Olsson, Peter Geissinger
Presentation Type	Seminar

Event Name	American Water Resources Association – Wisconsin Section Annual Meeting
Event Location	Wisconsin Dells, WI
Event Date	3/1/2007
Target Audience	Scientific audience
Audience Size	50
Description	

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Title	Optical Fiber Sensors with Microsphere-Templated, Porous Fiber Claddings for Remote Measurement in Aqueous Environments
Presenter(s)	Paul E. Henning, M. Veronica Rigo, Peter Geissinger
Presentation Type	Poster session
Event Name	American Water Resources Association – Wisconsin Section Annual Meeting
Event Location	Wisconsin Dells, WI
Event Date	3/1/2007
Target Audience	Mixed
Audience Size	50
Description	

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Title	Application of Microsphere Templating to Create Porous Optical Fiber Claddings for Crossed-Fiber Sensor Arrays
Presenter(s)	Paul E. Henning, M. Veronica Rigo, Peter Geissinger
Presentation Type	Poster session
Event Name	Pittcon 2007 – 58th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
Event Location	Chicago, IL
Event Date	2/25/2007
Target Audience	Scientific audience
Audience Size	300
Description	

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Title	Fiber Optic Surface Plasmon Resonance Sensor for Oxygen Measurement
Presenter(s)	M. Veronica Rigo, Peter Geissinger
Presentation Type	Poster session
Event Name	Pittcon 2007 – 58th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
Event Location	Chicago, IL
Event Date	2/25/2007
Target Audience	Scientific audience
Audience Size	300
Description	

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Title	Application of Microsphere Templating to Create Porous Optical Fiber Claddings for Crossed-Fiber Sensor Arrays
Presenter(s)	Paul E. Henning, M. Veronica Rigo
Presentation Type	Poster session
Event Name	2007 National Meeting - American Chemical Society
Event Location	Chicago, IL
Event Date	3/25/2007
Target Audience	Scientific audience
Audience Size	300
Description	

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Title	Improving Detection Limits in Optical Fiber Sensor Arrays through Metal Enhanced Fluorescence
Presenter(s)	M. Veronica Rigo, Peter Geissinger
Presentation Type	Poster session
Event Name	41st Midwest Regional Meeting - American Chemical Society
Event Location	Quincy, IL
Event Date	10/25/2006
Target Audience	Scientific audience
Audience Size	100
Description	

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Title	Nanosphere Templating for Rigid, Porous Optical Fiber Claddings for Use in Large Crossed-Fiber Sensor Arrays
Presenter(s)	Paul E. Henning, M. Veronica Rigo, Peter Geissinger
Presentation Type	Poster session
Event Name	41st Midwest Regional Meeting - American Chemical Society
Event Location	Quincy, IL
Event Date	10/25/2006
Target Audience	Scientific audience
Audience Size	100
Description	

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Title	High-Spatial Resolution Optical Fiber Sensor Arrays for Application in Aqueous Environments
Presenter(s)	Peter Geissinger
Presentation Type	Seminar
Event Name	Intelligent Optical Systems Corporation

Event Location	Torrance, CA
Event Date	6/19/2007
Target Audience	Other
Audience Size	
Description	Presentation for staff scientists of Intelligent Optical Systems Corporation.

Students & Post-Docs Supported

Student Name	Paul Henning
Campus	University of Wisconsin-Milwaukee
Advisor Name	Peter Geissinger
Advisor Campus	University of Wisconsin-Milwaukee
Degree	Expected PhD
Graduation Month	August
Graduation Year	2008
Department	Chemistry & Biochemistry
Program	Physical Chemistry
Thesis Title	Design and Fabrication of a Large Array of Evanescent Optical Fiber Sensors with High-Spatial-Resolution Readout
Thesis Abstract	

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Student Name	M. Veronica Rigo
Campus	University of Wisconsin-Milwaukee
Advisor Name	Peter Geissinger
Advisor Campus	University of Wisconsin-Milwaukee
Degree	Expected PhD
Graduation Month	August
Graduation Year	2008
Department	Chemistry & Biochemistry
Program	Physical Chemistry
Thesis Title	Optical Fiber Chemo- and Biosensors for High-Spatial Resolution, Multi-Parameter Sensing in Gas and Aqueous Environments
Thesis Abstract	

Enhanced Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons: Molecular and Biochemical Analyses

