

**Water Resources Institute
Annual Technical Report
FY 2008**

Introduction

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

With nearly 65% of its current base budget targeted for research, the WRI supports a total of 24 individual research projects that address a wide range of water-related issues and problems. Research projects fall into the following four thematic areas: groundwater, surface water, groundwater/surface water interactions and drinking water initiatives. Participants in WRI-supported projects include faculty, staff and students at UW System campuses at Madison, Milwaukee, Stevens Point, Green Bay; UW-Extension; Wisconsin Geological and Natural History Survey; Beloit College, Wisconsin Department of Natural Resources, U.S. Geological Survey, and individuals in private industry.

In May 1984, Comprehensive Groundwater Protection legislation for Wisconsin (1983 Act 410, Wisconsin Statutes) was signed into law. One of the provisions of the bill was to establish a state Groundwater Coordinating Council (GCC) appointed by the legislature and the governor. Advisory to the GCC is the Groundwater Advisory Council (GRAC), which is appointed by the UW-Madison Chancellor. Because groundwater protection is deemed a priority issue by the WRI, the GRAC serves as an important advisory committee for the WRI. Composed of a diversity of representatives with a great deal of scientific, political and administrative experience, the GRAC has helped the WRI identify current and anticipated water problems and issues and establish priorities for initiating research projects.

Since July 1989, the state has provided line item funding for groundwater research to the UW System. This Groundwater Research Program, administered by the WRI, currently funds 18 projects that provide a balanced program of laboratory, field, and computer-modeling studies and applications designed to preserve or improve groundwater quality. Charged with the primary mission to plan, develop and coordinate research programs that address present and emerging water-related and land-related issues, the WRI has developed a broadly-based statewide program of basic and applied research that has effectively confronted a spectrum of societal concerns.

Institute staff; UW System faculty, staff and students; state administrators and other public officials; industry, and the public have come to rely on the WRI for objective, timely scientific information about water resources issues. The WRI ensures that this information reaches these individuals through its strong information dissemination/technology transfer program. An integral part of the WRI's total program is the training of students. Research projects have provided support and training for graduate and undergraduate students pursuing degrees in a wide range of disciplines. 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 through our institute's library and website. Given the limited funding available through the annual 104(B) allocation, the Wisconsin WRI has decided to use its funds to participate in the WGRMP by supplementing this funding source and providing additional opportunities for groundwater research in the UW System.

Our priorities for research are established annually by the Wisconsin Groundwater Research Advisory Council (GRAC), and they are 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 a rigorous external peer review (coordinated by the WRI) and a thorough 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.

Research Program Introduction

None.

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

Basic Information

Title:	Grant No. 04HQGR0034 The Role of Dissolved Organic Carbon in Aquatic Mercury Cycling The Transport, Fate and Cycling of Mercury in Watersheds and Air Sheds
Project Number:	2005WI150S
Start Date:	11/15/2003
End Date:	9/14/2008
Funding Source:	Supplemental
Congressional District:	
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Jim Hurley

Publication

1. Gorski, P.R., DE. Armstrong, J.P. Hurley and M.M. Shafer. 2006. Speciation of aqueous methylmercury influences uptake by a freshwater alga (*Selenastrum capricornutum*). *Environmental Toxicology and Contamination*. 25 (2): 534-540.
2. Branfireun, B.A., D. P. Krabbenhoft, H. Hintelmann, R. J. Hunt, J. P. Hurley, and J.W.M. Rudd. 2005. The Transport And Speciation Of Atmospheric Mercury In A Boreal Forest Wetland: A Stable Mercury Isotope Approach. *Water Resources Research*, v. 41, W06016, oi:10.1029/2004WR003219, 2005.
3. Hall, B.D., H. Manolopoulos, J.P. Hurley, J. J. Schauer, V.L. St. Louis, D. Kenski, J. Graydon, C.L. Babiarz, L.B. Cleckner, and G.J. Keeler. 2005. Methyl and total mercury in precipitation in the Great Lakes region. *Atmospheric Environment*. 39(39):7557-7569.
4. Stoor, R.W., J.P. Hurley, C.L. Babiarz and D.E. Armstrong. 2006. Subsurface Sources of Methylmercury to Lake Superior from a Wetland-Forested Watershed. *Science of the Total Environment*. 368(1) pp99-110
5. Chadwick, S.P., C.L. Babiarz, J.P. Hurley and D.E. Armstrong. 2006. Influences of iron, manganese, and dissolved organic carbon on the hypolimnetic cycling of amended mercury. *Science of the Total Environment*. 368(1) pp177-188
6. Reed Harris , Marc Amyot , Christopher Babiarz , Ken Beaty , Paul Blanchfield , R. A. (Drew) Bodaly , Brian Branfireun , Cynthia Gilmour , Jennifer Graydon , Andrew Heyes , Holger Hintelmann , James Hurley , Carol Kelly , David Krabbenhoft , Steve Lindberg , Robert Mason , Michael Paterson , Cheryl Podemski , Art Robinson , Ken Sandilands , George Southworth , Vincent St. Louis and Michael Tate. 2007. Whole-Ecosystem Study Shows Rapid Fish Mercury Response to Changes in Mercury Deposition. *Proc. Nat. Acad. Sci.* v104 pp16586-16591
7. Engle, M.A., Tate, M.T., Krabbenhoft, D.P., Kolker, A., Olson, M.L., Edgerton, E.S., DeWild, J.F., and McPherson, A.K. 2008. Characterization and cycling of atmospheric mercury along the central

