Water Resources Institute
Annual Technical Report
FY 2009

Introduction

The University of Wisconsin WRI serves as the gateway to federal WRRI grants for all Wisconsin colleges and universities. While the WRI.s federal base funding from the U.S. Geological Survey totals less than $100,000 per year, every federal dollar is matched with at least two nonfederal dollars. All WRRI grants are awarded on a competitive, peer-reviewed basis. WRI funds are leveraged with additional funding from the UW System Groundwater Research Program, part of Wisconsin's Groundwater Research and Monitoring Program. Faculty members and research who have achieved PI status from any UW System campus are eligible to apply for this funding. Guided by the Wisconsin Groundwater Coordinating Council, this program is the mechanism whereby the UW System and the state departments of Natural Resources, Commerce, and Agriculture, Trade & Consumer Protection pool limited state and federal resources to support a coordinated, comprehensive and multidisciplinary response to the state's critical water resource issues. Together, these programs have helped establish the University of Wisconsin as a national leader in groundwater research.

The Wisconsin WRI funds an average of 15 short-term research projects of either a fundamental or applied nature that typically involve about 50 faculty, staff and students at a half-dozen campuses around the state each year. By supporting short-term projects, the institute is able to quickly respond to issues as they emerge. WRI annually provides 25 to 30 graduate and undergraduate students in the UW System with opportunities for training and financial support while they work toward their degrees. During 2007, a total of 34 students/trainees (12 undergraduates, seven master's degree students, 15 Ph.D. students and four post-doctoral students) received WRI support.

WRI research and other water-related information are readily accessible via a Web site (www.wri.wisc.edu) and the Water Resources Library (WRL), a nationally unique collection of documents covering every major water resource topic. The library's catalog is available online and searchable via the Internet, making the WRL a national and global resource. In 2003, the WRL became the first academic library in the state to make its collection available online to the public when it developed Wisconsin's Water Library" (www.aqua.wisc.edu/waterlibrary), which permits Wisconsin residents to check out WRL books and other documents free of charge via their local libraries. WRI also helps organize and cosponsors state and regional conferences on water issues.

The WRI is housed in the Aquatic Sciences Center which also houses the UW Sea Grant Institute, part of another federal-state partnership of 30 university programs that promote research, education, and outreach on Great Lakes and ocean resources. This unique administrative union of Wisconsin's federal Water Resources Research Institute and Sea Grant programs enables the UW Aquatic Sciences Center to address the full range of water-related issues in Wisconsin, from surface water to groundwater, from the Mississippi River to the shores of Lakes Michigan and Superior.

Research Program Introduction

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 Web site.

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.

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:	6/30/2009
Funding Source:	104G
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Models, Groundwater, Water Quantity
Descriptors:	
Principal Investigators:	Stephen J. Ventura, John Norman, Cynthia A. Stiles

Publications

1. Arrington, KE, and SJ Ventura. 2010. Modeling and Mapping Soil Infiltration Rates in Dane County, WI. ESRI Southeast Regional User Group Conference Proceedings, 2010. April 26-28, 2010, Charlotte NC.
2. Arrington, KE, SJ Ventura, JM Norman. 2010. Developing Saturated Hydraulic Conductivity Estimates that Include Macropore Flow. Soil Science of America Journal. In Press.
3. Arrington, K. 2009. Mapping Infiltration Rates in Dane County, WI. Ph.D. Soil Science, University of Wisconsin-Madison.

Annual Progress Report

Selected Reporting Period: 3/1/2008 - 2/28/2009

Submitted By: ventura stephen
Submitted: 6/1/2010

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

Steady-state infiltration rates were measured and soil samples collected at 49 locations across Dane County, Wisconsin in 2007 and 2008. Preliminary analysis of the 2007 data (infiltration measurements at 19 locations) indicated that landcover and the percentage of organic matter in the surface soil (0-15cm) were important predictors of Ksat, thus these two properties were used to stratify the county into landcover/organic matter categories. Data from the National Landcover Database (USGS, 2003) was used to divide the county into five landcover categories: forest, grassland, residential, pasture/hay and cropland. These five categories cover all but 7.5% of the county; the majority of the remaining area is water and a small percentage is barren land and wetlands. The county was also divided into two categories of organic matter, low (<3% organic matter) and medium (3-9% organic matter) based on the representative values of the surface horizon of soil mapping units in the Soil Survey. An overlay of these two data layers resulted in a county map of ten predicted landcover/organic matter combinations. Potential sites for infiltration measurements were randomly selected within each of these ten categories. At each site, two or three replicate infiltration measurements (2-3 m apart) were made using a rectangular stainless steel infiltrometer: 1m long, 0.5m wide (5,000 cm2) and 0.3m deep. Such a large infiltrometer was selected to filter out local soil heterogeneity and minimize the variance between replicate infiltration measurements. Variance in steady-state infiltration rates decreased by over 90% when infiltrometer size increased from 50cm2 to 400cm2 (Haws et al., 2004). At each location, soil cores (7.5cm diameter) were taken by hand at 4 depths: 0-15cm, 15-30cm, 30-45cm, and 45-60cm. All soil samples were analyzed in the laboratory for bulk density and texture; only surface samples (0-15cm and 15-30cm) were analyzed for organic matter content.

For each site, the average values for Ksat, soil properties, and topographic attributes were used to create a database for the development of pedo-transfer functions (PTFs). Best subsets regression was done in Minitab (Minitab, 2000), first including only soil properties as predictors and then adding landcover and topographic information. This technique uses multiple regression analysis to select the best model for a given number of predictors. The best model for each number of predictors was added to the list of candidate models until adding another predictor no longer resulted in an increase in

the adjusted R2 value. The accuracy of other Ksat estimates was assessed by comparing the Ksat values calculated from measurements in the infiltration database to values predicted by the following sources: the Soil Survey (NASIS database), the texture/porosity table (Rawls et al., 1998), the Kozeny-Carman equation (using coefficients given by Rawls et al, 1998), Rosetta (Schaap et al., 2001) and PALMS (Bonilla et al., 2008).

Ksat values ranged over nearly four orders of magnitude: from 1mm/hr to (a low spot in a newly-planted corn field) to 914 mm/hr (an upland spot of a mature forest). Most of the grassland, residential, pasture and cropland sites had low Ksat values (<100mm/hr) although a few sites had moderate Ksat values (100-300mm/hr). Ksat averages by textural class were considerably higher than estimates given by Rawls et al. (1992) and Rawls et al. (1998) for all textures except sand (Table 2). Textural class averages were closer to Ksat estimates used in PALMS. Percent sand (0-15cm) and bulk density (15-30cm) were the two soil properties that best predicted Ksat, although the adjusted R2 value of the model based on these two predictors is only 0.2 (Table 3). The root mean squared error (RMSE) values of several existing Ksat models were higher than the RMSE of the PTFs developed in this study, as calculated using leave-one-out cross-validation.

Principal Findings and Significance

Principal Findings and Significance

Description

Our first hypothesis was correct: when evaluated with the dataset collected for this study, the local PTFs have lower RMSE values than several other existing models, including Soil Survey estimates, the texture/porosity table, the Kozeny-Carman equation and PALMS. The PTFs presented here may represent an improvement to these Ksat estimates, however they should be evaluated with an independent dataset, rather than just cross-validation. The PTFs may have lower RMSE values than existing models because they were evaluated with the same dataset from which they were developed. While the cross-validation technique was used to account for this bias, it may still persist.

The second hypothesis was not correct: the local PTFs that include landcover and topographic information (elevation) in addition to soil properties had very similar RMSE values to the PTF based on soil properties alone. While the regression analysis indicated that adding landcover and elevation to soil properties improved the PTFs, the improvement did not persist in the cross-validation analysis. Thus the PTFs that include landcover and elevation as predictors cannot be expected to perform better than the PTF based only on soil properties when applied to an independent dataset.

The data collected for this study confirm that the texture-based Ksat estimates given by Rawls et al. (1998) and Rawls et al. (1992) are generally too low for predicting infiltration rates for soils in Dane County, Wisconsin because they assume that macropore flow is insignificant. However, at least for the agricultural sites in this study, the average Ksat value for each textural class corresponds fairly well with the estimates used in PALMS, which are adjusted to include the effect of macropore flow. In addition, the PALMS Ksat estimates performed nearly as well as the PTFs in the cross-validation analysis. Thus the texture-specific infiltration-multipliers used in PALMS appear to produce reasonable macropore-adjusted Ksat estimates. The infiltration multipliers used in PALMS may need to be modified so that they are appropriate for both agricultural and non-agricultural land uses.

Description

We have developed and evaluated a model of soil infiltration rates in Dane County WI. The maps generated from this analysis can be used for local to regional scale land use planning,

building on previous RGIS-supported technology transfer to local governments. In areas that depend on groundwater for potable water supplies or irrigation, planners and developers should be cognizant of potential impacts of land use changes on groundwater supplies. To do this, they need reliable models for predicting soil infiltration rates leading to maps depicting areas critical for groundwater recharge.

The rate at which precipitation moves into soil and recharges groundwater aquifers is spatially variable, depending on several soil properties such as texture and structure. Land use activities also influence soil infiltration through a direct effect on surface land cover and long term effects on soil properties. Undisturbed soils, such as forests, typically have abundant macropores - large spaces in the soil that allow for rapid water movement. Disturbed soils, particularly those that have been tilled, tend to have fewer macropores and slower infiltration rates.

An empirical model of soil infiltration rate (a pedotransfer function) was developed through detailed measurements at 50 sites throughout Dane County. Steady-state infiltration rates were measured with a large-frame infiltrometer to preserve macropore flow. Soil properties, including texture, bulk density and organic matter were measured at each site, along with site conditions such as land use and topography. Regression based techniques were used to determine the best combination of soil and other properties to predict infiltration rates. The locally derived models were a substantial improvement over most published pedotransfer functions, which tend to underestimate soil infiltration rates because they assume macropore flow is insignificant.

Adding a land cover parameter to the soil infiltration model provided modest improvement over a model based on soil properties alone. The best model was used to predict soil infiltration rates at unsampled locations, based on texture (percent sand), bulk density, and land cover. The grain (spatial resolution) of land cover data are much finer than the soil survey, which is otherwise the sole basis for predicting infiltration. Thus a soil infiltration model that includes landcover is the basis for spatially-detailed predictive infiltration maps.

Committees, Memberships & Panels

Group Name	National Cooperative Soil Survey
Description	This work was presented and discussed during an ad hoc committee meeting in Madison, WI.
Start Date	6/6/2007
End Date	6/7/2007

Interactions

Description	We have been in contact with Chuck Dunning, a Hydrologist at the USGS Water Science Center in Middleton, Wisconsin. Chuck is leading a project to establish a state standard for measuring infiltration rates in Wisconsin in order to design management practices to promote infiltration of stormwater runoff. He is planning to determine if a single-ring infiltrometer (10 inch

	diameter) is an appropriate device for such a standard. At three of the locations where we measured infiltration rates in 2007, a student working with Chuck joined us and measured infiltration rates using both a single and double-ring infiltrometer.
Event Date	9/1/2007

Journal Articles & Other Publications

Publication Type	Electronic Publication
Title	Modeling and Mapping Soil Infiltration Rates in Dane County, WI
Author(s)	K.E. Arrington, S.J. Ventura
Publication/Publisher	" ESRI Southeast Regional User Group Conference Proceedings, 2010. April 26-28, 2010, Charlotte NC.
Year Published	2010
Volume & Number	
Number of Pages	
Description	
Any Additional Citation Information	

Publication Type	
Title	Developing Saturated Hydraulic Conductivity Estimates that Include Macropore Flow
Author(s)	K.E. Arrington, S.J. Ventura, J.M. Norman
Publication/Publisher	Soil Science of America Journal
Year Published	In Review
Volume & Number	
Number of Pages	
Description	
Any Additional Citation Information	

Other Project Support

Source	National Center for Rural Geospatial Innovations (USDA-CSREES)
Dollar Value	$1
Description	In-kind technical and GIS support for the project.
Start Date	
End Date	

Partners

Name/Organization	Michelle Richardson

Affiliation	Dane County Land and Water Resources Department
Affiliation Type	Local & State
Email	michelle.richardson@co.dane.wi.us
Description	Michelle provided the GIS data layers of land use and parcels in Dane County. These were used extensively in the site selections for the infiltration measurements made in 2007.

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	20
Description	This presentation provided and overview of the goals of the project and the field work planned for 2007.

Title	Modeling and Mapping Soil Infiltration Rates in Dane County, WI
Presenter(s)	S.J. Ventura
Presentation Type	Professional meeting
Event Name	ESRI Southeast Regional User Group Conference
Event Location	Charlotte NC
Event Date	4/27/2010
Target Audience	Scientific audience
Audience Size	35
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	
Thesis Abstract	

Grant No. 07HQGR0170 ACAP Test Section Exhumation

Basic Information

Title:	Grant No. 07HQGR0170 ACAP Test Section Exhumation
Project Number:	2007WI200S
Start Date:	8/15/2007
End Date:	3/30/2009
Funding Source:	Supplemental
Congressional District:	02
Research Category:	Engineering
Focus Category:	Radioactive Substances, Groundwater, None
Descriptors:	
Principal Investigators:	Craig H Benson, Craig H Benson

Publications

There are no publications.

Completion Report

Submitted By: Craig Benson
Submitted: 6/1/2009

Start Date: 8/15/2007
End Date: 12/31/2008

Project Title

WR07R009: ACAP Test Section Exhumation

Project Investigators

Craig Benson, University of Wisconsin-Madison

Results

The objective of this project was to gather information needed to project the long-term performance of final covers and to interpret the performance of the landfill final cover test sections that were constructed and monitored as part of the Alternative Cover Assessment Program (ACAP). This information was gathered as we exhumed 24 of the 27 ACAP test sections along with two full-scale final covers at operating landfills.

Field and laboratory testing has shown that the hydraulic properties of final cover soils change in response to pedogenic processes that affect soil structure. These changes occur fairly rapidly (within 3-5 yr) and their magnitude is a function of the initial structure of the soil (larger changes in hydraulic properties occur for soils that are denser and less conductive when initially placed). An overall loosening of the soil occurs, which results in an increase in saturated hydraulic conductivity, as well as a change in soil water storage capacity. In addition, the hydraulic properties converge to a relatively narrow band after several years of weathering. In particular, regardless of the initial condition, the saturated hydraulic conductivity ultimately falls within 10-5 to 10-3 cm/s, van Genuchten's alpha parameter falls within 0.01-0.1 kPa-1, and van Genuchten's n parameter falls within 1.2-1.5.

These findings have two important practical implications for alternative covers. First, the universally narrow ranges for the hydraulic properties reduce the uncertainty in predictions of long-term cover performance and build confidence in alternative cover technology. Second, the findings suggest that alternative cover soils should not be densely compacted, and should be constructed with less plastic fine-textured soils when possible. Adopting both of these recommendations for cover soil selection and placement will result in covers that undergo smaller changes in hydraulic behavior over time, and therefore will exhibit more uniform performance over time.

Changes in the properties of geosynthetic materials have been less significant (except for geosynthetic clay liners). Wide-width tensile strengths, melt flow indices, and oxidation induction times of the geomembranes have remained essentially unchanged during the ACAP study. Small reductions (2x) in the transmissivity of geocomposite drainage layers have been observed. The permittivity of the overlying and underlying geotextiles in geocomposite drainage layers has also diminished modestly (2-3x) due to intrusion of fines. These changes are not significant enough to affect performance in the near term. However, performance may be affected over decades or centuries, which can be important for wastes with very long life spans (e.g., radionuclides). Interface shear strengths have remained essentially unchanged. However, appreciable reductions in the ply adhesion of

geocomposite drainage layers have been observed at several sites, which may have implications for long-term stability.

Significant increases in the hydraulic conductivity of geosynthetic clay liners (GCLs) have been observed in some cases, even if the GCL is covered by a geomembrane. The increases in hydraulic conductivity are due to replacement of native Na in the bentonite with divalent cations (predominantly Ca, but also Mg) combined with dehydration of bentonite surfaces or lack of sufficient hydration prior to cation exchange. For most sites where the GCL is covered by a geomembrane, low hydraulic conductivity can be maintained by ensuring the subgrade water content is at least 10% and that the total cation charge per mass (TCM) in the subgrade is less than 0.8 cmol+/kg. However, this recommendation does not ensure universal success. At two sites where the GCL was covered with a geomembrane, preferential flow was observed in GCLs even though they were sufficiently hydrated. The preferential flow paths appear to form in response to cation exchange in bentonite surrounding bundles of needle-punching fibers.

Impacts

No answer has been submitted for this question.

Most Significant Benefit/Application

No answer has been submitted for this question.

Follow-Up

A draft final report for this project has been submitted. After review and revision, the final report needs to receive widespread dissemination.

The findings from the study need to be published in peer-reviewed journals. Six journal manuscripts have been drafted from this project and will be submitted for review and publication.