Basic Information

Title:	Enhanced Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons: Molecular and Biochemical Analyses
Project Number:	2007WI164B
Start Date:	7/1/2006
End Date:	6/30/2008
Funding Source:	104B
Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Toxic Substances, Geochemical Processes, None
Descriptors:	
Principal Investigators:	Bill Hickey

Publication

Annual Progress Report

Reporting Period: 7/1/2006 - 6/30/2007

Submitted By: Ameesha Shetty
Submitted: 6/15/2007

Project Title

WR06R002: Enhanced Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons: Molecular and Biochemical Analyses

Project Investigators

William Hickey, University of Wisconsin-Madison

Progress Statement

Progress Statement:
The major objective accomplished during this period has been method development. Regular soil was used in the microcosms, instead of field samples, for method development work.
One of the objectives proposed was to describe the dynamics of chlorinated aliphatic hydrocarbon degradation in microcosm samples. The microcosms were set up using regular soil in order to determine the different analytical methods, before using the field samples. Reductive dechlorination of Trichloroethylene (TCE) to dichloroethylene (DCE) was detected in the microcosms. A sequential decrease in trichloroethylene (TCE) was accompanied by an increase in DCE. No further dechlorination to vinyl chloride or ethene has been detected so far. Assays have been standardized for the detection of TCE, DCE and Vinyl chloride (VC). Work is needed on establishing a high sensitivity detection method for VC. This will be done by varying conditions in the GC such a split ratios, head pressure and temperature to determine the optimum analysis conditions. Abiotic samples were set up as a control, which contained autoclaved soil. Dechlorination of TCE to DCE has not been observed in the abiotic samples. Lower detection limits of about 50 ppb have been obtained for ethene, ethane and methane. Detection methods have therefore been established for most of the analytes. Two different temperature conditions were studied, 10º C, which is close to the condition found at the depth of the aquifer and at room temperature, 22º C. Temperature can affect the microbial composition and activity. Conversion to DCE occurred sooner at room temperature i.e. 15 days as compared to 60 days at 10º C. The microcosms were periodically respiked with TCE, which was followed by a subsequent decrease in TCE. Methane was also detected in the microcosms (250 – 450 mg/L), which confirms the presence of methanogenic conditions. The data from methanogenic conditions can be compared with non-methanogenic ones to get a better understanding of its effect on dechlorination activity. The analysis techniques have been established with regular soil, which can then be used for chemical analysis of field samples.
The next aim of delineating the microbial community dynamics induced by the carbon augmentation is being worked upon. Automated Ribosomal Intergenic Sequence Analysis (ARISA) has been performed in order to understand the microbial diversity and composition of the microcosm at 10º C. A number of peaks were obtained (3 – 4 major peaks). A clone library of bacterial 16S rDNA - ITS needs to be established to yield organism identification. PCR amplification of these 16S rDNA-ITS has been done. The setting up of the clone library is being worked upon. PCR amplification using Dehalococcoides specific 16S rDNA primers was also done and an amplification product was obtained. These can be cloned and sequenced to ascertain that the amplicons belong to Dehalococcoides. PCR amplification of the RDase genes was also seen. However, once the presence of Dehalococcoides is confirmed, then these gene specific primers can be used for cloning and sequencing the reductases. The presence or absence of specific reductases can be confirmed only after they are sequenced. Work is in progress towards meeting these goals. Conclusions can be drawn from the molecular studies only after the ARISA peaks are identified and a

complete community profile is obtained. Once these methods are made certain, then samples of microcosm solids can be taken periodically and used for DNA extraction.
Work, that will completed in the immediate future, includes improving the sensitivity for vinyl chloride and DCE assays, setting up of a bacterial 16S DNA – ITS clone library and determining the molecular markers such as RDases.

Impacts

Description	Impact - Methods have been set up and standardized to assess dechlorination activity. These can be applied to study of the field samples. Changes in microbial communities and genetic markers are being studied. These can be correlated with changes in dechlorination activity which enables to understand the dynamics in microbial communities and their involvement in reductive dechlorination. Benefit - A good knowledge of the microbial activity and its role in enhanced reductive dechlorination will help augment the application of ERD for bioremediation of chlorinated aliphatic hydrocarbon contaminated groundwater.