U.S. Gulf of Mexico Coast. *Applied Geochemistry* 23: 419–437.

NOTE: Your report is not complete until you click on the **Submit Report** button.

[<< Back](#)[Submit Report](#)

Annual Progress Report

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

Submitted By: Jim Hurley

Submitted: 6/11/2009

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

The project team continues to make good progress towards understanding the sources and cycling of mercury in airsheds and watersheds. During the past year we conducted studies in two coastally situated settings: Weeks Bay, Alabama, and Cape Romaine, South Carolina. In addition, to add to the interpretation of our results, our project has begun development of a generally applicable dry-phase mercury deposition model that will facilitate estimates of ionic and elemental mercury to surfaces. The model is calibrated by the use of atmospheric mercury speciation measurements made in the field.

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 deposition 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.

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	

NOTE: Your report is not complete until you click on the **Submit Report** button.

[<< Back](#)[Submit Report](#)

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

Publication

NOTE: Your report is not complete until you click on the **Submit Report** button.

[<< Back](#)[Submit Report](#)

Annual Progress Report

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

Submitted By: Jim Hurley

Submitted: 6/11/2009

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

In Summer 2007, we measured infiltration rates at 20 locations in a watershed in western Dane County. The sites were selected with a random spatial pattern in the watershed. Sites were selected to represent nine classes created from the combination of two variables with three levels each: estimated Ksat (low, medium and high) and land use (agricultural, residential and open). For this stratification, Ksat estimates were made using the textural class and bulk density of the surface horizon for the corresponding soil mapping units in the NASIS database. A table of national averages for Ksat in each textural class of both high and low bulk density was used to estimate Ksat. Land uses categories were determined from a GIS data layer developed by the Dane County Regional Planning Commission from 2005 orthophotos.

At each site, two infiltration measurements were made using steel frames (1m long, 0.5m wide, 0.3m deep and 0.3cm thick), which were placed 2 to 3 meters apart. A pond depth of approximately 5cm was established and maintained in each frame until the steady-state infiltration rate is reached, defined as three consecutive readings within 10% of each other with no clear trend. After the infiltration measurements were completed, soil cores (7.5cm diameter) were taken by hand at four depths: 0-15cm, 15-30cm, 30-45cm, and 45-60cm from the center of each frame. Soil samples (0-15cm) were analyzed in the laboratory for particle size (hydrometer method), bulk density and organic matter. Steady-state infiltration rates (assumed to be the average of the last three

measurements taken) were converted to Ksat using the equations given by Reynolds (1993).