A webinar series should be developed to present the findings from this study to a broad audience.

Awards, Honors & Recognition

Title	J. James Croes Medal
Event Year	
Recipient	
Presented By	ASCE
Description	

Committees, Memberships & Panels

Group Name	US Department of Energy
Description	Chair, Independent Technical Review Committee for On-Site Disposal Facilities
Start Date	
End Date	

Group Name ASTM
Description D18 Executive Committee
Start Date
End Date

Group Name Geo Institute
Description Board of Governors
Start Date
End Date

Interactions

Description This project is a collaborative effort between the US Nuclear Regulatory Commission, US National Science Foundation, US Department of Energy, US Environmental Protection Agency, and the Environmental Research and Education Foundation. The Desert Research Institute of Reno, NV and California Polytech University are collaborators
Event Date

Other Project Support

Source Multilple Agencies
Dollar Value $1
Description This project is benefiting from funding being provided by the following agencies as part of a collaborative effort to understand the temporal evolution of the characteristics of landfill final covers: US National Science Foundation, US Nuclear Regulatory Commission, US Department of Energy, US Environmental Protection Agency, and the Environmental Research and Education Foundation.
Start Date
End Date

Partners

Name/Organization William H. Albright
Affiliation Desert Research Institute
Affiliation Type
Email bill@dri.edu
Description Co-PI

Presentations & Public Appearances

Title Design and Construction of Alternative Covers
Presenter(s) Craig H. Benson, and William H. Albright Presentation Type: Workshop Event Name: Event location: Event Date: February 2008 Target Audience: Audience Size: 100 Description:
Presentation Type
Event Name

	Design and Construction of Alternative Covers
Event Location	Portland, OR
Event Date	2/1/2008
Target Audience	
Audience Size	100
Description	3-d workshop for engineering consultants, state regulators, and federal regulators

Students & Post-Docs Supported

Student Name	Matthew Bennett
Campus	University of Wisconsin-Madison
Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month	December
Graduation Year	2009
Department	and Environmental Engineering
Program	Geo Engineering
Thesis Title	
Thesis Abstract	

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Student Name	Seunghak Lee
Campus	University of Wisconsin-Madison
Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison
Degree	Post Doc
Graduation Month	April
Graduation Year	2009
Department	Civil and Environmental Engineering
Program	Geo Engineering
Thesis Title	
Thesis Abstract	

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Student Name	A. Hakan Oren
Campus	University of Wisconsin-Madison
Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison

Degree	Post Doc
Graduation Month	August
Graduation Year	2009
Department	Civil and Environmental Engineering
Program	Geo Engineering
Thesis Title	
Thesis Abstract	

Student Name	Paul Schlicht
Campus	University of Wisconsin-Madison

Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison

Degree	Masters
Graduation Month	December
Graduation Year	2009
Department	Civil and Environmental Engineering
Program	Geo Engineering
Thesis Title	
Thesis Abstract	

Controls on Methylation of Groundwater Hg(II) in Hyporheic Zones of Wetlands.

Basic Information

Title:	Controls on Methylation of Groundwater Hg(II) in Hyporheic Zones of Wetlands.
Project Number:	2007WI202O
Start Date:	7/1/2007
End Date:	6/30/2009
Funding Source:	Other
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	Groundwater, Hydrogeochemistry, Models
Descriptors:	
Principal Investigators:	Martin Shafer

Publications

1. Creswell, J. E., Kerr, S. C., Meyer, M. H., Babiarz, C. L., Shafer, M. M., Armstrong, D. E., Roden, E. E. 2008. Factors controlling temporal and spatial distribution of total mercury and methylmercury in hyporheic sediments of the Allequash Creek wetland, northern Wisconsin. J. Geophys. Res. Biogeosciences 113:G00C02. DOI: 10.1029/2008JG000742
2. Creswell, J. E., Babiarz, C. L., Shafer, M. M., Armstrong, D. E., Roden, E. E. 2009. Controls on Methylation of Groundwater Hg(II) in Hyporheic Zones of Wetlands. Water Resources Institute, University of Wisconsin, Madison. 15p. Final_WR07R008.pdf

Controls on Methylation of Groundwater Hg(II) in Hyporheic Zones of Wetlands

(WR07R008)

Project Completion Report

J.E. Creswell, C.L. Babiarz, M.M. Shafer, D.E. Armstrong
Environmental Chemistry & Technology Program
University of Wisconsin – Madison
660 North Park Street
Madison, WI 53706

and

E.E. Roden
Department of Geoscience
University of Wisconsin – Madison
1215 West Dayton Street
Madison, WI 53706

Table of Contents

List of Figures and Tables

Project Summary

Title: Controls on Methylation of Groundwater Hg(II) in Hyporheic Zones of Wetlands
Project I.D.: WR07R008
Investigators:

Principal Investigators:

Martin M. Shafer – Associate Scientist, Christopher L. Babiarz – Assistant Scientist, David E. Armstrong – Professor Emeritus, Environmental Chemistry & Technology Program
Eric E. Roden – Professor, Department of Geoscience

Research Assistant:

Joel E. Creswell – Doctoral Student, Environmental Chemistry & Technology Program

Period of Contract: July 1, 2007 to June 30, 2009

Background/Need: This project addressed the groundwater-related problem of methylmercury (MeHg) formation in hyporheic zones, the subsurface regions of stream- and lake beds where the active exchange of surface and groundwater occurs. MeHg formation involves the methylation of Hg(II), in the hyporheic zone, by bacteria. Subsequent transport of the MeHg into surface waters leads to accumulation of this highly toxic substance in aquatic food webs.

Objectives: Our research was focused on determining the main factors controlling the bioavailability of inorganic Hg(II) for production of MeHg in wetland hyporheic zones. Our objectives included:

1. Experimentally determining rates of mercury methylation and demethylation using isotopic tracer techniques .
2. Determining whether observed MeHg concentrations were allochthonous or produced *in situ.*
3. Assessing the influence of strong Hg-binding ligands on methylation rate potential and determining whether sulfide or dissolved organic carbon (DOC) played the greatest role in regulating Hg(II) bioavailability (as probed by methylation rate potential measurements) to methylating bacteria.
4. Determining whether neutral complexes of mercury and sulfide, such as HgS^0, are the most bioavailable form of Hg(II) to bacteria.
5. Comparing two geochemically different sites within the wetland, with different groundwater flow patterns, to determine if Hg(II) bioavailability and methylation were influenced by the contrasting redox conditions.

Methods: This study was conducted in the Allequash Creek Wetland, in the Trout Lake region of Vilas County, northern Wisconsin. We collected sediment cores from two sites, one in the groundwater-fed headwaters of Allequash Creek ("Upper Springs" site), and one in the riparian wetland roughly half-way between the headwaters and the creek's discharge into Allequash Lake, 4 km downstream ("Middle Wetland" site). Cores were collected in July and October, 2008, and February and July, 2009.

Some cores were kept intact and were injected with isotopically labeled mercury for methylation and demethylation rate potential measurements. Others were sliced at 2 cm intervals, and porewater was extracted for measurements of geochemical parameters. Parameters measured included sulfide, sulfate, Fe(II), Fe(III), DOC, total Hg (HgT), MeHg, strong Hg-binding ligand concentrations, concentrations of negatively-charged Hg species, and major ion concentrations.

Results and Discussion: HgT and MeHg concentrations in porewater varied considerably, spatially and temporally, from 2.8 to 50.3 ng/L for HgT and from 0 to 1.8 ng/L for MeHg. HgT concentrations were generally higher at the upper springs site than at the middle wetland, but did not show any consistent trend with depth at either site. MeHg concentrations were generally higher at the middle wetland site than

at the upper springs, and tended to peak within the upper 4 cm of sediment before declining with increasing depth. This trend of declining MeHg concentration with depth was reversed in the February, 2009 sampling, with MeHg concentrations peaking either at the deepest (8-10 cm at the middle wetland site) or second-deepest (6-8 cm at the upper springs site) horizon sampled.

Methylation rate potentials, like HgT and MeHg concentrations, varied widely, both spatially and temporally, while demethylation rates were more uniform. The relative uniformity of demethylation rates suggests that demethylation is a process that either occurs under a wider range of redox conditions, than methylation, or is possibly carried out by a greater number of bacterial species. An alternate possibility is that demethylation has an abiotic component. The range of observed methylation rates was 0 to 9.5 fmol MeHg/g sediment/hr (0-34.5% of introduced spike/day), while the range of observed demethylation rates was 0.5 to 9.6 fmol MeHg/g sediment/hr (0-302.2% of introduced spike/day). Methylation rates were lowest in February, 2009, when porewater temperatures were lowest, however, demethylation rates in these samples were the highest measured. These findings indicate that methylation rates may be more sensitive to low temperatures than demethylation rates.

The poor correlation observed between porewater MeHg and HgT concentrations suggests that the abundance of HgT is not directly limiting to methylation. The relatively stronger correlations observed between MeHg and DOC concentrations, as well as between DOC concentrations and methylation rate potentials, suggest that DOC plays an important role in regulating the production of MeHg in this system, and perhaps also its retention in the porewater or export to the stream. Correlations between MeHg and sulfide concentrations, as well as between sulfide concentrations and methylation rates were also stronger than correlations between MeHg and HgT, suggesting that sulfide plays a role in regulating methylation. Strong correlations between MeHg concentrations and methylation/demethylation rates, combined with low MeHg concentrations in upwelling groundwater, suggest that the majority of the MeHg in this system is produced *in situ*. Multiple regression analysis showed DOC concentration to be the most important factor in explaining the variability in the observed methylation rates, in most cases, with sulfide being the second most important variable.

Conclusions/Implications/Recommendations: The majority of the MeHg present at this site is produced *in situ*, in the hyporheic zone, however rates of production are highly variable by depth, sampling site, and season. In spite of predictions, generated by speciation modeling in previous studies, that sulfide will dominate Hg speciation (and therefore potential bioavailability) at this site, DOC appears to be the most important factor controlling Hg(II) methylation in this system. The findings of this study can aid in the creation of more targeted fish consumption advisories, can help improve mercury cycling computer models, and can lead to better wetland management practices to limit MeHg production. Future studies should focus on gaining a better understanding of the roles of DOC and sulfide in MeHg production and export.

Related Publications: Creswell, J.E., Kerr, S.C., Meyer, M.H., Babiarz, C.L., Shafer, M.M., Armstrong, D.E., and Roden, E.E. 2008. Factors controlling temporal and spatial distribution of total mercury and methylmercury in hyporheic sediments of the Allequash Creek wetland, northern Wisconsin. Journal of Geophysical Research – Geosciences. 113(G00C02):1-9.

Key Words: Methylmercury, mercury, wetland, hyporheic zone, dissolved organic carbon, methylation, sulfide

Funding: UWS Groundwater Research

Introduction

The accumulation of methylmercury (MeHg), the most toxic form of mercury (Hg), in aquatic food webs is a major problem in freshwaters across the U.S. (U.S. EPA, 2001). Production of MeHg occurs through the methylation of inorganic Hg(II) by bacteria in anoxic environments such as wetlands (Morel *et al*., 1998, Benoit *et al*., 1999). Groundwater and surface water have been demonstrated to transport some Hg(II) into these environments, but contribute little to no MeHg, implicating *in situ* production of MeHg as the primary source (Meyer, 2005; Stoor *et al*., 2006; Armstrong *et al*., 2006). Although information is emerging, the factors and mechanisms controlling MeHg production are not well understood. To design management strategies that would limit MeHg production, an understanding of factors regulating MeHg concentrations is essential.

Recent research provides some insight into the formation of MeHg in aquatic environments. Briefly, MeHg is produced in anoxic environments through bacterial activity, especially sulfate-reducing bacteria (Benoit *et al*., 1999), but other species may also be involved, such as Fe(III)-reducing bacteria (FeRB) (Warner *et al*., 2003; Fleming *et al*., 2006; Kerin *et al*., 2006). Factors believed to be important in controlling methylation rates include the activity of bacteria, concentration of Hg(II), and the speciation of Hg(II). Speciation is important because it influences the bioavailability of Hg(II) to bacteria (Hammerschmidt and Fitzgerald, 2004). Neutral species such as HgS^0, $Hg(HS)_2^0$, $HgCl_2^0$, and $Hg(OH)_2^0$ are believed to be bioavailable due to their lipophilic character and enhanced ability to pass through bacterial membranes (Morel *et al*., 1998). Ionic species such as $HgCl_3^-$ or $HgHS_2^-$ are expected to be unavailable (Barkay *et al*., 1997). In addition, binding to large organic molecules or natural dissolved organic matter is, under certain conditions, expected to prevent the uptake of Hg(II) by bacteria (Hammerschmidt *et al*., 2004). In anoxic environments, Hg(II)-sulfide complexes are expected to dominate Hg(II) speciation due to the especially strong binding of Hg(II) to sulfide. Under these conditions, the bioavailability of Hg(II) should be mainly controlled by sulfide concentration and pH (Benoit *et al*., 1999; Hammerschmidt and Fitzgerald, 2004). However, Hg(II) also associates with natural organic matter (NOM) through strong binding to reduced sulfur groups (Haitzer *et al*., 2002), and our recent work indicates that Hg(II)-NOM complexes may play a role in regulating methylation, even in the presence of sulfide (Armstrong *et al*., 2006; Chadwick, 2006; this study). The exact role of NOM on Hg(II) bioavailability is not clear. For example, the partitioning and transport of Hg(II) with NOM is well-established (cf. Hammerschmidt *et al*., 2004; Babiarz *et al*., 1998), and this binding might be expected to reduce the bioavailability of Hg(II). However, concentrations of MeHg also tend to correlate with NOM concentrations, which could suggest the opposite: that Hg(II) is more available in the presence of NOM. The MeHg-NOM correlation, however, could also be explained if NOM plays an important role in MeHg partitioning and transport. Possible explanations for the observed correlations between MeHg and NOM include: (a) non-equilibrium conditions at the time of sampling that allow Hg-NOM complexes in the presence of Hg(II) and sulfides (Hammerschmidt *et al*., 2004); (b) covariation of Hg(II)-NOM complexes with a separate pool of bioavailable Hg(II); or (c) a NOM buffering effect on Hg(II) activities, whereby dissociation of Hg(II)-NOM complexes in association of microbial uptake provides a pool of Hg(II) for methylation.

The hyporheic zone of streambeds is a subsurface, three-dimensional region in which the active exchange of typically oxic surface water and sub-oxic or anoxic groundwater produces sharp chemical gradients with depth (Alley *et al*., 2002). These changing chemical conditions, along with a supply of labile organic matter, give rise to substantial biological activity, and can provide conditions conducive to production of MeHg. Our prior work at the Allequash Creek wetland in northern Wisconsin documents intense redox cycling in large areas of the hyporheic zone – highly reducing groundwater mixing with DOM and sulfate from surface water produces conditions that support active sulfate reduction, as well as zones of iron oxidation and reduction. Past studies in our group have also implicated the hyporheic zone as an important exporter of MeHg to surface water and downstream environments (Armstrong *et al*.,

2006; Meyer *et al*., 2005). It is for these reasons that this study focused on Hg(II) methylation in the hyporheic zone of the Allequash Creek wetland.

The goal of our research was to determine the main factors controlling the bioavailability of inorganic Hg(II) for production of MeHg in wetland hyporheic zones. Our objectives included:

1. Experimentally determining rates of mercury methylation and demethylation using isotopic tracer techniques .
2. Determining whether observed MeHg concentrations were allochthonous or produced *in situ.*
3. Assessing the influence of strong Hg-binding ligands on methylation rate potential and determining whether sulfide or dissolved organic carbon (DOC) played the greatest role in regulating Hg(II) bioavailability (as probed by methylation rate potential measurements) to methylating bacteria.
4. Determining whether neutral complexes of mercury and sulfide, such as HgS^0, are the most bioavailable form of Hg(II) to bacteria.
5. Comparing two geochemically different sites within the wetland, with different groundwater flow patterns, to determine if Hg(II) bioavailability and methylation were influenced by the contrasting redox conditions.

Procedures and Methods

Site Description: This study was conducted in the Allequash Creek wetland, in the Trout Lake basin, in Vilas County, northern Wisconsin (Figure 1). This area is in the Northern Highland Lake District of Wisconsin, and is dominated by glacial terrain. The creek is spring-fed, consisting of several groundwater point discharges at the base of a dominating hillslope (Armstrong *et al*., 2006; Kerr, 2007; Creswell *et al*., 2008). It receives groundwater discharge along most of its course, although the length and origin of groundwater flow paths discharging to the stream varies widely (Pint *et al*., 2003). The wetland plant community is dominated by sphagnum moss, leatherleaf, tussocks sedge, and black spruce, while the surrounding hillslope is covered in a mix of coniferous and deciduous forest (Armstrong *et al*., 2006; Creswell *et al*., 2008).