Students & Post-Docs Supported

Student Name	Ameesha Shetty
Campus	University of Wisconsin-Madison
Advisor Name	William Hickey
Advisor Campus	University of Wisconsin-Madison
Degree	PhD
Graduation Month	
Graduation Year	
Department	
Program	
Thesis Title	
Thesis Abstract	

Information Transfer Program

University of Wisconsin Water Resources Institute - Information Transfer

Basic Information

Title:	University of Wisconsin Water Resources Institute - Information Transfer
Project Number:	2005WI89B
Start Date:	3/1/2005
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Stephen Wittman, Jim Hurley

Publication

Information Transfer

Highlights of the reporting period, March 1, 2006 through February 28, 2007, include the Eight International Conference on Mercury as a Global Pollutant and a new Water Resources Library Web site, Wisconsin's Water Library for Kids (*aqua.wisc.edu/waterlibrary/kids*). In addition, WRI continued to publish a quarterly newsletter, maintain several Web sites, cosponsor the AWRA Wisconsin Section conference, support a library and issue additional publications.

Conferences

The Eighth International Conference on Mercury as a Global Pollutant was held in Madison on August 6-11, 2006. This conference is the preeminent international forum for formal presentation and discussion of scientific advances concerning environmental mercury pollution. The depth, breadth, and pace of scientific discovery on the sources, environmental transport and fate, biogeochemical cycling, and adverse effects of mercury have increased enormously since the inaugural conference was convened in Sweden in 1990. The 2006 conference presented a timely opportunity to assimilate, synthesize, and disseminate scientific knowledge and technical information in a form useful to policy discussions involving mercury in the environment. To learn more, visit the conference Web site at www.*mercury2006.org*

The Water Resources Institute once again cosponsored the American Water Resources Association, Wisconsin Section annual meeting. "The Future of Wisconsin's Water Resources: Science & Policy" was held March 1-2, 2007 in Wisconsin Dells. Plenary, oral and poster sessions addressed both surface water and groundwater issues in Wisconsin. Other sponsors of the conference were the UW-Stevens Point Center for Watershed Science and Education, the Wisconsin Department of Natural Resources and the Wisconsin District of U.S. Geological Survey.

UW Water Resources Library Outreach Activities

During the past year, the UW Water Resources Library maintained its involvement in outreach while continuing to serve university system faculty, staff and students.

Library staff also continued to be involved in the "Allied Drive Story Hours" doing a story hour in November 2006 based on picture books about frogs. A UW Arboretum educator also did a presentation on frogs for the kids. Allied Drive is a neighborhood of Madison, Wisconsin which is pocket of poverty and crime. The "Allied Drive Story Hours" began during the summer 2004 when the Water

Resources Library launched the first of a series of story hour programs. The project has since become a partnership between eight other specialized campus libraries, the UW-Madison School of Library and Information Studies, and the Madison School and Community Recreation Safe Haven Childcare Program. The library's July story hour received television coverage.

Web Sites

During the past year, work began on the redesign of the main **UW Water Resources Institute Web Site** (*wri.wisc.edu*) to expand the information offered and make it more easily navigated. The main site links to the following sites which also contain WRI-related information:

The **ASC Publications Store** (*www.aqua.wisc.edu/publications*) features publications from the Water Resources as well as the Sea Grant Institutes. Many of the publications are free and/or available as PDFs.

Library Web Sites

The **Water Resources Library Web Site** (*wri.wisc.edu/library*) introduces UW-Madison faculty, staff and students to the library services tailored to them. Two of the most popular pages on that site are "Guide to Finding a Water-Related Job" (*wri.wisc.edu/library/finding_jobsall.html*) and "Guide to Finding Water-Related Information" (*library.wisc.edu/guides/WaterResources/index.htm*).

Wisconsin's Water Library (*aqua.wisc.edu/waterlibrary*) is an outreach project for those who want to know more about our state's water resources. It makes the books and other materials of the Water Resources Library available to any Wisconsin resident. During the past year, staff produced bi-monthly lists of Recent Acquisitions and added several special features or annotated reading lists on popular topics, including "Making Maps, Mapping History", "Climate Change in the Great Lakes Region", and "Arsenic in Groundwater". The most popular pages on the Water Library are "Wisconsin Water Facts" (*aqua.wisc.edu/waterlibrary/facts.asp*), "Native Americans and the Environment" (*aqua.wisc.edu/waterlibrary/nativeamericans.asp*) and "Environmentally-friendly Lawn and Garden Care" (*aqua.wisc.edu/waterlibrary/lawn.asp*).