Principal Findings and Significance

Description	Fieldwork for the project only began in May 2007, so results and impacts have not yet been generated. The test infiltrometer described above is a UW innovation. Thus far, it appears to be superior to traditional methods for measuring in-field infiltration. It was vetted with a multi-agency group of infiltration specialists at the recent national conference of the National Cooperative Soil Survey. This group thought it was a useful direction and may eventually incorporate it or similar idea in national soil testing standards.
Description	<p>For the 40 infiltration measurements taken in 2007, the average calculated Ksat steady-state infiltration rate was 221mm/hr. Ksat values ranged from 931mm/hr (a forested site that has been undisturbed since 1937) to 21 mm/hr (an agricultural field that has been planted in corn since 1975). The average Ksat value calculated for three land use categories was 90 mm/hr for Agriculture, 220 mm/hr for Residential and 274 mm/hr for Open land. The high average Ksat values for residential land can be attributed to two extraordinarily samples – high infiltration rates measured above a septic system and in a mulched garden area with large trees.</p> <p>The data collected for this project in 2007 suggest that topographic and land cover data improve our ability to predict measured infiltration rates in Dane County compared to using soil properties alone. Best subsets regression was done to identify the best predictors among multiple soil properties. For this data set, percent organic matter, percent sand, and texture (R-squared adjusted: 0.18) provided the strongest regression, though this is still a generally weak model. When terrain variables calculated from a Digital Elevation Model (DEM) and land cover data were added to the analysis, the highest R² (adjusted) value increased to 0.67 for the model that used the following predictors: percent organic matter, percent clay, elevation, aspect, planform curvature, and land cover. While this model still only accounts for about two-thirds of the variability of measured Ksat values, this analysis suggests that predictions of infiltration rates should be based on land cover and topographic information in addition to soil properties. Land cover information appears to be particularly valuable. In the regression analyses performed on the 2007 data, land cover was the best single predictor of measured infiltration rates.</p>

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

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 an overview of the goals of the project and the field work planned for 2007.

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

NOTE: Your report is not complete until you click on the **Submit Report** button.

<< Back

Submit Report

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

Basic Information

Title:	Grant No. 07HQGR0025 Effectiveness of Engineered Covers: From Modeling to Performance Monitoring
Project Number:	2006WI179S
Start Date:	12/1/2006
End Date:	2/28/2009
Funding Source:	Supplemental
Congressional District:	2
Research Category:	Engineering
Focus Category:	Solute Transport, Models, None
Descriptors:	landfills
Principal Investigators:	Craig H Benson

Publication

Completion Report

Submitted By: Craig Benson

Submitted: 6/1/2009

Start Date: 12/1/2006

End Date: 2/28/2009

Project Title

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

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 Multiple 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

.....

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

.....

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 Joseph Scalia
Campus University of Wisconsin-Madison

Advisor Name Craig Benson
Advisor Campus University of Wisconsin-Madison

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

.....

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

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

Basic Information

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

Publication

1. Lepore, B.J. and Barak, P. 2009. A Colorimetric Microplate Method for Determining Bromide Concentrations. *Soil Sci Soc Am J*, 73: 1130-1136.
2. 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*. (accepted).

Enhanced Reductive Dechlorination of Chlorinated Aliphatic Hydrocarbons :

Molecular and Biochemical Analyses

Ameesha Shetty and William J. Hickey

Department of Soil Science

Molecular and Environmental Toxicology Center

University of Wisconsin – Madison

TABLE OF CONTENTS

PROJECT SUMMARY	3
INTRODUCTION	5
PROCEDURES AND METHODS	6
RESULTS AND DISCUSSION	7
CONCLUSIONS	12
REFERENCES	15

PROJECT SUMMARY

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

Project I.D. – WR06R002

Investigators – Principal Investigator – Dr. William Hickey; Professor; Dept. Soil Science, Molecular and Environmental Toxicology, University of Wisconsin – Madison.

Research Assistant – Ms. Ameesha Shetty, Graduate student, Molecular and Environmental Toxicology

Period of contract – July 2006 to June 2008.

Background/need – Chloroalkenes are widespread groundwater contaminants for which enhanced reductive dechlorination (ERD) via electron donor augmentation can serve as an effective, *in situ* bioremedial strategy. A major goal of ERD is to stimulate late stage dechlorination reactions, which are needed to prevent accumulation of toxic intermediates. Establishment of methanogenic conditions is important for the onset and support of late stage dechlorination processes that involve reduction of dichloroethene (DCE) to vinyl chloride (VC), and VC reduction to the non-toxic end-point compound, ethene. However, little is known about the composition of microbial communities that are active in late-stage dechlorination. Elucidating the structure and function of microbial communities associated in the field with late stage dechlorination reactions could help establish a mechanistic foundation that would advance the science of ERD, and consequently enhance the effectiveness with which the process might be applied and managed.