Samples were collected at two locations within the wetland. The upper springs site is located in a beaver pond at the eastern end of the watershed, where the stream originates (Figure 1). The sediment here is relatively low in organic matter and iron, and oxidized sulfur compounds are more prevalent than sulfide species (Creswell *et al*., 2008). Groundwater discharging to this area has traveled along relatively short flow paths of 25-50 years (Pint *et al*., 2003), and is less reducing than groundwater at the other study site. The middle wetland site is defined by a three meter wide riparian zone on either side of the main stream channel, roughly half-way between the headwaters and the discharge point into Allequash Lake (Figure 1). This site is characterized by peat soils over six meters in depth, high concentrations of dissolved organic matter, higher iron concentrations, and a greater proportion of reduced sulfur compounds (Armstrong *et al*., 2006; Creswell *et al*., 2008). Groundwater discharging at this site has traveled along relatively long flow paths of 50-150 years (Pint *et al*., 2003) and is characteristically anoxic and sulfidic. These sites were chosen in order to take advantage of data collected by prior studies in our research group (Meyer, 2005; Armstrong *et al*., 2006; Meyer *et al*., 2005; Creswell *et al*., 2008; Kerr *et al*., 2008), as well by the North Temperate Lakes Long Term Ecological Research (NTL-LTER) project and the U.S. Geological Survey's Water, Energy, and Biogeochemical Budgets (WEBB) project.

Field Methods: All sampling was carried out following trace metal clean techniques developed in our laboratory (Hurley *et al*., 1996; Shafer *et al*., 1999) to ensure sample integrity and to minimize contamination. Hyporheic zone sediment cores were collected from the upper springs and middle wetland sites during four different field campaigns in July and October, 2008, and February and July, 2009.

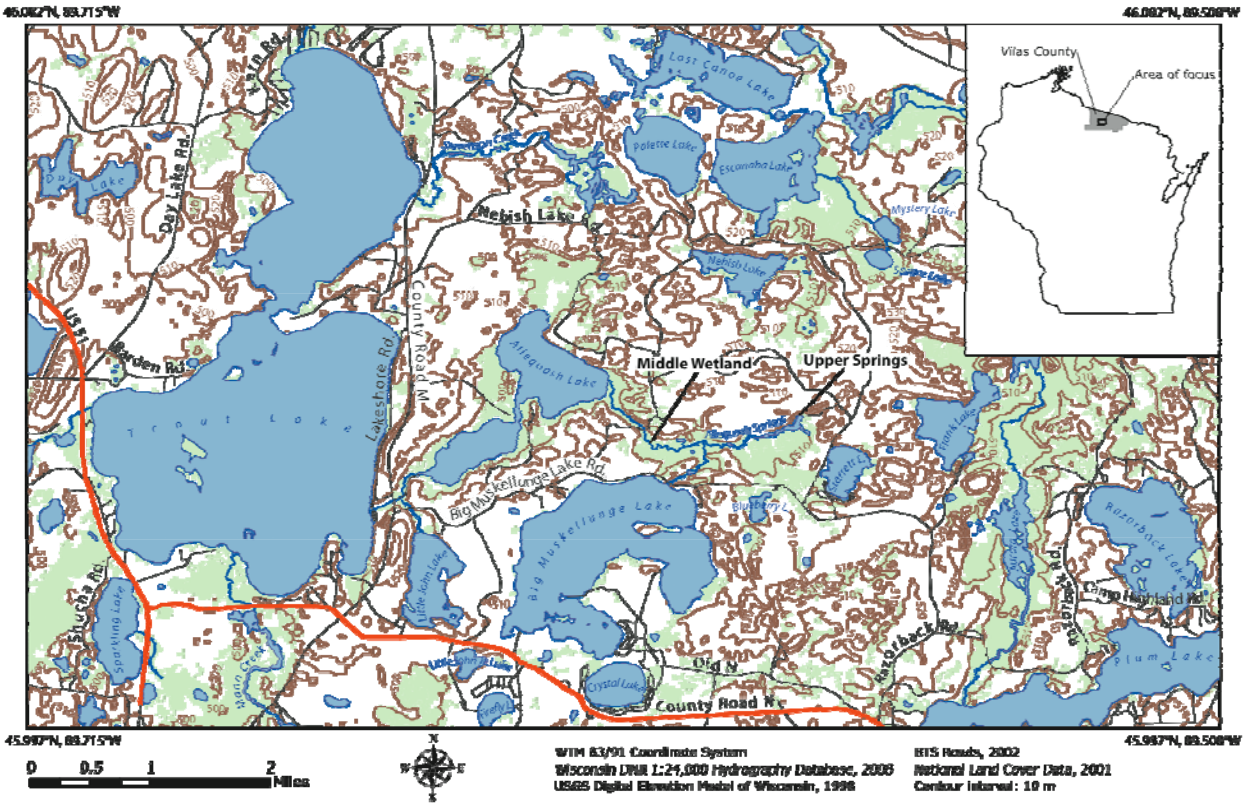

Figure 1: Map of the study area, showing the locations of the sampling sites. Wetlands, as delineated in the National Land Cover Database, are shown in green. Contour interval: 10 m.

Laboratory and Analytical Methods: Cores were transferred to the nearby UW Trout Lake Station for processing. Four replicate cores from each site were collected for geochemical analysis. These were sectioned in five 2 cm increments in an anoxic glove box, and composited by depth horizon. Porewater was removed from the composited core sections by centrifugation, and was then passed through acid-cleaned 0.45 µM filters using all-plastic syringes. Porewater and sediments were then subsampled for geochemical analyses, described below. In most cases, porewater was kept in the glove box until it was preserved for storage and transport, in order to minimize the oxidation of redox-sensitive analytes.

Methylation/Demethylation Rate Potential Measurements: Two cores from each site were collected for this analysis. The cores for methylation rate potential measurements were injected with pH-neutral amendments of isotopically enriched Hg(II), (^{200}Hg) which were diluted to the appropriate concentration using Allequash Creek water. Injections were made through silicone septa in the wall of the core tube. Cores for demethylation rate measurements were injected with isotopically enriched amendments of MeHg (Me^{199}Hg), prepared as described above. Amendments typically increased the HgT and MeHg burden of the sediment by 1-2%. Cores were incubated at porewater temperature for 7-13 hours. Incubations were terminated by slicing and freezing.

Sediments were analyzed following the direct distillation method (Horvat *et al*., 1993). After distillation, samples analyzed by GC-ICP-MS, following standard methods for isotopic Hg measurement (Hintelmann *et al*., 1995). In samples amended with ^{200}Hg(II), any ^{200}MeHg measured was methylated during the incubation. In samples amended with Me^{199}Hg, the difference between the introduced Me^{199}Hg and what remained at the end of the incubation was what was demethylated (Hintelmann *et al*., 2000).

HgT/MeHg: Samples for mercury and methylmercury analysis were analyzed using Cold Vapor Atomic Fluorescence Spectrometry (CVAFS), following established methods (Babiarz *et al*., 1998; Bloom and Telliard, 2001a; Bloom and Telliard, 2001b).

Reducible Mercury Titrations: This method provided an estimate of the concentration of strong mercury-binding ligands in porewater. It involves amending replicate porewater samples with a range of Hg(II) concentrations, and allowing the amended mercury to equilibrate with the natural ligands overnight. Samples are then reduced with $SnCl_2$, a weak reductant, purged with nitrogen, and the evaded Hg is measured. The ligand concentrations are calculated from the difference between introduced and measured Hg (Lamborg *et al*., 2003; Lamborg *et al*., 2004). Because the reductant used in this analysis is weak, the ligands measured are operationally defined to be strong. Although sulfide species would generally be considered strong Hg-binding ligands in hyporheic porewater, these samples were not stored under anoxic conditions prior to analysis, thus it is assumed that all sulfide present was oxidized.

Ion Exchange Resin: Porewater samples were passed through columns containing diethylaminoethyl resin in order to isolate negatively charged aqueous complexes (e.g. DOM, free anionic Hg species) from porewater (Chadwick, 2006). After passing through the columns, the porewater, containing only positive and neutral aqueous complexes, was analyzed for HgT. The negatively charged complexes were eluted from the resin using weak acid and were also analyzed for HgT.

Ancillary Geochemistry: Iron and sulfide in porewater were measured colorimetrically, following the methods of Stookey (1970) and Cline (1969), respectively. Dissolved organic carbon was measured using a Shimadzu TOC-V/CSH instrument. Sulfate concentrations were measured by ion chromatography. Major ions and metals were measured by high resolution ICP-MS.

Results and Discussion

HgT and MeHg concentrations in porewater varied considerably, spatially and temporally, from 2.8 to 50.3 ng/L for HgT and from 0 to 1.8 ng/L for MeHg (Figure 2). HgT concentrations were generally higher at the upper springs site than at the middle wetland, but did show any consistent trend with depth at either site. MeHg concentrations were generally higher at the middle wetland site than at the upper springs, and tended to peak within the upper 4 cm of sediment before declining with increasing depth. This trend of declining MeHg concentration with depth was reversed in the February, 2009 sampling, with MeHg concentrations peaking either at the deepest (8-10 cm at the middle wetland site) or second-deepest (6-8 cm at the upper springs site) horizon sampled. MeHg concentrations showed little apparent correlation with HgT concentrations within each core, but did generally correlate well with DOC, sometimes positively, sometimes negatively. This finding suggests that DOC either plays an important role in MeHg formation in this system, or that it is responsible for MeHg retention in the hyporheic porewaters sampled. The lack of correlation between MeHg and HgT suggests that Hg(II) concentration is not a directly limiting factor in MeHg production at this site.

Methylation rate potentials, like HgT and MeHg concentrations, varied widely, both spatially and temporally, while demethylation rates were more uniform. The relative uniformity of demethylation rates suggests that demethylation is a process that either occurs under a wider range of redox conditions, than methylation, or is possibly carried out by a greater number of bacterial species. An alternate possibility is that demethylation has an abiotic component. The range of observed methylation rates was 0 to 9.5 fmol MeHg/g sediment/hr (0 to 34.5% of introduced spike/day), while the range of observed demethylation rates was 0.5 to 9.6 fmol MeHg/g sediment/hr (0 to 302.2% of introduced spike/day). These methylation rate potentialss span a wider range than those found in nearshore marine sediments (1.4 to 8.2% d^{-1}; Hammerschmidt and Fitzgerald, 2004) and Ontario lakes (1.2 to 1.6 % d^{-1}; Hintelmann *et al.*, 2000). The mean of the methylation rates in this dataset (3.9% d^{-1}) is comparable to that in the marine sediment

dataset (3.8% d^{-1}), but is higher than that of the Ontario dataset (1.4% d^{-1}). Demethylation rates measured in this study (208.3% d^{-1} mean) are higher than in the Ontario lakes study (~40% d^{-1}). Methylation rates in this study were lowest in February, 2009, when porewater temperatures were lowest, however, demethylation rates in these samples were the highest measured. These findings indicate that methylation rates may be more sensitive to low temperatures than demethylation rates.

Methylation rate potentials only twice showed a strong positive correlation (r^2>0.7) with porewater (upper springs site, October, 2008) or sediment (upper springs site, July, 2008) MeHg concentrations. There were no strong negative correlations between sediment or porewater MeHg concentrations and demethylation rate potentials. If the MeHg present within a given core section were produced within that section, one would expect it to correlate positively with the methylation rate potential, and negatively with the demethylation rate potential. Given the observed lack of correlation, however, we conclude that the highly dynamic flow patterns in this system rapidly transport MeHg from where it is produced to other locations in the hyporheic zone or stream. In spite of the lack of correlation between methylation rate potentials and hyporheic zone MeHg concentrations, the very low MeHg concentrations found in the upwelling groundwater at both sites lead us to conclude that the majority of the MeHg observed in the hyporheic zone was methylated *in situ*. The mean MeHg concentration in upwelling groundwater measured in 2003 and 2004 was 0.09 ng/L (Meyer *et al*., 2005), while the mean porewater concentration measured in this study was 0.46 ng/L.

Site/Date	DEAE+/0	DEAE-	DOC	Sulfide	r^2
July, 2008	-0.010	-0.021	*5.508*	1.131	0.452
October, 2008	0.007	0.029	-2.605	*3.927*	0.911*
February, 2009	0.004	0.006	*-0.555*	0.031	0.922*
Upper Springs (All Dates)	-0.004	-0.001	*-1.234*	-0.111	0.455
Middle Wetland (All Dates)	0.017	-0.044	*7.674*	2.761	0.553

Table 1: Multivariate regression results. The geochemical parameters listed were regressed against methylation rates. Numbers in the DEAE+/0, DEAE-, DOC, and Sulfide columns are regression coefficients. The largest coefficients from each regression are shown in italics. The r^2 value in each row corresponds to fit of the multivariate regression to the data. Regressions were run by date, in which case data from both sites were included, and by site, in which case data from all dates were included. * indicates a significant result at the p=0.05 level.

Reducible mercury titrations showed considerable variability in the strong Hg-binding ligand concentrations (1.73-113.09 nN, mean: 40.62 nN). These data fall mostly within the range found in previous studies (0.3 to 60 nM; Lamborg *et al.*, 2003; Lamborg *et al.*, 2004), and the mean value from this study is similar to the value measured for a Minnesota bog, the most similar site for which published data exist (60 nN). Although there were generally no discernable trends with depth, by season, or between sites in these data, it is important to note that all of the measured ligand concentrations are at least an order of magnitude higher than the highest measured HgT concentration. We assume that the majority of the ligands measured using this method are organic (Lamborg *et al*., 2003) and correspond to a fraction of the measured DOC concentrations. This finding of strong ligand concentrations well in excess of HgT concentrations, in sediments in which methylation is nonetheless taking place, supports the hypothesis that there is a complex relationship between Hg(II), DOC, and methylation. Based on the assumption that strong ligand binding of Hg(II) makes it unavailable for methylation, we would not expect to see methylation in waters with strong ligand concentrations in excess of HgT concentrations. The fact that methylation is occurring in these porewaters, however, indicates either that some ligand-bound Hg(II) is being made available for methylation, or that non-equilibrium conditions exist between Hg(II) and strong organic ligands in this system, leaving a fraction of Hg(II) free for methylation.

The ion exchange resin data do not show discernable trends with depth, by season, or between sites. At the upper springs site in February, 2009, the positive correlation between the concentration of positive and neutral Hg species with the methylation rate potential (r^2=0.78) was stronger than the correlation of the methylation rate with any of the other parameters considered (negatively charged Hg species, DOC, sulfide). This correlation implies that, in this instance, positive and neutral Hg species do a better job of explaining the observed variability in methylation rates than the other factors. While this result may suggest an important role for neutrally charged Hg-S complexes in controlling methylation, the fact that such a strong correlation occurred only once prevents us from drawing broad conclusions.

Multivariate regression analysis of methylation rates against selected geochemical parameters (Table 1) shows that DOC is most often the most significant factor in explaining the observed variability in methylation rates. Sulfide is generally the second most significant factor. It is interesting to note, however, that the sign of the relationship between DOC and methylation rate varies. This relationship suggests that DOC sometimes stimulates and sometimes inhibits methylation.

Conclusions and Recommendations

Selected conclusions, as they relate to our research objectives, are outlined below:

1. Experimentally determining rates of mercury methylation and demethylation using isotopic tracer techniques .

The range of observed methylation rates was 0 to 9.5 fmol MeHg/g sediment/hr (0 to 34.5% of introduced spike/day), while the range of observed demethylation rates was 0.5 to 9.6 fmol MeHg/g sediment/hr (0 to 302.2% of introduced spike/day).

2. Determining whether observed MeHg concentrations were allochthonous or produced *in situ.*

Based on our results, we conclude that the majority of the MeHg present in the Allequash Creek wetland hyporheic zone is produced *in situ.* Hyporheic porewaters are a mixture of surface and groundwater, thus porewater MeHg could theoretically be transported into the hyporheic zone from either source. Because the stream flow is composed almost entirely of groundwater, however, MeHg transport in upwelling groundwater is the primary possible source for allochthonous inputs. The very low measured concentrations of MeHg in upwelling groundwater thus led us to the conclusion that MeHg is being produced in the hyporheic zone.

3. Assessing the influence of strong Hg-binding ligands on methylation rate potential and determining whether sulfide or dissolved organic carbon (DOC) played the greatest role in regulating Hg(II) bioavailability (as probed by methylation rate potential measurements) to methylating bacteria.

While we measured organic ligands in much greater concentrations than HgT in our porewater samples, methylation was still taking place in this system, suggesting either that Hg(II) complexation with organic matter does not prevent methylation, or that non-equilibrium conditions exist, allowing some Hg(II) not to be complexed with organic matter. DOC often showed a strong correlation with methylation rates (Table 1), both in univariate and multivariate models, suggesting that it plays an important role in controlling rates of methylation, however the relationship between DOC and methylation was sometimes positive and sometimes negative. Sulfide concentrations were also correlated with methylation rate potentials, but generally not as strongly as DOC. However, correlations between sulfide and methylation rate potentials were positive in every instance, suggesting strongly that increased sulfide concentrations lead to increased methylation. It is thus not entirely clear which geochemical parameter plays the most significant role in regulating Hg(II) bioavailability, however, sulfide appears to be the primary promoter of Hg(II) methylation.