Wisconsin's Water Library for Kids (aqua.wisc.edu/waterlibrary/kids) features children's books with aquatic themes that have won awards or appeared on best books lists. Most books are for preschool through second grade children, although there are also materials for older kids. Besides fiction and nonfiction books, the Web site also has ideas and resources for story hours. Users can browse recommended reading lists by topic (frogs, fish and fishing, Great Lakes, water pollution, etc.) and age group. Any adult Wisconsin resident can check out books online and pick them up at their local public library.

The popularity of the library Web sites continues to grow. From August 2003 to February 2007, the number of visits per day to the Water Library Web site has grown from 45 to over 300. The average user likes what he sees and spends about 10 minutes on the site. Our library sites (Wisconsin's Water Library + Water Resources Library + our material on the UW-Madison Libraries site) currently receive over 500 unique visits per day.

New Information Transfer Activities

The Wisconsin Water Resources Institute is conducting a one-year information transfer project to document the accomplishments, impacts and benefits of the federal Water Resources Research Institutes (WRRI) Program in the state as well as Wisconsin's nationally unique Groundwater Coordinating Council (GCC) and Groundwater Research and Monitoring Program, which were established the same year as the WRRI. The primary goal of the project is to develop an illustrated booklet about the WRRI, GCC and GRMP, plus a series of fact sheets on Wisconsin's most important groundwater resource issues, to illustrate the crucial role of the WRRI, GRMP and GCC in addressing those issues over the last 20 years. The booklet—tentatively titled Saving Wisconsin's Buried Treasure: Twenty Years of Coordinated Groundwater Research and Monitoring—is scheduled be published in August 2007 and distributed statewide along with a news release presenting the highlights of the GCC's 2007 Annual Report to the State Legislature.

The booklet and fact sheets are designed to provide a complementary packet of information with long-term usefulness. It is hoped this effort will draw greater attention from state and federal government officials, news media and citizens to the impacts and benefits of the WRRI, GCC and GRMP over the last two decades.

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	5	0	0	7	12
Masters	2	1	0	2	5
Ph.D.	3	2	0	7	12
Post-Doc.	0	0	0	2	2
Total	10	3	0	18	31

Notable Awards and Achievements

2007 WRI Research Highlights

Establishing baseline concentrations data on 40 chemical elements found in groundwatermany of which are potentially toxic yet rarely, if ever, measuredfor understanding and predicting the geochemical mechanisms that result in high arsenic levels in drinking water;

Developing a computer model of the types of landscapes and weather events that result in rapid infiltration of storm water and lead to increased groundwater contamination;

Establishing critical baseline physical and ecological data on natural springs in Waukesha and Iowa counties for assessing the vulnerability of these water resources to groundwater pumping by high-capacity wells and other types of development;

Determining that antibiotic-resistant bacteria occur naturally in groundwater, lessening concerns about the proliferation of such bacteria from septic tank effluents;

Testing an infiltrometer invented at UW-Madison to identify high-infiltration groundwater recharge areas, which may be adopted by the National Cooperative Soil Survey if it proves superior to traditional methods for measuring water infiltration of soil, and

Assessing the effectiveness of the engineered covers and monitoring methods used to protect groundwater around decommissioned waste containment facilities at eight locations around the United States.

Publications from Prior Projects

1. 2001WI35O ("Effect of Clean and Polluted Groundwater on Reproduction and Development of Daphnia") - Articles in Refereed Scientific Journals - Kashian, D.R. 2004. Toxaphene detoxification and acclimation in Daphnia magna: do cytochrome P-450 enzymes play a role? Comp. Biochem. And Physiol. C-Toxicol. Pharmacol. 137 (1): 53-63.