Objectives - 1) Delineate the microbial community dynamics induced by soluble carbohydrate augmentation in field samples and during progress in ERD. 2) Elucidate the composition of communities that effect complete dechlorination of CAH in field samples.

Methods – Cells in the groundwater samples were collected by filtration and DNA was extracted from them to use in Automated Ribosomal Intergenic Spacer Analysis (ARISA) in order to determine microbial community diversity. PCR was done using fluorescently labeled primers, and then the profile of fluorescent peaks for each sample was determined. ARISA however provides information of community diversity but does not define community structure since organisms cannot be identified. 16S-ITS clone libraries were set up for identification of the organisms represented by major peaks on the community profiles, or were consistently present over time. The DNA extracted from the groundwater samples was used to amplify the 16S-ITS regions of the template. These were then used for ligation and transformation to set up the clone libraries. The clones were screened and the ones that contained the ARISA fragment of interest were sequenced. Sequence similarities with the 16S gene were used for organism identification. These clone libraries were used to identify some of the major peaks seen in the microbial community profiles. The time period during which this study was undertaken was September 2006 to July 2008.

Results and Discussion – Microbial community diversity was studied in locations that differed from each other by the stage of dechlorination. The community profile at these locations was studied over the span of a year as ERD continued. In the locations showing late stage dechlorination, the predominant species were affiliated with *Clostridia*, *Bacteroidetes*, *Mollicutes* and *Spirochaetes*. This corresponded with the other studies on microbial characterization of reductive dechlorination sites. These communities were absent in the location demonstrating only early stage processes. At this site, the predominant classes there were *Delta proteobacteria* and *epsilon proteobacteria*. Therefore a distinct community profile was associated with VC stalling conditions. The community dynamics was studied and the profile did not change substantially within a location over the period of 1 year.

Conclusions - Distinct community profiles seem to be associated with early and late stage of dechlorination. The species that are previously known to be affiliated with dechlorination sites are not observed in the location showing stalling of dechlorination at vinyl chloride. Late stage processes are preferred since it does not lead to the accumulation of toxic by-products. Therefore, understanding the difference in microbial communities stimulated in areas showing early and late stage processes is imperative. This study also gives an insight into populations other than dechlorinators in a field site undergoing ERD. A greater understanding of the role played by these species is needed for complete and successful ERD treatment.

Key words – Trichloroethylene, Bioremediation, Enhanced Reductive Dechlorination

Funding – University of Wisconsin System Groundwater Research Program; U.S. Geological Survey

INTRODUCTION - Chlorinated aliphatic hydrocarbons (CAH) such as perchloroethylene (PCE), trichloroethylene (TCE), and trichloroethane (TCA) are toxicants and pervasive groundwater contaminants. Thus, sites with CAH-impacted groundwater are one of the most (if not the most) commonly targeted locations for cleanup, for which bioremediation utilizing enhanced reductive dechlorination (ERD) mediated by anaerobic bacteria has become a major process for *in situ* treatment.

Reductive dechlorination involves sequential removal of chlorines from CAH, ultimately resulting in the non-toxic end-products ethene or ethane. Under natural conditions, the process frequently stalls, resulting in accumulation of *cis*-dichloroethylene (c-DCE) and vinyl chloride (VC). Since VC is considered more toxic than any of its parent compounds, a major goal of ERD is to establish conditions conducive to the late stage dechlorination processes (reduction of c-DCE and VC to ethene) that are essential for effective remediation. Data from field sites where ERD has been implemented indicate that the onset of late stage transformations typically coincides with establishment of methanogenic conditions [2, 3]. However, the microbial communities, interactions and activities that underlay effective ERD at these sites are poorly understood.

Because of its ability to mediate VC reduction to ethene, the chloridogenic (dehalorespiring) bacterium *Dehalococcoides ethenogenes* initially attracted much attention. But, VC reduction by *D. ethenogenes* is slow, and microcosm and field screening studies have indicated that this transformation can occur in the absence of *D. ethenogenes* [4-7]. Recently, VC-respiring strains of *Dehalococcoides* sp. that are highly efficient in VC reduction have been isolated, and genes encoding reductive dehalogenases (RDases) mediating VC reduction to ethene have been identified [8].