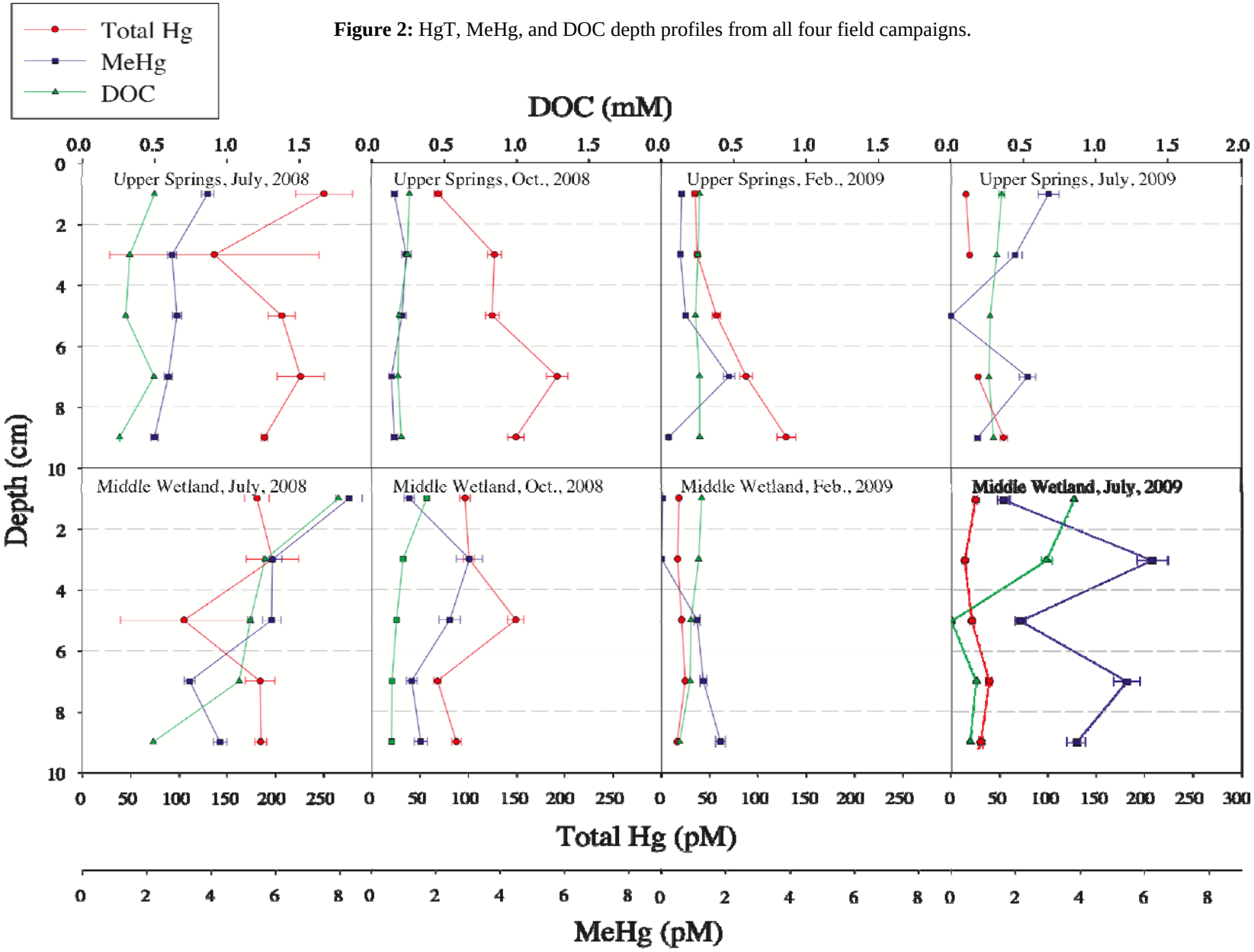

Figure 2: HgT, MeHg, and DOC depth profiles from all four field campaigns.

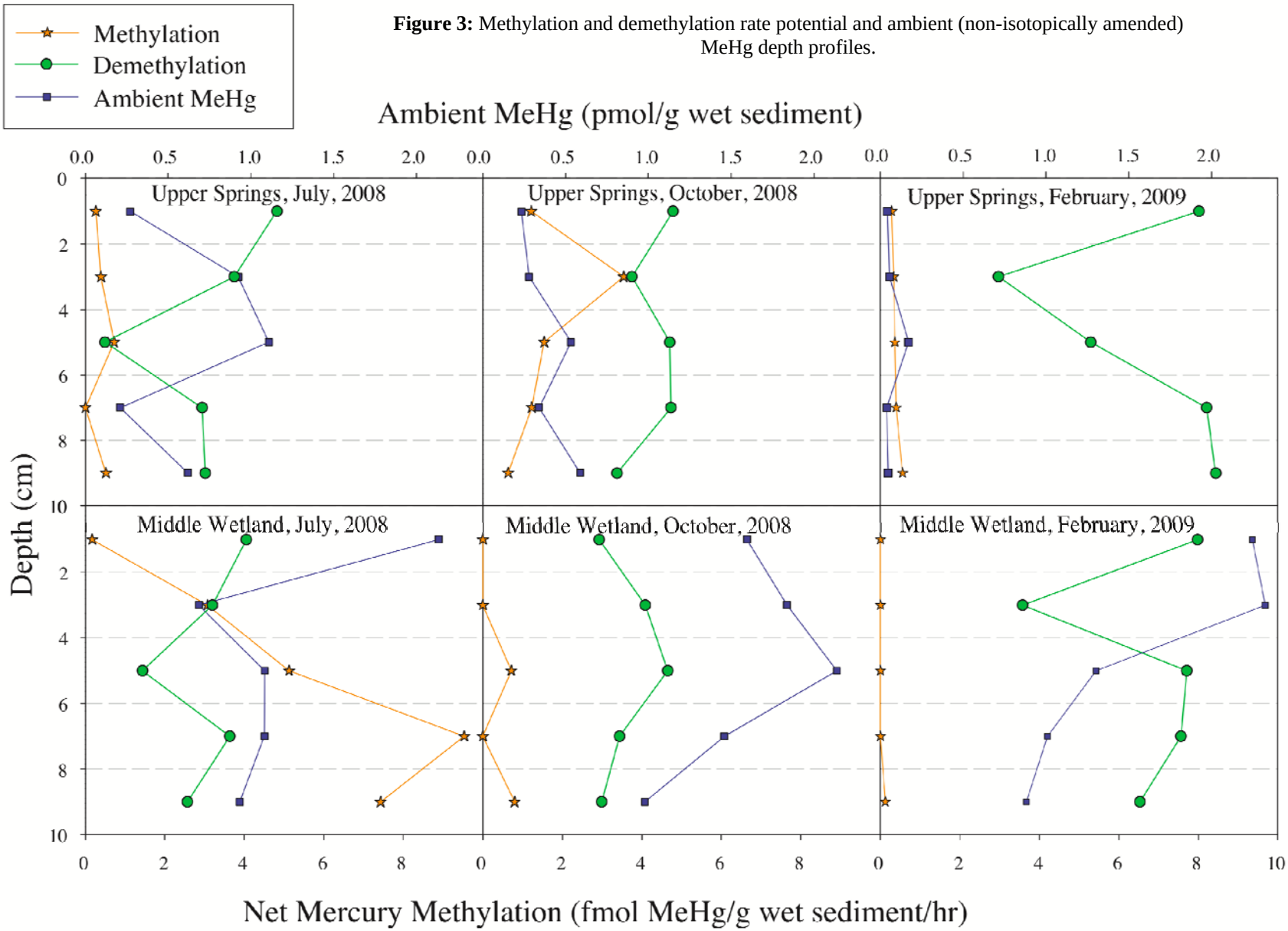

Figure 3: Methylation and demethylation rate potential and ambient (non-isotopically amended) MeHg depth profiles.

4. Determining whether neutral complexes of mercury and sulfide, such as HgS^0, are the most bioavailable form of Hg(II) to bacteria.

There was no clear correlation between the concentration of neutral and positive Hg complexes and methylation rates. It is thus unclear, based on the data presented here, whether these complexes are more bioavailable, and therefore more readily methylated.

5. Comparing two geochemically different sites within the wetland, with different groundwater flow patterns, to determine if Hg(II) bioavailability and methylation were influenced by the contrasting redox conditions.

While there are clear and consistent geochemical differences between the two sites studied, methylation rates at one site do not consistently differ from the other. This finding suggests that methylation and bioavailability are highly variable, and likely the result of several different factors that can change rapidly at each site.

Further investigation of controls on methylation in hyporheic zones should involve experimental manipulation of hyporheic sediments from the Allequash Creek wetland, in order to determine the specific influence of each on methylation and bioavailability. The key finding of this study, from a management perspective, is that the majority of the MeHg in this system is produced internally, rather than imported from external sources. The findings of this study can aid in the creation of more targeted fish consumption advisories, can help improve mercury cycling computer models, and can lead to better wetland management practices to limit MeHg production.

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

Publications:

Creswell, J.E., Kerr, S.C., Meyer, M.H., Babiarz, C.L., Shafer, M.M., Armstrong, D.E., and Roden, E.E. 2008. Factors controlling temporal and spatial distribution of total mercury and methylmercury in hyporheic sediments of the Allequash Creek wetland, northern Wisconsin. J. Geophys. Res. - Biogeosciences. **113:**1-9.

Presentations:

Creswell, J.E., Babiarz, C.L., Shafer, M.M., Roden, E.E., and Armstrong, D.E. 2007. Mercury Methylation, Demethylation, and Bioavailability in the Hyporheic Sediments of a Northern Wisconsin Wetland. Poster presentation. American Geophysical Union Fall Meeting, San Francisco, CA, 10-14 December, 2007.

Creswell, J.E., Babiarz, C.L., Shafer, M.M., and Armstrong, D.E. Measurements of mercury methylation rates and bioavailability in the Allequash Creek Wetland, Northern Wisconsin. Poster presentation. American Geophysical Union Fall Meeting, San Francisco, CA, 15-19 December, 2008.

Creswell, J.E., Babiarz, C.L., Shafer, M.M., Armstrong, D.E., and Roden, E.E. Mercury methylation, demethylation, and bioavailability in the hyporheic sediments of a northern Wisconsin wetland, USA. Oral presentation. Ninth International Conference on Mercury as a Global Pollutant, Guiyang, China, 7-12 June, 2009.

Creswell, J.E., Babiarz, C.L., Shafer, M.M., Armstrong, D.E., and Roden, E.E. Bioavailability of mercury to methylating bacteria in a northern Wisconsin wetland: Results from a year of field sampling. Oral presentation. American Chemical Society National Meeting, Washington, D.C., 16-20 August, 2009.

Influence of Wetland Hydrodynamics on Subsurface Microbial Redox Transformations of Nitrate and Iron.

Basic Information

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Principal Investigators:	, Jean Bahr

Publications

1. Bahr, J.M. and E.E. Roden. 2009. Influence of Wetland Hydrodynamics on Subsurface Microbial Redox Transformations of Nitrate and Iron. Water Resources Institute, University of Wisconsin, Madison. 15p. Final_WR07R007.pdf
2. Miller, C.A. 2009. Influence of Wetland Dynamics on Microbial Redox Transformations of Nitrate and Iron. Master of Science (Geology). University of Wisconsin-Madison.
3. Miller, C.A. , J.M. Bahr, and E.E. Roden, Influence of wetland hydrodynamics on subsurface microbial redox transformations of nitrate and iron, AWRA WI Section 33rd Annual Meeting, p. 40.

INFLUENCE OF WETLAND HYDRODYNAMICS ON MICROBIAL REDOX TRANSFORMATIONS OF NITRATE AND IRON

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Project Summary

Title: Influence of Wetland Hydrodynamics on Microbial Redox Transformations of Nitrate and Iron

Project ID: WRI Project Number WR07R007

Investigators:

PIs: Jean M. Bahr, Professor, Geoscience; Eric E. Roden, Professor, Geoscience
Research Assistant: Cassidy A. Miller, Graduate Student, Geoscience
Research Associate: Evgenya Shelobolina, Post-doc, Geoscience

Period of Contract: 7/1/07-6/30/09

Background/Need:
Nitrogen (N) is a limiting nutrient in many aquatic ecosystems, particularly in estuarine and coastal marine environments. The anthropogenic N delivered in surface waters to coastal environments is a non-point source pollutant that originates primarily from agricultural activities. Thus, understanding controls on the transport and fate of N in inland waters is critical to maintaining the ecological health and economic viability of coastal resources. In addition to effects on ecosystems, nitrate contamination of groundwater is a well-documented problem throughout the world. In Dane County an estimated 30% of private wells contain nitrate concentrations that exceed drinking water standards.

Objectives:
This research sought to explore the interaction of nitrate and iron redox cycles in freshwater aquifers, a poorly understood but potentially significant influence on the fate of nitrate in the environment, through monitoring the geochemical and microbial properties of groundwater over a one year period.

Methods:
Several multilevel sampling devices were installed in the wetland sediments for the collection of groundwater samples. Three different locations in the wetland were chosen for this project and are referred to as ML1, the western transect, and the eastern transect. Groundwater samples were collected monthly using a peristaltic pump and the geochemistry of each sample was determined though a combination of in-field and laboratory analyses. Due to time constraints samples for microbial analysis were collected only once during the sampling period. These samples were analyzed using the most-probable number (Woomer, 1994) and 16S rDNA clone library analyses.

Results and Discussion
At ML1, redox conditions, and therefore iron and nitrate concentrations, varied considerably. Oxic conditions were associated with elevated nitrate concentrations and decreased iron concentrations. When concentrations shifted towards anoxic, a decrease in nitrate concentrations and an increase in iron concentrations were observed. Microbial results from this location

indicate the presence of at least low concentrations of bacteria related to the nitrate and iron cycles. This suggests that coupling of the two redox cycles is likely occurring in the aquifer sediments surrounding ML1.

Nitrate was never observed along the western transect. Conditions were consistently anoxic with significant concentrations of ferrous iron observed throughout the study period. Microbial data indicates the strong presence of nitrate-reducing and iron-reducing bacteria at this location.

Along the eastern transect low levels of nitrate were observed under oxic conditions at the upgradient wells while anoxic conditions were observed downgradient. Although microbial and geochemical sampling failed to identify the coupling of the two redox cycles, some process is removing nitrate from groundwater upgradient of ML8.

Conclusions:
Observations of nitrate and iron concentrations at ML1 are consistent with the conceptual model and are most likely a result of microbial activity. MPN counts and 16S rDNA clone library data indicate the presence of at least low concentrations of bacteria related to the nitrate and iron cycles. This suggests that coupling of the two redox cycles is likely occurring nearby and may occur at this location in the event of a shift to more reducing conditions.

Although nitrate was never observed along the western transect, geochemical and microbial data indicate that iron and nitrate redox cycles are likely coupled in the sediments immediately upgradient of ML4. Geochemical data indicates that nitrate is likely flowing towards the transect after leaching out of the vadose zone of the nearby field. Microbial analyses indicate that microbially-mediated nitrate reduction removes all nitrate from groundwater prior to the groundwater reaching ML4.

Along the eastern transect, nitrate is removed as dissolved oxygen concentrations decrease downgradient. Insufficient microbial data along this transect prevents indentifying the microbial community that may be responsible for nitrate removal. However, abundant concentrations of ferrous iron observed downgradient indicate that the coupling of nitrate and iron cycles may be one of the responsible processes affecting the fate of nitrate along the transect.

Related Publications:
Miller, C.A. 2009, Influence of wetland dynamics on microbial redox reactions of nitrate and iron, MS Thesis, UW Madison Department of Geoscience

Miller, C.A. , J.M. Bahr, and E.E. Roden, Influence of wetland hydrodynamics on subsurface microbial redox transformations of nitrate and iron, AWRA WI Section 33rd Annual Meeting, p. 40.

Key Words: Nitrate, Iron

Funding: UWS

Introduction

Nitrate has become one of the most prominent contaminants in groundwater systems world-wide since the 1970's. Consequences of nitrate contamination of groundwater include both health concerns such as methemoglobinemia and environmental concerns such as excessive amounts of nitrate in the Mississippi River Basin flowing into the Gulf of Mexico (Burden, 1982).