2. 2001WI35O ("Effect of Clean and Polluted Groundwater on Reproduction and Development of Daphnia") - Articles in Refereed Scientific Journals - Kashian D.R. and S.I. Dodson. 2004. Effects of vertebrate hormones on development and sex determination in Daphnia magna. Environ. Toxicol. Chem. 23 (5): 1282-1288.
3. 2000WI8G ("Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study") - Dissertations - Chadwick , S.P. 2006. Fate and Transport of Ambient and Amended Mercury in a Stratified Temperate Lake. Ph.D. Thesis, Environmental Chemistry and Technology Program, University of Wisconsin-Madison.
4. 2000WI8G ("Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study") - Articles in Refereed Scientific Journals - Chadwick, S.P., C.L. Babiarz, J.P. Hurley and D.E. Armstrong. 2006. Influences of iron, manganese, and dissolved organic carbon on the hypolimnetic cycling of amended mercury. Sci. Tot. Environ. 368 (1): 177-188.
5. 2000WI8G ("Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study") - Articles in Refereed Scientific Journals - Hurley, J.P., D.P. Krabbenhoft, J.G. Wiener, and C.L. Babiarz. 2007. Preface to the Madison declaration and critical synthesis papers on mercury pollution - Eighth International Conference on Mercury as a Global Pollutant Madison, Wisconsin, USA - 6-11 August 2006. Ambio. 36 (1): 2.
6. 2006WI180S ("Mercury Speciation along a Groundwater Flowpath") - Articles in Refereed Scientific Journals - Stoor, R.W., J.P. Hurley, C.L. Babiarz and D.E. Armstrong. 2006. Subsurface Sources of Methylmercury to Lake Superior from a Wetland-Forested Watershed. Sci. Total Environ. 368: 99-110.
7. 2003WI63O ("An Assessment of Aquifer Storage Recovery for Selected Generic Hydrogeologic Settings in Wisconsin") - Articles in Refereed Scientific Journals - Lowry, C.S. and M.P. Anderson. 2006. An Assessment of Aquifer Storage Recovery Using Ground Water Flow Models. Ground Water 4: 661667.
8. 2004WI78B ("Design and Evaluation of Rain Gardens for Enhancement of Groundwater Recharge") - Water Resources Research Institute Reports - Atchison, D., K. Potter and L. Severson. 2006. Design Guidelines for Stormwater Bioretention Facilities. Madison: University of Wisconsin Water Resources Institute. 33p.
9. 2004WI126O ("Mercury Speciation along a Groundwater Flowpath") - Water Resources Research Institute Reports - Armstrong, D.E., C.L. Babiarz, M.M. Shafer and S.C. Kerr. 2006. Mercury Speciation Along a Groundwater Flowpath. Water Resources Institute, University of Wisconsin, Madison. 20p.
10. 2004WI128O ("Monitoring Environmental Effects at an Established Phytoremediation Site") - Water Resources Research Institute Reports - DeVita, W.M. and M. Dawson. 2006. Monitoring Environmental Effects at an Established Phytoremediation Site - Phase III. Water Resources Institute, University of Wisconsin, Madison. 11p.
11. 2004WI79B ("Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics in Subsurface Environments") - Water Resources Research Institute Reports - Karthikeyan, K.G. and J.A. Pedersen. 2006. Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics In Subsurface Environments. Water Resources Institute, University of Wisconsin, Madison. 17p.
12. 2004WI129O ("Foundry Slag for Treating Arsenic in Groundwater and Drinking Water") - Water Resources Research Institute Reports - Metz, S.E. and C.H. Benson. 2006. Iron Foundry Slags for Removing Arsenic from Water. Water Resources Institute, University of Wisconsin, Madison. 10p.
13. 2004WI127O ("Occurrence of Estrogenic Endocrine Disruptors in Groundwater") - Water Resources Research Institute Reports - Sonzogni, W., J. Hemming M, Barman and S. Geis, 2006. Occurrence of Estrogenic Endocrine Disruptors in Groundwater. Water Resources Institute, University of Wisconsin,

Madison. 13p.

14. 2004WI129O ("Foundry Slag for Treating Arsenic in Groundwater and Drinking Water") - Dissertations - Metz S. 2006. Using Gray Iron Slags for Treating Arsenic in Groundwater M.S. Thesis. University of Wisconsin-Madison Dept. of Geological Engineering.
15. 2004WI129O ("Foundry Slag for Treating Arsenic in Groundwater and Drinking Water") - Dissertations - Eberhardt, M. 2006. Metals Leaching from Gray Iron Slags Used in Permeable Reactive Barriers. M.S. Thesis. Department Civil and Environmental Engineering, University of Wisconsin-Madison.
16. 2005WI153O ("A Combined Hydrogeologic/Geochemical Investigation of Groundwater Conditions in Waukesha County, Wisconsin") - Water Resources Research Institute Reports - Grundl, T., K. Bradbury, D. Feinstein, S. Friers and D. Hart. 2006. A Combined Hydrologic/Geochemical Investigation of Groundwater Conditions in the Waukesha County Area, WI. Water Resources Institute, University of Wisconsin, Madison. 72p.