While VC dechlorinators and other dehalorespiring bacteria have key roles in CAH bioremediation, their activity is dependent upon that of commensalistic fermentative organisms, which generate the hydrogen, electron donors and growth factors chloridogens require. There is also growing recognition that varying composition and activities of fermentative consortia may have significant effects on the activities of dechlorinators [6], but the nature and activities of fermentative organisms that are predominant in methanogenic ERD are poorly understood. Microcosm studies with model ERD amendments (organic acids and alcohols) have shown that the nature of the electron donor has a significant effect on the structure and activity of the microbial community stimulated [6], but little is known about the microbial communities established in response to ERD amendments (*e.g.*, molasses) that are actually used in the field.

Finally, to the best of the authors' knowledge, there are only two reports that have examined microbial communities associated with CAH bioremediation in field studies [1, 9]. Both reports were significant in demonstrating that integrating data on molecular microbial community structure with biogeochemical measurements provided new insights into biodegradative processes operative at the sites, which could facilitate site management. Likewise, elucidating the structure and function of microbial communities associated in the field with late stage dechlorination reactions could help establish a mechanistic foundation that would advance the science of ERD, and consequently enhance the effectiveness with which the process might be applied and managed.

PROCEDURES AND METHODS -

1) Field site, ERD biostimulation and field sampling. This study was done in collaboration with ARCADIS, an environmental consulting and engineering firm that was contracted to carry-out remediation of the study site. The site (located in southeastern Wisconsin) was developed in the early 1940's for heavy manufacturing, and operated until 1992 when the plant closed. Since 1992, the site has not been utilized. The predominant groundwater contaminants are TCE (120,000 µg/L to non-detectable (ND)), 1,1,1-trichloroethane (1,1,1-TCA; 14,000 µg/L to ND), c-DCE (19,000 µg/L to ND), and VC (4,300 µg/L to ND).

An anaerobic reactive zone was established within the groundwater plume through the addition of a carbon amendment solution (100:3.5:2 (v:v:v), potable water:granular cheese whey:blackstrap molasses). Approximately 100, 2-inch diameter injection wells were installed in the areas of impacted groundwater. Each well had an approximate depth of 15 feet, and a screened interval of 5 to 10 ft. Approximately 300 gallons of carbon amendment solution was injected into each well, or as an alternative 300 gallons of a 100:7 solution of potable water to blackstrap molasses be injected into each well. The carbon amendment injections began in April 2006.

Samples of aquifer water and sediment cores were obtained during the installation of the injection wells. Water samples were processed for chemical and microbiological analyses as described below. The progress of ERD was monitored by chemical analysis of groundwater samples acquired from a monitoring well network; groundwater being sampled quarterly during the period. Samples of groundwater used for molecular analysis were shipped to the laboratory on ice by overnight courier. Chemical analysis was also done on groundwater samples, was carried out by a certified environmental analysis laboratory contracted by ARCADIS and samples of groundwater were sent from the locations to the laboratory for further molecular analysis.

2.) Molecular microbial community analyses. Molecular analysis of microbial communities was applied to DNA extracted from field samples of groundwater. Groundwater samples were acquired from locations showing high levels of cDCE/VC reduction, and for comparison, a location inactive in cDCE/VC reduction was obtained. Field groundwater samples (500-mL) were acquired as discussed above, transported to lab and processed (filtration through polyethersulfone membranes, 0.2 µm pore diam). The membranes were processed for extraction of Bacterial DNA using the Mobio Soil DNA extraction kit ().

Whole community profiles were developed using Automated Ribosomal Intergenic Spacer Analysis (ARISA) with bacterial primers 1406f and 23Sr [10]. The forward primer was synthesized with a fluorochrome label (5'-FAM). PCR conditions were optimized for the present application as 94°C for 2min, followed by 30 cycles of 94°C for 15 sec, 50°C for 15 sec, 72°C for 45 sec and finally 72°C for 2 min. For each sample, fluorescent DNA fragment analysis was done in duplicate through the UW-Madison Biotechnology Center by using an ABI 3700 automated sequencer to generate electropherograms, and Genemarker v 1.5 for profile alignment. Individual peaks were treated as operational taxonomic units (OTUs). Peak areas were normalized within ARISA profiles, and expressed as fraction of the total peak area comprising the profile termed as relative intensity.