Goolsby et al. (1999) showed that nonpoint sources, stemming from the application of fertilizers related to agricultural activity, accounted for approximately 74% of the total nitrogen flux to the Gulf of Mexico. Point sources from other agricultural, domestic, and industrial activities also have the potential to contribute to the flux of nitrate into groundwater systems (Smith and Duff, 1988; Smith et al., 1991). The relative contribution of each of these sources varies greatly depending on seasonal variations in the amount and timing of precipitation. Episodic events, such as the 1993 flooding of Midwestern states, have been shown to double the yearly influx of nitrate to the Gulf as a result of increased runoff and increased leaching from vadose zones, which may act as massive storage reservoirs for nitrate as it accumulates during dry periods (Goolsby et al., 1999).

Wetlands and riparian zones have been shown to be efficient at removing nitrate from groundwater, and several different processes affecting the fate of nitrate may occur in aquifer sediments. One poorly understood mechanism that may act as a pathway for nitrate removal is the coupling of nitrate and iron redox cycles. In this process, ferrous iron is oxidized via the reduction of nitrate under anoxic conditions. Unlike denitrification, this process does not necessarily result in the production of nitrogen gas, and may instead result in several different end products including NH_4^+, NO, NO_2^-, N_2O, or N_2 (Weber et al., 2006; Shelobolina et al., 2003). This process must be microbially-mediated in order to occur under conditions commonly found in aquifers and requires close coupling of the nitrate and iron cycles, such that nitrate and ferrous iron meet in opposing diffusion gradients. Within the zone where the two diffusion gradients meet, nitrate is reduced via the oxidation of ferrous iron, precipitating Fe(III)-oxides that may then be reduced by heterotrophic Fe(III)-reducing bacteria, thus replenishing the available supply of ferrous iron for use in the reduction of nitrate.

The objective of this study was to identify coupled microbial redox metabolism of nitrate and iron in sediments underlying a wetland through geochemical and microbial analyses of groundwater. From the geochemical data, potential locations for active iron and nitrate cycling were identified and the relative abundances of bacteria related to the nitrate and iron cycles were determined. The geochemical parameters combined with the microbial analyses were then used to assess the significance of microbially-mediated nitrate reduction in relation to microbial Fe redox metabolism.

Procedures and Methods

Location of Study

The research for this project was conducted in the Dorn Creek Marsh State Fishery Area in Dane County, Wisconsin. The Dorn Creek sub-watershed has an area of approximately 32.9 km^2, 25.6 km^2 of which are agricultural lands and 5.3 km^2 are wetlands (Rogers, 2006). The high percentage and close proximity of agricultural land use surrounding the Dorn Creek Marsh

results in high nutrient loading in the surface water and groundwater in the watershed, making it an ideal site for studying the coupling of nitrate and iron cycles in wetlands.

Dorn Creek flows from west to east through the wetland and empties into nearby Lake Mendota. Surface water chemistries observed during the summer of 2006 by Craig (2007) indicated that nitrate concentrations decrease by 90% over the reach of the stream, with a significant decrease in nitrate concentrations observed between sampling points 6 and 7 (Figure 1). Based on this information, two transects of multilevel sampling devices and piezometers were installed in the wetland, focusing primarily on the region where the greatest decrease in nitrate concentrations was observed (Figure 2). Additionally, a multilevel sampler (ML1) was installed near County Road Q based on groundwater nitrate concentrations observed in an 11.5 ft deep well installed during the 2006 season (Craig, 2007).

Figure 1: Nitrate concentrations of surface water samples collected during summer of 2006. Nitrate concentrations in mgL^{-1} NO_3-N (Craig, 2007).

Figure 2: Location of multilevel samplers and piezometers installed in the Dorn Creek Marsh State Fishery Area.

Site stratigraphy of the study area is characteristic of post-glacial lake sediments in the region. Core taken at ML1 consists of 0.76 meters of peat, underlain by a silty sand layer, a homogeneous clay layer, and highly variable layers of silt, sand, and gravel (Figure 3). The boring reached a depth of 8.1 meters before hitting bedrock.

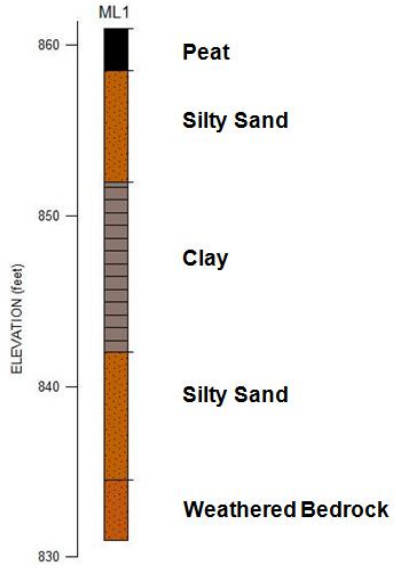

Figure 3: Stratigraphy at ML1 in the Dorn Creek Marsh State Fishery Area.

Core recovered from the eastern transect, which consists of ML5, ML6, ML7, ML8, and ML9, was also very heterogeneous. Groundwater along this transect flowed from south to north (ML9 to ML5), and stratigraphy varied from well-sorted sand and gravel on the southern end of the transect to a complex distribution of peat, clay, silt, and sand on the northern end (Figure 4). The western transect, which consisted of ML2, ML3, and ML4, was relatively uniform by comparison. Along this transect groundwater flows from south to north (ML4 to ML2) and sediments consisted of approximately 1 meter of peat underlain by silty sand, well-sorted sand, and clay (Figure 5).

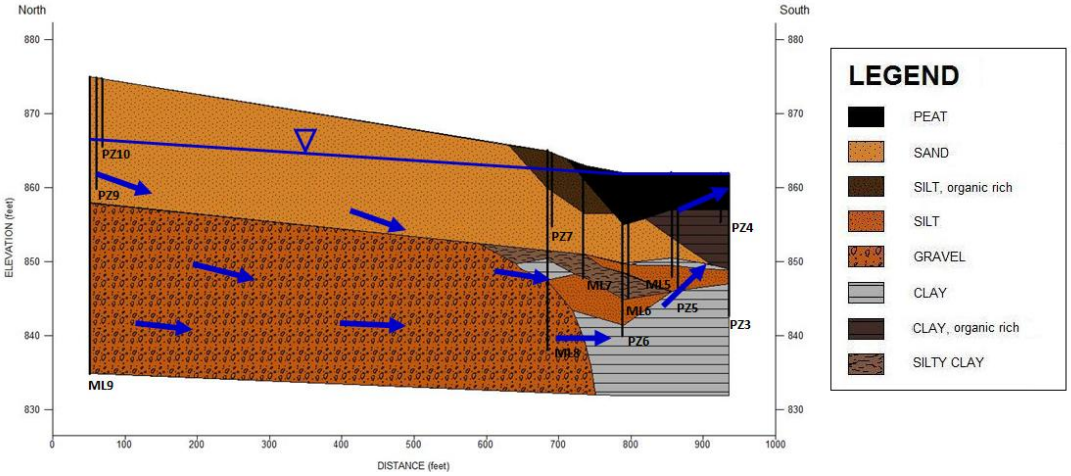

Figure 4: Stratigraphy of the eastern transect in the Dorn Creek Marsh State Fishery Area.

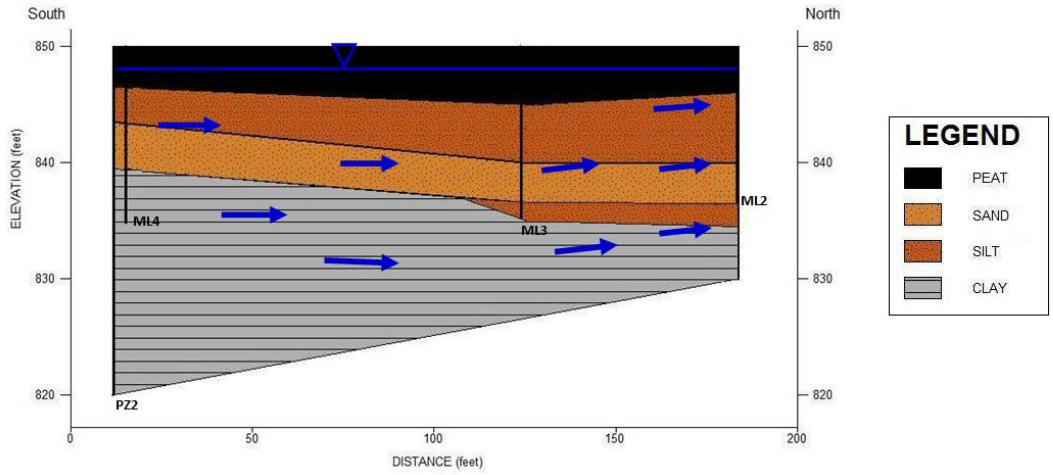

Figure 5: Stratigraphy of the western transect in the Dorn Creek Marsh State Fishery Area.

Field Methods and Laboratory Analysis

Groundwater samples were collected for chemical analyses from every multilevel sampling device except for ML2 and ML6. These two locations failed to produce groundwater in sufficient amounts for sampling due to malfunction of the multilevel sampling device. Groundwater was collected from multilevel samplers using a peristaltic pump and the geochemistry of each sample was determined though a combination of in-field and laboratory analyses. Each sampling point was purged by pumping at least 500 ml of groundwater prior to sampling. Specific conductance and temperature were determined in-situ using a YSI Model 30 handheld conductivity meter. Analyses for dissolved oxygen were also performed in-situ using CHEMets® R-7501 and K-7512 field test kits. Anions chloride, sulfate, and nitrate were analyzed with a Dionex ion chromatograph model ICS 1000. Iron concentrations were determined in the method outline by Stookey (1970) using a Shimadzu UV Mini 1240 Spectrophotometer. Some groundwater samples were also analyzed for various metals, including Ca, Cu, Fe, Mg, and Mn, using a Varian Vista-MPX CCD Simultaneous ICP-OES. Microbial samples were analyzed using the most-probable number (Woomer, 1994) and 16S rDNA clone library analyses.

Results and Discussion

ML1

Geochemical results at ML1 indicate two distinct geochemical environments. The first is located above the clay layer, at depths of less than 3.0 meters. This shallow zone is characterized by highly variable concentrations of nitrate, iron, and oxygen. Increases in nitrate concentrations at this location are associated with decreased ferrous iron and elevated oxygen concentrations, while decreasing nitrate concentrations are associated with elevated ferrous iron and decreased oxygen concentrations (Figure 6a). No microbial data were acquired from sampling points within this zone of groundwater, making it difficult to infer the mechanism responsible for nitrate reduction.

In the deeper zone of groundwater at ML1, geochemical data indicated consistently oxic conditions with high nitrate concentrations and very low ferrous iron concentrations.

Groundwater samples for microbial analysis were obtained from the deepest sampling point at ML1 (Table 1). Results of the microbial analysis and indicated that the dominant process is nitrate reduction, with microbes related to the iron and sulfur cycles also present (Table 2; Table 3).

Western Transect

Groundwater samples from ML3 and ML4 indicated primarily reducing conditions along the western transect, and nitrate was never observed at either location during the sampling period (Figure 6b). Geochemical results indicate two distinct flow paths along the transect, one that is observed in the shallow sampling points and contains high ion concentrations, and one that is deeper in the sediments and contains a low concentration of ions. The distinction between the two flowpaths is well-demonstrated by calculating the molar ratio of calcium to magnesium in groundwater from each sampling point. In the deeper flow path, which is observed in the deepest two sampling points at ML4, the calcium-to-magnesium ratio is approximately 0.4, while in the shallow sampling points the ratio increases to approximately 1.0 (Figure 7). Most likely, the differences observed are a result of fertilizer application on the cornfield immediately south of ML4 which provides a steady influx of nutrients to the shallow groundwater flow path. Aside from the relative concentrations of calcium and magnesium, the fertilizer impact is also observed in concentrations of sulfate and chloride (Figure 8). Typically, elevated nitrate concentrations would also be observed. However, it appears that all nitrate is removed from groundwater via microbially-mediated pathways prior to reaching ML4. Given the significant concentration of ferrous iron along the transect, there is great potential for this to occur lithotrophically, with the nitrate and iron cycles coupled in the vicinity of ML4. Microbial observations at ML4 are consistent with geochemical results. The 16S rDNA clone library developed for ML4 indicated the presence of iron-reducing bacteria (Table 2), while MPN results indicate that nitrate-reducing bacteria dominate the microbial community (Table 3).

East Transect

Groundwater samples from the eastern transect indicate oxidizing conditions at ML9 and a transition to reducing conditions downgradient at ML8, ML7, and ML5. Groundwater samples were not collected at ML6 due to inadequate flow from sampling points. Groundwater from ML9 contained low levels of nitrate during the sampling period (<6.0 mg/L) and very low ferrous iron concentrations. Downgradient, nitrate concentrations were below detection throughout the sampling period and ferrous iron concentrations were significantly elevated (Figure 6c). Overall, sampling points with elevated nitrate concentrations were oxic and contained very low ferrous iron concentrations, while sampling points that did not contain nitrate were anoxic and contained elevated ferrous iron concentrations. This is consistent with the conceptual model that significant concentrations of ferrous iron and nitrate will not be observed together, as the nitrate would be reduced via the microbial oxidation of Fe(II). As would be expected under the oxic conditions observed at ML9, both MPN and 16S rDNA clone library analyses indicated aerobic heterotrophs dominated the microbial community (Table 2; Table 3).

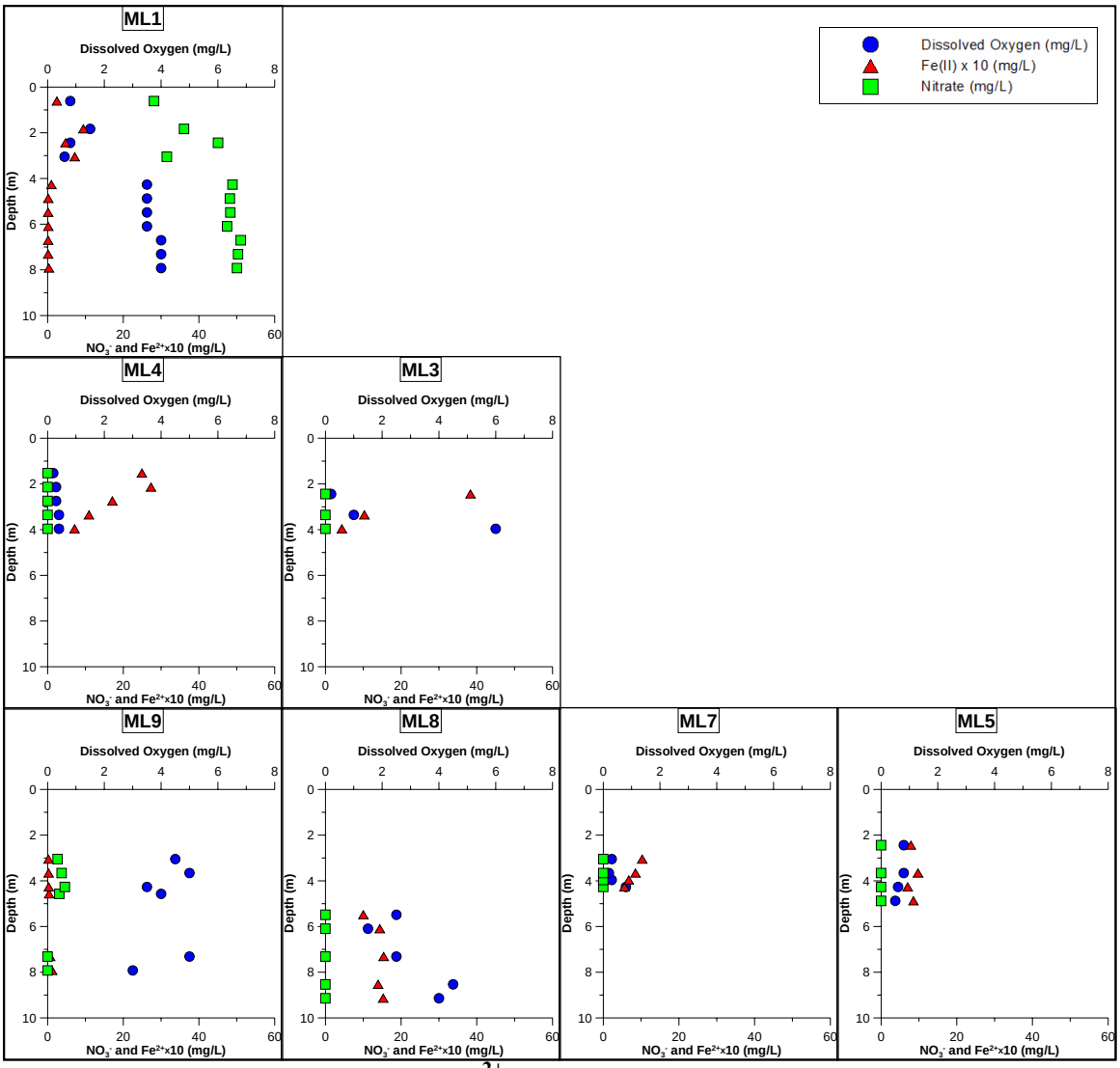

Figure 6: Concentration of NO_3^-, Fe^{2+} and Dissolved Oxygen during the November 2008 sampling round.

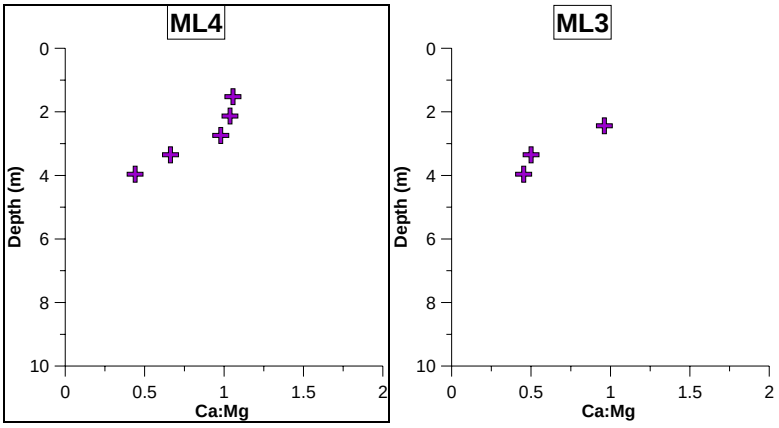

Figure 7: Ratio of calcium to magnesium at the western transect during the November 2008 sampling round.

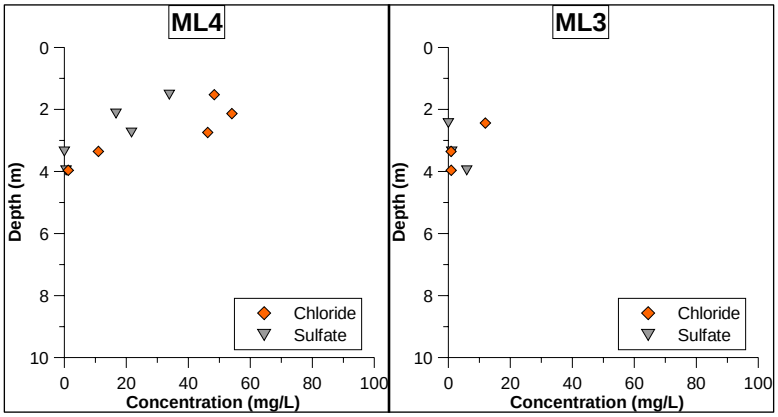

Figure 8: Concentration of sulfate and chloride during the November 2008 sampling round.

Table 1: Geochemistry of groundwater samples collected for microbial analyses.

Well	Depth (m)	T (°C)	Cond. µs/cm	D.O. (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	DOC mg/L)	NO_3^- (mg/L)	Fe(II) (mg/L)
ML1	7.9	13.9	682	4.0	44.0	19.2	1.34	65.7	0.06
ML4	2.7	14.0	738	0.3	42.9	25.0	1.69	0.0	1.36
ML7	4.0	10.9	551	0.4	1.42	12.5	1.54	0.0	0.69
ML9	4.6	13.3	897	2.5	3.19	38.4	2.41	3.7	0.09

Table 2: Summary of phylogenetic affiliation and distribution of 16S rDNA gene clones from clone libraries of groundwater from wells ML1, ML4, and ML9

Phylogenetic group	Nearest relative (GenBank accession no.)	Base pairs considered	% similarity	Potential physiology	No. of related clones in groundwater from:		
					ML1	ML4	ML9
α-Proteobacteria	*Sphingomonas mathurensis* strain SM13 (EF424400)	1422	94%	Aerobic heterotroph	0	0	6
	Uncultured α-Proteobacterium (EU244149)	652	98%	?	4	0	2
β-Proteobacteria	*Polaromonas jejuensis* strain JS12-13 (EU030285)	1288	98%	Aerobic and denitrifying	2	0	14
	Uncultured β-Proteobacterium (GQ105041)	592	91%	Aerobic and nitrate-reducing	0	0	3
	Massilia aurea strain AP13T (AM231588)	1441	99%	Aerobic heterotroph	0	0	10
δ-Proteobacteria	*Geobacter psychrophilus* strain P35 (AY653549)	665	96%	Fe(III) reduction	4	6	0
	Desulforegula conservatrix strain Mb1PaT (AF243334)	1436	98%	Sulfate reduction	8	12	0

Table 2 (continued)							
ε-Proteobacteria	Uncultured ε-Proteobacterium (AM086106)	1399	92%	?	4	0	0
	Pseudomonas veronii strain S3 (AY179328)	1463	99%	Aerobic and denitrifying	0	0	136
	Pseudomonas fragi strain B531 (AY581136)	604	97%	Aerobic heterotroph	0	0	1
Verrucomicrobia	Uncultured Verrucomicrobia bacterium (DQ676300)	1467	89%	Aerobic heterotroph	4	4	0
Cyanobacteria	Uncultured Cyanobacterium (EF520515)	1436	97%	Fermentation or aerobic heterotrophy	2	4	0
Acidobacteria	Uncultured Acidobacterium (FJ479521)	506	97%	Fermentation	0	0	2
Bacteroidetes	*Pedobacter agri* strain PB92 (EF660751)	1454	99%	Aerobic heterotroph	0	0	6
Clostridia	Syntrophomonas zehnderi strain OL-4 (DQ898277)	1420	89%	Syntrophic organic matter degrader	0	4	0
	Uncultured Desulfosporosinus (EU981221)	634	96%	Sulfate reduction	0	2	0
	Clostridium cellulolyticum strain H10 (X71847)	1415	92%	Fermentation	4	0	0
Chloroflexi	Uncultured Chloroflexi (DQ811890)	639	84%	Fermentation	2	0	0
Candidate divisions OD1 and OP11	Uncultured bacterium (AB252962)	1414	85%	Sulfur cycle	6	6	6

Table 3: Results of the most-probable number method

Microbial Group	Most probable number (MPN) per ml of GW			
	ML1A	ML4	PZ9	ML7
Nitrate reducers using acetate as the e donor	$(2.39 \pm 1.74)^* 10^2$	$(2.39 \pm 1.74)^* 10^2$	$(4.62 \pm 1.75)^* 10$	$(1.10 \pm 0.39)^* 10$
Fe(III) reducers using acetate as the e donor	$(1.12 \pm 0.64)^* 10^{-1}$	2.40 ± 1.74	< 0.03	$(1.12 \pm 0.64)^* 10^{-1}$
Lithotrophic Fe(II) oxidizers using nitrate as the e acceptor	$(1.12 \pm 0.64)^* 10^{-1}$	$(1.12 \pm 0.64)^* 10^{-1}$	$(1.12 \pm 0.64)^* 10^{-1}$	< 0.03
Fe(II) oxidizers using nitrate as the e acceptor and acetate as C source	$(1.12 \pm 0.64)^* 10^{-1}$	$(1.12 \pm 0.64)^* 10^{-1}$	$(1.12 \pm 0.64)^* 10^{-1}$	< 0.03
Aerobic heterotrophs using acetate as the e donor	4.62 ± 1.75	$(2.39 \pm 1.74)^* 10$	$(2.39 \pm 1.74)^* 10^3$	$(4.62 \pm 1.75)^* 10$

Conclusions and Recommendations

In the upper sediments at ML1 the geochemical data indicate that redox cycles of iron and nitrate are coupled at this location. Redox conditions appear to be highly variable and fluctuate between

oxic and anoxic conditions during the monthly sampling rounds. Oxic conditions are associated with high concentrations of nitrate and low concentrations of dissolved iron. When anoxic conditions are present, however, nitrate concentrations decrease significantly and soluble iron concentrations increase. These observations are consistent with the conceptual model and are most likely a result of microbial activity. Iron reducing bacteria are likely creating abundant supplies of soluble iron under anoxic conditions. The soluble Fe(II) is then available for use by lithotrophic nitrate-reducing bacteria, which use the reduced iron species as an election donor. At depths greater than 10 feet at ML1, conditions were consistently oxic, with high concentrations of nitrate and low concentrations of soluble iron observed throughout the 12 month sampling period. Although the geochemical data do not indicate the coupling of nitrate and iron redox cycles at this depth, MPN counts and 16S rDNA clone library data indicate the presence of at least minor concentrations of bacteria related to the nitrate and iron cycles. This suggests that coupling of the two redox cycles is likely occurring nearby and may occur at this location in the event of a shift to more reducing conditions.

Although nitrate was not detected along the western transect during the sampling period, geochemical and microbial data indicate that iron and nitrate redox cycles are likely coupled in the sediments immediately upgradient of ML4. At ML4, reducing conditions were consistently observed throughout the sampling period and also in the sediment iron extractions. These anoxic conditions were characterized by high concentrations of soluble iron and an absence of nitrate. As stated previously, the impact of agricultural fertilizers along this transect is detected through elevated measurements of sulfate, chloride, calcium, magnesium, and conductivity. Although fertilizers also contain high concentrations of nitrate, it appears that all nitrate is removed prior to the groundwater reaching ML4. Microbial analysis results indicate that heterotrophic nitrate reducers are primarily responsible for nitrate removal as they dominate the MPN counts. However, the abundance of reduced iron at this location and the presence of lithotrophic Fe(II) oxidizing bacteria that use nitrate as an electron donor suggests that the two redox cycles are coupled at this location and are at least partially responsible for the reduction of nitrate upgradient of ML4.

Along the eastern transect, geochemical and microbial data did not indicate where iron and nitrate redox cycles are potentially coupled. However, that does not preclude coupling of the two redox cycles, as water chemistry and sediment iron extractions indicate that redox conditions along the transect transition from oxic conditions with low concentrations of nitrate and iron at ML9 to anoxic conditions with no nitrate and high dissolved iron concentrations at ML8, ML7 and ML5. Nitrate is likely leaching from the vadose zone of the nearby field and is removed from the groundwater prior to reaching ML8. Although attempts to build a 16S rDNA clone library from groundwater samples at ML7 failed due to low microbial concentrations, MPN analysis results at this location do indicate the presence of heterotrophic nitrate reducers as well as iron reducing bacteria. Therefore, the redox cycles of nitrate and iron are likely coupled upgradient of ML8. However, further evaluation of this transect is necessary to fully understand the processes occurring in the subsurface.

Future work at this location that would enhance the knowledge obtained through this project includes a more comprehensive microbial analysis. A comprehensive microbial analysis of all sampling points in the wetland at three different points throughout the year would be a

significant step towards meeting the goal of the project by revealing the spatial and temporal variations in the microbial community throughout the wetland.

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Award No. 08HQGR0148 The Transport, Fate and Cycling of Mercury in Watersheds and Air Sheds

Basic Information

Title:	Award No. 08HQGR0148 The Transport, Fate and Cycling of Mercury in Watersheds and Air Sheds
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End Date:	9/14/2013
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Congressional District:	2nd
Research Category:	Water Quality
Focus Category:	Toxic Substances, Wetlands, Water Quality
Descriptors:	mercury, catchment processes
Principal Investigators:	Jim Hurley, David P. Krabbenhoft

Publications

1. Kolker, A., Olson, M., Krabbenhoft, D.P., Tate, M.T., and Engle. M.A., 2010, Patterns of mercury dispersion from local and regional emission sources, rural Central Wisconsin, USA, Atmos. Chem. Phys., 10, 1–10, 2010.
2. Engle, M.A., Tate, M.T., Krabbenhoft, D.P., Schauer, J.J., Kolker, A., Shanley, J.B., Bothner, M.H. 2010, Comparison of Atmospheric 1 Mercury Speciation and Deposition at Nine Sites across Central and Eastern North America, Geophysical Research (in press).

Annual Progress Report

Selected Reporting Period: 3/1/2009 - 2/28/2010

Submitted By: Jim Hurley
Submitted: 6/10/2010

Project Title

WR08R005: The Transport, Fate and Cycling of Mercury in Watersheds and Air Sheds

Project Investigators

James Hurley, University of Wisconsin Sea Grant Institute

Progress Statement

This project looks at two mercury related questions: (1) mercury in watersheds; and, (2) mercury cycling and transport in the atmosphere. During reporting period the project completed its first year of "recovery" (i.e., no longer loading mercury to the study watershed) on the Mercury Experiment to Assesses Atmospheric Loadings in Canada and the US (METAALICUS) project. Our portion of the project is to monitor the watershed-scale response of the artificial load of mercury that was administered from 2001 through 2007 using three different stable isotopes (198Hg, 201Hg, 202Hg) to the study wetland, uplands and lake, respectively. During the current phase of the project, we will ensue with monitoring the response of the watershed to a mercury "load reduction". On the atmospheric studies, the project performed two assessments: (1) a large scale assessment of mercury concentrations and speciation at nine sites spanning most of the US including Puerto Rico; and (2) a detailed study of mercury deposition spanning time and space domain near a emission stack in central Wisconsin..

Principal Findings and Significance

Principal Findings and Significance

Description

Our results show that in coastal settings, the intersection of terrestrially based mercury emission sources interacting with chemical oxidants formed in the marine boundary layer result in exacerbated mercury deposition in the near coastal environments. These finds have direct implications for water-resource rich ecosystems along the East Coast of the US, and

people who fish in those waters. Also, the application of the mercury depositon model developed by this project to these field settings provides a scientifically based explanation for why coastal areas in the southeastern US are among the highest mercury deposition zones.

Description

Results from the past year of data collection revealed that despite the cessation of loading the watershed on the METAALICUS project, concentrations in runoff continued to increase. This phenomenon reveals the inherent time lags that are part of the natural response to changes in loading watersheds. On the atmospheric studies portion of the project the assessment revealed the importance of the marine boundary layer for facilitating atmospheric mercury reactions and deposition.

Journal Articles & Other Publications

Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Characterization and cycling of atmospheric mercury along the central U.S. Gulf of Mexico Coast
Author(s)	Engle, M.A., Tate, M.T., Krabbenhoft, D.P., Kolker, A., Olson, M.L., Edgerton, E.S., DeWild, J.F., and McPherson, A.K.
Publication/Publisher	Applied Geochemistry 23 (2008), pp. 419–437.
Year Published	2008
Volume & Number	23
Number of Pages	19
Description	
Any Additional Citation Information	

Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Patterns of mercury dispersion from local and regional emission sources, rural Central Wisconsin, USA
Author(s)	Kolker, A., Olson, M., Krabbenhoft, D.P., Tate, M.T., and Engle. M.A.,
Publication/Publisher	Atmos. Chem. Phys.,
Year Published	2010
Volume & Number	10, 1–10
Number of Pages	10
Description	Abstract. Simultaneous real-time changes in mercury (Hg) speciation- reactive gaseous Hg (RGM), elemental Hg (Hg°), and fine particulate Hg (Hg-PM2.5), were determined from June to November, 2007, in ambient air at three locations in rural Central Wisconsin. Known Hg emission sources within the airshed of the monitoring sites include: 1) a 1114 megawatt (MW) coal-fired electric utility generating station; 2) a Hg-bed chlor-alkali plant; and 3) a smaller (465 MW) coal-burning electric utility. Monitoring sites, showing sporadic elevation of Hg°, Hg-

	PM2.5, and RGM were positioned at distances of 25, 50 and 100 km northward of the larger electric utility. Median concentrations of Hg°, Hg-PM2.5, and RGM were 1.3–1.4 ng m−3, 2.6 –5.0 pg m−3, and 0.6–0.8 pg m−3, respectively. A series of RGM events were recorded at each site. The largest, on 23 September, occurred under prevailing southerly winds, with a maximum RGM value (56.8 pg m-3) measured at the 100 km site, and corresponding elevated SO2 (10.4 ppbv; measured at 50 km site). The finding that RGM, Hg°, and Hg-PM2.5 are not always highest at the 25 km site, closest to the large generating station, contradicts the idea that RGM decreases with distance from a large point source. This may be explained if: 1) the 100 km site was influenced by emissions from the chlor-alkali facility or by RGM from regional urban sources; 2) the emission stack height of the larger power plant promoted plume transport at an elevation where the Hg is carried over the closest site; or 3) RGM was being generated in the plume through oxidation of Hg°. Operational changes at each emitter since 2007 should reduce their Hg output, potentially allowing quantification of the environmental benefit in future studies.
Any Additional Citation Information	

Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Comparison of Atmospheric Mercury Speciation and Deposition at Nine Sites across Central and Eastern North America
Author(s)	Engle, M.A., Tate, M.T., Krabbenhoft, D.P., Schauer, J.J., Kolker, A., Shanley, J.B., Bothner, M.H.
Publication/Publisher	Geophysical Research
Year Published	In Press
Volume & Number	
Number of Pages	
Description	
Any Additional Citation Information	

From Sandbags to Sanity: Lessons from the Midwest Floods of 2008

Basic Information

Title:	From Sandbags to Sanity: Lessons from the Midwest Floods of 2008
Project Number:	2009WI215B
Start Date:	3/1/2009
End Date:	2/28/2010
Funding Source:	104B
Congressional District:	2
Research Category:	Social Sciences
Focus Category:	Law, Institutions, and Policy, Floods, Hydrology
Descriptors:	None
Principal Investigators:	Donald Patrick Moynihan

Publication

1. Donald P. Moynihan (ed); Roxanne Gray, Gerry Galloway, Gerry Galloway, Ray Burby, Sandra McLellan, Tom A nderson, Keith Lang, Terri Leece, Daniel A lesch, Joan Ballweg, Larry Larson. 2010. From Sandbags to Sanity: Dealing with Flood Risk in Wisconsin. Water Resources Institute. In Press.