3) 16S-ITS Clone library - ARISA profiles are coupled with 16S rDNA-ITS clone libraries in order to yield organism identification. By doing so, ARISA peaks of interest can be tracked to the ITS contained in these clones, and identification made by sequencing of the associated 16S rDNA [11] To create the Bacterial 16S rDNA-ITS clone libraries, PCR primers

27f [12] and 23Sr were used to amplify the majority of the Bacterial 16S rDNA gene as well as the adjoining ITS. The PCR parameters were 94° (2min), followed by 30 cycles of 94°C for 15sec, 43°C for 15sec and 72°C for 2 min, finally 72°C for 7 min. Purified PCR products will be cloned ligation into pGEM-T Easy (Promega) and transformed into *E. coli* JM109 competent cells. Clone libraries were established with DNA extracted from a sediment sample obtained from a methanogenic reactive zone showing high levels of c-DCE/VC dechlorination and from locations showing stalling at c-DCE/ VC dechlorination.

The procedure of Grant and Ogilvie [13] was used to screen clones for ARISA peaks of interest for 16S rDNA sequencing. Briefly, clones were propagated in 96-well plates, and ARISA done as described above on clones pooled across rows and across columns. An ARISA peak of interest was associated with a clone by identifying the combination of reactions from a row pool and a column pool that possess the peak, and then locating the well at the intersection of the row and column. Plasmid DNA was isolated from clones of interest, and sequencing of 16S rDNA by BigDye (Applied Biosystems) cycle sequencing will be done as in the PI's previous work. Sequence similarities will be determined by BLAST-N searches against GenBank.

4) DNA sequence analysis. Each clone was sequenced by the dideoxy termination method by using an Applied Biosystems (Foster City, CA) automated sequencing system available at University of Wisconsin-Madison. GenBank database searches were carried out using the National Center for Biotechnology Information BLAST web server.

RESULTS AND DISCUSSION –

Each location had a distinct ARISA profile, and each location showed variation in ARISA profile over the course of one year (Figs. 2-4). The identities of major peaks could be determined from sequencing clones recovered from the Bacterial 16S rDNA-ITS libraries. However, many of the fragments relatively low in abundance (*i.e.*, smaller peaks in Figs. 2-4) eluded recovered in the libraries. Thus, the identifies of the organisms yielding these peaks were not determined.

At the first time point, the predominant fragments at Location 1 had the greatest sequence identity to members of the *Clostridia*, *Mollicutes* and CFB (*Cytophaga-Flavobacterium-Bacteroides*) groups of bacteria (Fig 2a, Table 1). A fragment identified as *Pseudomonas* sp. was also prominent. Over the next three time points, the diversity of the community appeared to expand (*i.e.*, increase in number of peaks, Fig. 2b) and then contract. The final profile (Fig. 2d) was similar to that developed at the first sampling point one year earlier. Notable trends were the consistent identification of *Clostridia* as prevalent organisms across the one-year time span, and the disappearance of *Pseudomonas* sp. after the first time point. At Location 2, the predominant clones at the first and second sampling times were identified as *Bacteroidetes* and *Spirochaetes* (Fig. 3a, Table 1). At the two later time points, a new peak identified as a *betaproteobacteria* was prominent. At Location 3, *deltaproteobacteria* and *epsilonproteobacteria* were initially most abundant; the former represented the single peak resolved in the final sample.

The groups predominating at the late stage locations (*Clostridia*, *Bacteroides*, *Mollicutes* and *Spirochaetes*) have been previously identified in TCE-contaminated aquifers, and in microcosms established to study CAH degradation [1, 15]. In the present study, its notable that these groups were absent form Location 3, which was stalled at the early dechlorination stage for the duration of the study. This finding indicates that late stage dechlorination requires establishment of a particular community of microbes, which enhance and/or complement the activity of chloridogenic organisms, such as *Dehalococcoides* sp.

To the best of the authors' knowledge, the present study is the first to document the variation occurring in microbial community structure through the dechlorination process at an actual field site. The relative abundance of the predominant species appeared to reflect changes in the chemical profile of the groundwater. For Location 1, late stage dechlorination increased substantially between the first and second time points, and remained high thereafter (Fig. 1a). A corresponding change in community structure was documented to occur between these sampling points (Fig. 2a,b); the later time points were similar in the predominance of *Clostridia*. Location 2 showed the opposite trend, with late stage dechlorination high at the first and second time points, and then decreasing for the third and fourth (Fig. 1b). Again a corresponding change occurs in the community structure (Fig. 3a-d).