Annual Progress Report

Selected Reporting Period: 3/1/2009 - 2/28/2010

Submitted By: Donald Moynihan
Submitted: 6/10/2010

Project Title

WR09R001: From Sandbags to Sanity: Lessons from the Midwest Floods of 2008

Project Investigators

Donald Moynihan, University of Wisconsin-Madison

Progress Statement

This project funded a day-long seminar that welcomed more than 130 representatives from local government, state agencies, engineering firms, academia, non-profits, public health and the Wisconsin Legislature. The event took place on April 20, 2009, at the Monona Terrace, Madison, Wisconsin.

The event was coordinated by emergency management scholar Donald Moynihan and the La Follette School of Public Affairs at the University of Wisconsin-Madison, and by the Water Resources Institute. It included contributions from two national experts, Gerry Galloway, of the University of Maryland, and Ray Burby, of the University of North Carolina at Chapel Hill, as well as more than a dozen University of Wisconsin researchers and government officials to discuss these issues.

The meeting was timed to have a direct input on public policy. It included representatives from Gov. Jim Doyle's Wisconsin Recovery Task Force and the Wisconsin Legislative Council's Special Committee on Emergency Management & Continuity of Government, including and Rep. Joan Ballweg. Their sessions allowed a back-and-forth discussion between state policymakers and local government officials who are the front line of response.

Principal Findings and Significance

Principal Findings and Significance

Description

The projects main goal was to connect local government managers and state policymakers with new research from the US and elsewhere relevant to managing flood events. This basic goal was met in a number of ways. The conference had over 130 participants, most of whom were local government officials from across the state of Wisconsin. The participants gave high

marks for the conference. A post-conference survey, given to all participants, found that participants provided an average score of over 4.5 in response to the statement "overall, this symposium was worth attending" (on a scale where 1= strongly disagree, and 5 = strongly agree).

Rather than allow the seminar to become a one-off event, the project sought to maximize access to the seminar contents using the web. After the seminar was completed, all of the conference materials (including powerpoint presentations, speeches, and a video of proceedings) were made publicly available. A conference website has been maintained at: http://www.lafollette.wisc.edu/publicservice/floods/index.html

Currently, the Water Resources Institute and Professor Moynihan are completing a final report from the conference (scheduled publication date is August 20 2010) that will offer an accessible summary of the key lessons of the conference. This report will be disseminated to conference participants, local government officials, state policymakers, and the Association of State Floodplain Managers.

Journal Articles & Other Publications

Publication Type	Proceedings/Symposium
Title	From Sandbags to Sanity: Dealing with Flood Risk in Wisconsin
Author(s)	Donald P. Moynihan (ed); Roxanne Gray, Gerry Galloway, Gerry Galloway, Ray Burby, Sandra McLellan, Tom Anderson, Keith Lang, Terri Leece, Daniel Alesch, Joan Ballweg, Larry Larson
Publication/Publisher	Water Resources Institute
Year Published	In Press
Volume & Number	
Number of Pages	60
Description	This document summarizes the presentations of the main participants at the Sandbags to Sanity seminar.
Any Additional Citation Information	

Students & Post-Docs Supported

Student Name	Erikl Viel
Campus	University of Wisconsin-Madison
Advisor Name	Donald Moynihan
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month	May
Graduation Year	2010

Department	La Follette School of Public Affairs
Program	Masters in Public Affairs
Thesis Title	N/A for professional degree program
Thesis Abstract	

Combination of Co-Precipitation with Zeolite Filtration to Remove Arsenic from Contaminated Water

Basic Information

Title:	Combination of Co-Precipitation with Zeolite Filtration to Remove Arsenic from Contaminated Water
Project Number:	2009WI216B
Start Date:	3/1/2009
End Date:	2/28/2010
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Toxic Substances, Treatment, Groundwater
Descriptors:	None
Principal Investigators:	Zhaohui Li

Publications

1. Zhaohui Li, Andria J. Koski, Justin S. Merrill, Jeffrey J, Randolph, Stephan R. Kurdas, Jonathan H. Friend, Sarah J. Antinucci, Allison E. Reiley, Caren J. Ackley, Nancy A Fenske, Laura A . Schulz, Jiin-Shuh Jean, C.-C. Liu, A .H.M.S. Reza. 2010. Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred. Taylor Francis Group. Arsenic in the Environment.
2. Hanlie Hong, Ke Yin1, Xulong Lai, Yuansheng Du, Zhaohui Li, Jiin-Shuh, Jean. 2010. Occurrence of Arsenic in Mudstone of the Endemic Blackfoot Disease Region, Taiwan. Taylor Francis Group. Arsenic in the Environment.

Annual Progress Report

Selected Reporting Period: 3/1/2009 - 2/28/2010

Submitted By: Zhaohui Li
Submitted: 5/27/2010

Project Title

WR08R002: Combination of Co-Precipitation with Zeolite Filtration to Remove Arsenic from Contaminated Water

Project Investigators

Zhaohui Li, University of Wisconsin-Parkside

Progress Statement

Column tests were conducted during this period of time.

1. Determination of influence of pH on iron hydroxide precipitation and arsenic adsorption by iron hydroxide
2. Determination of the influence of added Fe to the removal of As from water
3. Determination of input Fe to the final concentration of Fe in water

The large column had a diameter of 5 cm and a 24 cm in length, and 400 g of 8-14 mesh zeolites was packed. 10 L of 100 ppb As (V) solution was made. Then 270 mg of FeCl3•6H2O was added to make a final Fe concentration of 5.6 ppm. Then, 3.1 mL of 1 M NaOH was added to raise the pH to 9.12. The mixture was stirred vigorously to induce precipitation. Samples were taken every liter. The flowrate is about 300 mL/min.

The results showed that using zeolite did not add advantages that the proposal hypothesized.

Principal Findings and Significance

Principal Findings and Significance

Description A large scale application tesst should be conducted this summer. The impact and benefit using zeolite instead of sand as the filtration media was assessed at batch and small column scale tests. The results were not distinguishable to that using sand statistically. The impact and benefit at larger scale shall be assessed this summer.

Description The inteded application will be using the technolgy for in situ treatment of arsenic

contaminated water at the point of use scale.

Awards, Honors & Recognition

Title	invited talk
Event Year	2010
Recipient	
Presented By	
Description	Was invited to present an invited talk at the 3rd International Conference on Arsenic in the Environment

Committees, Memberships & Panels

Group Name	Arsenic research
Description	Served as panelist for two sessions for the 3rd International Conference on Arsenic in the Environment.
Start Date	5/17/2010
End Date	5/21/2010

Journal Articles & Other Publications

Publication Type	Proceedings/Symposium
Title	Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred
Author(s)	Zhaohui Li, Andria J. Koski, Justin S. Merrill, Jeffrey J, Randolph, Stephan R. Kurdas, Jonathan H. Friend, Sarah J. Antinucci, Allison E. Reiley, Caren J. Ackley, Nancy A. Fenske, Laura A. Schulz, Jiin-Shuh Jean, C.-C. Liu, A.H.M.S. Reza
Publication/Publisher	Taylor Francis Group
Year Published	2010
Volume & Number	
Number of Pages	3
Description	This is part of the work that I conducted in Taiwan in conjunction with this project.
Any Additional Citation Information	

Publication Type	Proceedings/Symposium
Title	OCCURRENCE OF ARSENIC IN MUDSTONE OF THE ENDEMIC BLACKFOOT DISEASE REGION, TAIWAN
Author(s)	Hanlie Hong1, Ke Yin1, Xulong Lai1, Yuansheng Du1, Zhaohui Li2□3, Jiin-Shuh Jean3

Publication/Publisher	Taylor Francis Group
Year Published	2010
Volume & Number	
Number of Pages	2
Description	This project is part of my work conducted in Taiwan in conjunction with current project.
Any Additional Citation Information	

Other Project Support

Source	National Cheng Kung University
Dollar Value	$23,000
Description	Collaborative research among Auburn University, National Cheng Kung University and University of Wisconsin - Parkside. The amount is total value. I received 1/3 of the total value to cover my visit to Taiwan to conduct research and three of my colleagues from China University of Geosciences to conduct research in Taiwan
Start Date	6/1/2009
End Date	9/30/2009

Partners

Name/Organization	Prof. Jiin-Shuh Jean
Affiliation	National Cheng Kung University
Affiliation Type	Academic Institutions
Email	jiinshul@mail.ncku.edu.tw
Description	Conducted collaborative research on arsenic occurrance in Taiwan

Presentations & Public Appearances

Title	Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred
Presenter(s)	Zhaohui Li
Presentation Type	Speech
Event Name	to the 3rd International Conference on Arsenic in the Environment
Event Location	Tainan, Taiwan
Event Date	5/19/2010
Target Audience	International organization
Audience Size	200
Description	

Students & Post-Docs Supported

Student Name	Caren Ackley
Campus	University of Wisconsin-Parkside
Advisor Name	Zhaohui Li
Advisor Campus	University of Wisconsin-Parkside
Degree	Undergraduate
Graduation Month	May
Graduation Year	2011
Department	Geosciences
Program	B.S. in Geosciences
Thesis Title	NA
Thesis Abstract	NA

Student Name	Justin Merrill
Campus	University of Wisconsin-Parkside
Advisor Name	Zhaohui Li
Advisor Campus	University of Wisconsin-Parkside
Degree	Undergraduate
Graduation Month	December
Graduation Year	2009
Department	Geosciences
Program	B.S.
Thesis Title	NA
Thesis Abstract	NA

Student Name	Laura Schulz
Campus	University of Wisconsin-Parkside
Advisor Name	Zhaohui Li
Advisor Campus	University of Wisconsin-Parkside
Degree	Undergraduate
Graduation Month	May
Graduation Year	2011
Department	Geosciences
Program	B.S. in Geosciences

Thesis Title	NA
Thesis Abstract	NA

The Lethal and Sublethal Effects of Elevated Groundwater Nitrate Concentrations on Infaunal Invertebrates in the Central Sand Plains

Basic Information

Title:	The Lethal and Sublethal Effects of Elevated Groundwater Nitrate Concentrations on Infaunal Invertebrates in the Central Sand Plains
Project Number:	2009WI217B
Start Date:	3/1/2009
End Date:	2/28/2010
Funding Source:	104B
Congressional District:	6
Research Category:	Biological Sciences
Focus Category:	Nitrate Contamination, Groundwater, Ecology
Descriptors:	None
Principal Investigators:	Robert Scott Stelzer

Publication

1. R.S. Stelzer, B.L. Joachim. 2010. Effects of elevated nitrate concentration on mortality, growth, and egestion rates of Gammarus pseudolimnaeus amphipods. Archives of Environmental Contamination and Toxicology. 58:694-699.

Annual Progress Report

Selected Reporting Period: 7/1/2009 - 6/30/2010

Submitted By: Robert Stelzer
Submitted: 5/28/2010

Project Title

WR08R003: The Lethal and Sublethal Effects of Elevated Groundwater Nitrate Concentrations on Infaunal Invertebrates in the Central Sand Plains

Project Investigators

Robert Stelzer, University of Wisconsin-Oshkosh

Progress Statement

The research plan for Year Two of this project originally called for assessing the effects of elevated nitrate in porewater on amphipods in the field (in a stream that receives groundwater with very high nitrate concentration in the Central Sand Plains of Wisconsin). However, based on the equivocal results that we obtained from Year One (laboratory phase) it would probably not have been fruitful to move to the field phase of this project as originally conceived. Thus, we proposed to shift the focus of the work planned for Year Two. In a separate project, funded by the United States Forest Service, we have been measuring nitrate retention in Emmons Creek (in the Central Sand Plains). We have found, somewhat surprisingly, that nitrate retention is high in this high-N stream and that groundwater discharge is strongly related to the magnitude of nitrate retention. A paper from this work is currently in press in Biogeochemistry. It is unclear where the nitrate retention is occurring in Emmons Creek, although the positive relationship between groundwater discharge and nitrate retention suggests that processes in the sediments are involved. Because of the likely role of sediments in contributing to nitrate retention the focus of Year Two of our current WRI project is nitrogen biogeochemistry in stream sediments. The objectives for Year Two are:

1) To determine denitrification rates in the sediments of Emmons Creek and to assess if denitrification rates change with sediment depth
2) To determine nitrate and chloride concentration profiles in the sediments of Emmons Creek using a combination of porewater samplers (peepers) and piezometer nests.

We think this two-pronged approach will shed light on processes and patterns that contribute to reach-scale nitrate retention in Emmons Creek and in other groundwater-fed streams. We have measured denitrification rates and assessed variation in groundwater nitrate concentration in sediments from upwelling locations in Emmons Creek for three seasons (summer and fall 2009, spring 2010). Sediment cores to 30 cm depth were collected and acetylene inhibition was used to measure denitrification rates of core sections. Peepers and wells to a depth of 70 cm were used to measure gradients in groundwater nitrate concentration.

Principal Findings and Significance

Principal Findings and Significance

Description

Mean areal denitrification rate in Emmons Creek was 60 mg N2O-N m-2 h-1. Core sections deeper than 5 cm accounted for 66 percent of the areal denitrification rate. Nitrate profiles suggested that nitrate loss occurred along upwelling flow paths at sediment depths between 5 and 45 cm. Our results suggest than nitrate processing can be substantial at depth in groundwater-fed streams and are consistent with the positive relationship between nitrate retention and groundwater discharge in Emmons Creek. Our results also suggest that denitrification estimates based only on shallow sediment cores may underestimate denitrification rates in lotic ecosystems.

This project has resulted in the training of two undergraduate students and one graduate student at UW Oshkosh during the last year. One of the students, Jordan Geurts, is currently employed as a research technician with the United States Department of Agriculture in Madison, WI. The training that he received on the project helped prepare him for his current position at the USDA.

Committees, Memberships & Panels

Group Name	American Water Reources Associaion- Wisconsin Section
Description	Vice President
Start Date	3/5/2010
End Date	3/5/2011

Journal Articles & Other Publications

Publication Type	Peer-Reviewed Journal Article/Book Chapter
Title	Effects of elevated nitrate concentration on mortality, growth, and egestion rates of Gammarus pseudolimnaeus amphipods
Author(s)	R.S. Stelzer, B.L. Joachim
Publication/Publisher	Archives of Environmental Contamination and Toxicology
Year Published	2010
Volume & Number	58
Number of Pages	694-699
Description	
Any Additional Citation Information	

Other Project Support

Source	University of Wisconsin Oshkosh Faculty Development Program
Dollar Value	$6,153
Description	Augmented the current WRI project by providing a month summer salary and funds for additional supplies
Start Date	5/1/2009
End Date	2/2/2010

Source	United States Forest Service
Dollar Value	$45,579
Description	The capacity of forest streams for nutrient uptake: a comparison between a high nitrogen and low nitrogen ecosystem
Start Date	6/1/2006
End Date	12/31/2010

Partners

Name/Organization	Dr. William Richardson and Mr. Lynn Bartsch
Affiliation	Upper Midwest Environmental Sciences Center (USGS)
Affiliation Type	Federal
Email	wrichardson@usgs.gov
Description	The PI has collaborated with Dr. Richardson and Mr. Bartsch on the portion of the project involving measuring denitrification rates

Name/Organization	Dr. Eric Strauss
Affiliation	University of Wisconsin La Crosse
Affiliation Type	Local & State
Email	strauss.eric@uwlax.edu
Description	The PI has collaborated with Dr. Strauss on the portion of the project involving measuring denitrification rates

Presentations & Public Appearances

Title	The dark side of the hyporheic: nitrogen processing and profiles in deep stream sediments
Presenter(s)	Stelzer, R.S., L.A. Bartsch, W.B. Richardson, and E. Strauss
Presentation Type	Professional meeting
Event Name	Joint meeting of the North American Benthological Society and the American Society of

Event Name	Limnology and Oceanography
Event Location	Santa Fe, NM
Event Date	6/6/2010
Target Audience	Scientific audience
Audience Size	
Description	

Title	Nitrate processing below the hyporheic zone in a sand plains stream
Presenter(s)	Stelzer, R.S., L.A. Bartsch, W.B. Richardson, and E. Strauss
Presentation Type	Professional meeting
Event Name	American Water Resources Association (Wisconsin Section) Annual Meeting
Event Location	Madison, WI
Event Date	3/5/2010
Target Audience	Mixed
Audience Size	50
Description	

Title	Effects of elevated nitrate concentration on mortality, growth, and egestion rates of Gammarus pseudolimnaeus amphipods
Presenter(s)	Stelzer, R.S., B.L. Joachim, S.L. Eggert and M.A. Muldoon
Presentation Type	Poster session
Event Name	Annual Meeting of the North American Benthological Society
Event Location	Grand Rapids, MI
Event Date	5/17/2009
Target Audience	Scientific audience
Audience Size	100
Description	

Undergraduate Students Supported

New Students: **3**
Continuing Students: **1**

Grant No. G09AP00068 Influence of Coupling Erosion and Hydrology on the Long-Term Performance of Engineered Surface Barriers

Basic Information

Title:	Grant No. G09AP00068 Influence of Coupling Erosion and Hydrology on the Long-Term Performance of Engineered Surface Barriers
Project Number:	2009WI245S
Start Date:	5/15/2009
End Date:	5/15/2012
Funding Source:	Supplemental
Congressional District:	
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Anders W. Andren, Craig H Benson

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 3/1/2009 - 2/28/2010

Submitted By: Craig Benson
Submitted: 6/15/2010

Project Title

WR09R007: Influence of Coupling Erosion and Hydrology on the Long-Term Performance of Engineered Surface Barriers

Project Investigators

Craig Benson, University of Wisconsin-Madison

Progress Statement

The overall objective of this research project is to assess the performance of erosion controls for low-level radioactive waste disposal systems, and the coupling of erosion control strategies and hydrological performance of the cover. The specific objectives of this work are:

(1) Prepare an extensive literature review regarding erosion control strategies being employed for waste containment facilities in both humid and arid regions.

(2) Select a combination of models that can predict erosion and hydrological performance of covers in humid and arid regions and compare/validate the models with field data.

(3) Perform model simulations to identify strategies likely to be effective in managing erosion and hydrology of covers.

During the first year of study, we have focused on Objectives 1 and 3. We have conducted a literature review on models for simulating erosion processes and have evaluated a collection of models used to simulate variably saturated flow for cover systems. We have selected the SIBERIA model for simulating erosion and the SVFLUX model for simulating variably saturated flow.

We selected SIBERIA for several reasons. First, the model is mechanistic and thus properly represents the physics of erosion processes. Second, the model simulates landform evolution and therefore will be useful in evaluating long-term impacts of erosion. Third, the model has been applied to long-term erosion and landform evolution modeling at mine closure sites in Australia and Canada. These sites have many similarities to LLRW disposal facilities in North America.

We selected SVFLUX for three reasons. First, the code is well documented and can be used in 1, 2, or 3D modes. Second, SVFLUX has a reliable algorithm that simulates infiltration and runoff mechanistically with a high degree of realism, regardless of antecedent conditions or precipitation intensity. Third, SVFLUX includes algorithms for simulating soil-plant-

atmosphere interactions, which are key to predicting the hydrology of final covers.

We are using two UMTRA mill tailings disposal facilities as base cases for our simulations: Grand Junction, CO and Canonsburg, PA. The US Department of Energy's Division of Legacy Management has provided topographic information and cover profiles of these sites.

Principal Findings and Significance

Principal Findings and Significance

Description	This project is still in its early stages and thus significant applications and impacts have not yet been realized. However, this project will result in design methodologies for more sustainable and effective cover systems. New cover system profiles will be developed as an outcome of this study. These profiles will be more resistant to erosion and more effective in limiting percolation into underlying waste. As a result, they will require less maintenance and be more effective in protecting groundwater.

Awards, Honors & Recognition

Title	Diplomate Geotechnical Engineer
Event Year	2009
Recipient	Craig H Benson
Presented By	Academy of Geoprofessionals
Description	Inducted as a diplomate

Title	Academy of Distinguished Alumni
Event Year	2009
Recipient	Craig H Benson
Presented By	University of Texas at Austin
Description	Inducted into academy of distinguished alumni in Civil & Environmental Engineering.

Students & Post-Docs Supported

Student Name	Crystal Smith
Campus	University of Wisconsin-Madison
Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison
Degree	Masters

Graduation Month	December
Graduation Year	2010
Department	Geological Engineering
Program	Geological Engineering
Thesis Title	NA
Thesis Abstract	NA

Information Transfer Program Introduction

None.

University of Wisconsin Water Resources Institute - Information Transfer

Basic Information

Title:	University of Wisconsin Water Resources Institute - Information Transfer
Project Number:	2009WI214B
Start Date:	3/1/2009
End Date:	2/28/2010
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	Education, Conservation, Groundwater
Descriptors:	
Principal Investigators:	Stephen Wittman, Jim Hurley

Publications

1. Kline, Kathleen Schmitt 2010. Emerging Challenges for the Waters of Wisconsin: 34th Annual Meeting Program and Abstracts. American Water Resources Association – Wisconsin Section and Water Resources Institute, University of Wisconsin, Madison, Wis. 68 pages
2. White, Elizabeth, ed. 2009. Aquatic Sciences Chronicle, Spring issue. Madison: University of Wisconsin Aquatic Sciences Center, 8 pages.
3. Bahr, J.M. and E.E. Roden. 2009. Influence of Wetland Hydrodynamics on Subsurface Microbial Redox Transformations of Nitrate and Iron. Water Resources Institute, University of Wisconsin, Madison.
4. Creswell, J. E., Babiarz, C. L., Shafer, M. M., Armstrong, D. E., Roden, E. E. 2009. Controls on Methylation of Groundwater Hg(II) in Hyporheic Zones of Wetlands. Water Resources Institute, University of Wisconsin, Madison.
5. White, Elizabeth, ed. 2009. Aquatic Sciences Chronicle, Summer issue. Madison: University of Wisconsin Aquatic Sciences Center, 8 pages.
6. White, Elizabeth, ed. 2009. Aquatic Sciences Chronicle, Fall issue. Madison: University of Wisconsin Aquatic Sciences Center, 8 pages.
7. Deitchman R.S. and S.P. Loheide II. 2009. A thermal remote sensing tool for mapping spring and diffuse groundwater discharge to streams. Water Resources Institute, University of Wisconsin, Madison.
8. Li, J. and C.H. Yang. 2009. Transport and Survival of Pathogenic Bacteria Associated With Dairy Manure in Soil and Groundwater. Water Resources Institute, University of Wisconsin, Madison. 17p.

Information and Outreach Activities

A redesigned University of Wisconsin Water Resources Institute website, wri.wisc.edu, was launched on Feb. 15, 2008. Since that time and up until the conclusion of this reporting period, the site attracted 11,868 unique visitors who were responsible for 39,923 views. The site orients visitors to the Wisconsin program and includes a variety of information for those interested in water-related issues. One of the site's main audiences is researchers. To that end, the site provides a clear navigational path to the WRI project listing, project reports, groundwater research database, funding opportunities and conference information sections. The areas are updated on a regular basis to ensure currency of information transfer.

Wisconsin Water Resources Institute Publications

In recognition of the manner in which people increasingly access information – through the Internet – the Aquatic Sciences Center hosts an online publications store offering free PDF downloads of a number of relevant Wisconsin groundwater publications. Staff has produced print publications and has diligently distributed them to interested audiences. Importantly, the electronic distribution method also allows for the maximum convenience of information transfer to interested audiences. Through both methods – print and electronic – some of the most popular publications have been "Design Guidelines for Stormwater Bioretention Facilities," with ___ downloads and __ print copies distributed since February 2006; and "Protecting Wisconsin's Buried Treasure," with___ downloads and __ print copies distributed since November 2007.

Water Resources Research Highlighted in Newsletter

The Aquatic Sciences Chronicle is published quarterly and distributed to more than 2,500 subscribers. Chronicle readers include local and state water management agencies, academic faculty, staff and students; water-related non-governmental organizations; peer WRI personnel; and members of the news media. During this reporting period, Chronicle news stories have included details on researchers who have earned a patent on a water-treatment device, an intergenerational learning experience

called Grandparents University that spotlights water-related topics and announcements about water-related meetings.

AWRA 2010 Annual Conference

WRI cosponsors the annual conference of the Wisconsin Section of the American Water Resources Association, which is attended regularly by approximately 170 water resource managers, professionals and students from throughout the state. In 2010, the conference was held in Middleton on March 4 and 5 and featured more than 50 oral and poster presentations. The plenary session topics focused on groundwater-borne viruses and illnesses risk, Wisconsin's water laws and the implications of climate change on Wisconsin's water quality.

Other conference sponsors were the UW-Stevens Point Center for Watershed Science and Education, Wisconsin Department of Natural Resources, Wisconsin Geological and Natural History Survey and the U.S. Geological Survey's Wisconsin Water Science Center.

Wisconsin's Water Library Outreach Activities

The library provides outreach by answering many in-depth reference questions on a wide range of water-related topics. Some examples of reference queries answered in this reporting period include: researching the effects of the chemical bisphenol A on water quality, making an inventory of the literature related to citizen monitoring of water quality for the Bad River Watershed group, advising a local journalist on how to find historical materials relating to hidden streams in Dane County, researching the locations of natural springs near Stevens Point for a professor at University of Wisconsin-Stevens Point, researching tertiary wastewater treatment techniques for a student taking the wastewater operator's exam, and researching the intersection of groundwater regulations and land-use regulations for a University of Wisconsin-Madison professor in support of her research.

During the reporting period, in partnership with the Wisconsin Department of Natural Resources and the Wisconsin Wastewater Operator's Association (WWOA), the library continued its outreach to current and future wastewater operators of Wisconsin. The

library cataloged the essential technical manuals into the library catalog and provided loans to WWOA members around the state in support of their required state license examinations as well as in support of the educational needs of their daily work.

Wisconsin's Water Library continues to catalog all groundwater research reports from projects funded by the Water Resources Institute into WorldCat and MadCat, two library indexing tools that provide both worldwide and statewide access to WRI research. By having this information permanently indexed, the research results are easily available to other scientists throughout the University of Wisconsin System as well as across the nation and throughout the world.

The library applied for and won a *Friends of the UW Madison Libraries* grant. It is funding material acquisition related to water and climate change, expanding the titles the library owns on this important topic and creating a substantial collection for use by researchers.

Library staff also continued to be involved in the Allied Drive Story Hours project. Allied Drive is a Madison, Wisconsin neighborhood with the highest concentration of children of any urban neighborhood in Dane County and many families that live in poverty. The program is a partnership with eight special UW-Madison campus libraries, the UW-Madison School of Library and Information Studies, and the Madison School and Community Recreation Safe Haven Childcare Program. Each month, a different campus library hosts a reading hour with themes relating to their specialized subject area.

Library Websites

The library maintains several information transfer tools to reach library patrons and the most frequently accessed is the library's recently redesigned website (*aqua.wisc.edu/waterlibrary*). The library's site serves as an outreach site for those who want to know more about our state's water resources. The site's overhaul was designed to make books and other materials in the library easily accessible to any Wisconsin resident. There are three areas of the Web site, each designed to address the needs of the library user groups: There is an area for UW system faculty, staff and students; a section just for Wisconsin residents; and an area dedicated to just children, and their

guardians and parents. Library staff continually update the site with new topical reading lists, new links to useful water-related Web sites, and pages with the library's new books. These frequent updates encourage users to return to the site often.

During the past 12 months, the library site has 43,148 visitors with 58,431 page views. The average time spent on the site is almost six minutes, a sign that Web surfers are finding items of interest and are drilling deeper into the information on the site after their initial entry.

In addition to its website, Wisconsin's Water Library uses other technology tools to reach library patrons. Using e-mail, the library sends out a bimonthly *Recent Acquisitions List* to close to 500 contacts. The message also includes recent updates to the library website and contact information for users to ask any water-related question. The library also supports an e-mail at askwater@aqua.wisc.edu, which is monitored daily.

The library also employs web 2.0 tools to reach new library users and raise visibility. The library has a blog, AquaLog (*aqualog2.blogspot.com/*), where library staff reports on news, publications, and resources about water and the Great Lakes. The blog has seen increased usage over the time it has been active. It now sees approximately 30 hits per days, on average.

The library is also using the social media tools Facebook and Twitter. Users of both technologies can become followers of both and get the latest on water-related information instantly. Facebook (www.facebook.com/pages/Madison-WI/UW-Wisconsins-Water-Library/92090121028?ref=nf) is used often to announce events and display interesting links to its "fans". Twitter (*twitter.com/WiscWaterLib*) is an excellent way to communicate in a timely manner. Both tools have seen increased use by library patrons and both have loyal and an increasing numbers of followers.

Student Supported

Name: Omar Poler

Campus: University of Wisconsin-Madison

Advisor:

Advisor Campus: University of Wisconsin-Madison

Degree/Training: Master of Library Science

Graduation: May 2010

Department: Library and Information Studies

Program of Degree: Library and Information Studies

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	3	1	0	0	4
Masters	5	0	0	1	6
Ph.D.	0	1	0	2	3
Post-Doc.	0	0	0	1	1
Total	8	2	0	4	14

Notable Awards and Achievements

Deitchman, R.S., and S.P. Loheide II (2009), Characterization of groundwater flux using ground-based thermal remote sensing at the seepage face, American Water Resources Association – WI Section 2009 Annual Meeting, Stevens Point, WI. “Best Student Platform” award winner.

James P. Hurley, Assistant Director for Research and Outreach, Distinguished Service Award, American Water Resources Association, Wisconsin Chapter, 2009.

Publications from Prior Years

1. 2005WI91B ("Occurrence of Estrogenic Endocrine Disruptors in Groundwater ") - Articles in Refereed Scientific Journals - Gao, J., Pedersen, J.A. 2009. Sorption of sulfonamide antimicrobial agents to humic-clay complexes. J. Environ. Qual. J Environ Qual 39:228-235 (2009) DOI: 10.2134/jeq2008.0274
2. 2006WI135B ("Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil") - Articles in Refereed Scientific Journals - Lepore, B.J. and Barak, P. 2009. A Colorimetric Microplate Method for Determining Bromide Concentrations. Soil Sci Soc Am J, 73: 1130-1136.
3. 2006WI135B ("Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil") - Articles in Refereed Scientific Journals - Lepore, B.J., Morgan, C.L.S., Norman, J.M. and Molling, C.C. 2009. A Mesopore and Matrix Infiltration Model Based on Soil Structure. Geoderma. 152(3/4): 301-313
4. 2006WI135B ("Measuring and Modeling Macroporous Soil Water and Solute Flux Below the Root Zone of a Plano Silt-Loam Soil") - Articles in Refereed Scientific Journals - Lepore, B. J., A.M. Thompson and A. Petersen. 2009. Impact of polyacrylamide delivery method with lime or gypsum for soil and nutrient stabilization. Journal of Soil and Water Conservation 64: 223-231.
5. 2005WI152B ("Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation") - Articles in Refereed Scientific Journals - Li, Z., Hong, H. 2009. Retardation of Chromate through Packed Columns of Surfactant-Modified Zeolite. J. Hazard. Mater, 162, 1487-1493. http://dx.doi.org/10.1016/j.jhazmat.2008.06.061
6. 2005WI152B ("Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation") - Articles in Refereed Scientific Journals - Liu, Z., Li, Y., Li, Z. 2009. Relationship between land use and surface water quality in Wisconsin - a GIS approach. J. Integr. Environ. Sci., 6, 69-89.
7. 2007WI213O ("Geochemical Characterization of Sulfide Mineralization in Eastern Wisconsin Carbonate Rocks") - Conference Proceedings - Luczaj, J.A., McIntire, M.J., Steffel, A.M., and Duca, A.L. 2009. Geochemical Characterization of Sulfide Mineralization in Eastern Wisconsin Carbonate Rocks. 33rd American Association of Water Resources Wisconsin Section Meeting, Stevens Point, Wisconsin, March 5-6, 2009. Program and Abstracts, p. 38.
8. 2006WI182O ("Occurrence of Estrogenic Endocrine Disruptors in Groundwater") - Articles in Refereed Scientific Journals - Pedersen, J.A.; Karthikeyan, K.G.; Bialk, H.M. 2009. Sorption of human and veterinary antibiotics to soils. Natural Organic Matter and Its Significance in the Environment. Wu, F.; Xing, B. (eds); Science Press: Beijing, China, pp. 276-299.
9. 2005WI152B ("Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation") - Articles in Refereed Scientific Journals - Zhang, X., Hong, H., Li, Z., Guan, J. 2009. Removal of Azobenzene from Water by Kaolinite. J. Hazard. Mater. Oct 30;170(2-3):1064-9.
10. 2007WI204O ("Monitoring Septic Effluent Transport and Attenuation using Geophysical Methods") - Articles in Refereed Scientific Journals - Wilcox, J.D., J.M. Bahr, C.J. Hedman, J. D. C. Hemming, M.A.E.Barman and K. R. Bradbury. 2009. Removal of organic wastewater contaminants in septic systems using advanced treatment technologies. J. Env. Quality 38:149-156.