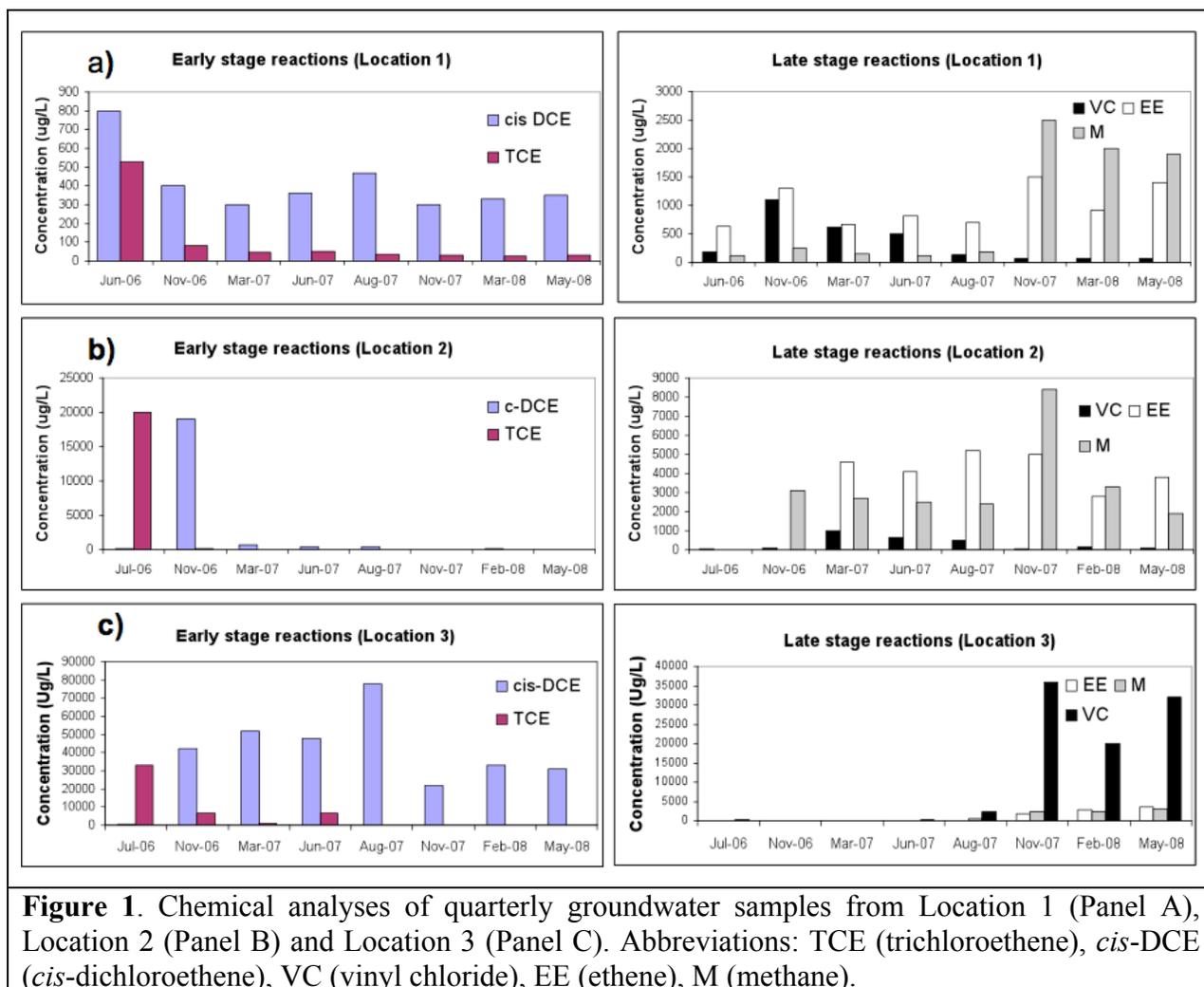


Figure 1. Chemical analyses of quarterly groundwater samples from Location 1 (Panel A), Location 2 (Panel B) and Location 3 (Panel C). Abbreviations: TCE (trichloroethene), *cis*-DCE (*cis*-dichloroethene), VC (vinyl chloride), EE (ethene), M (methane).

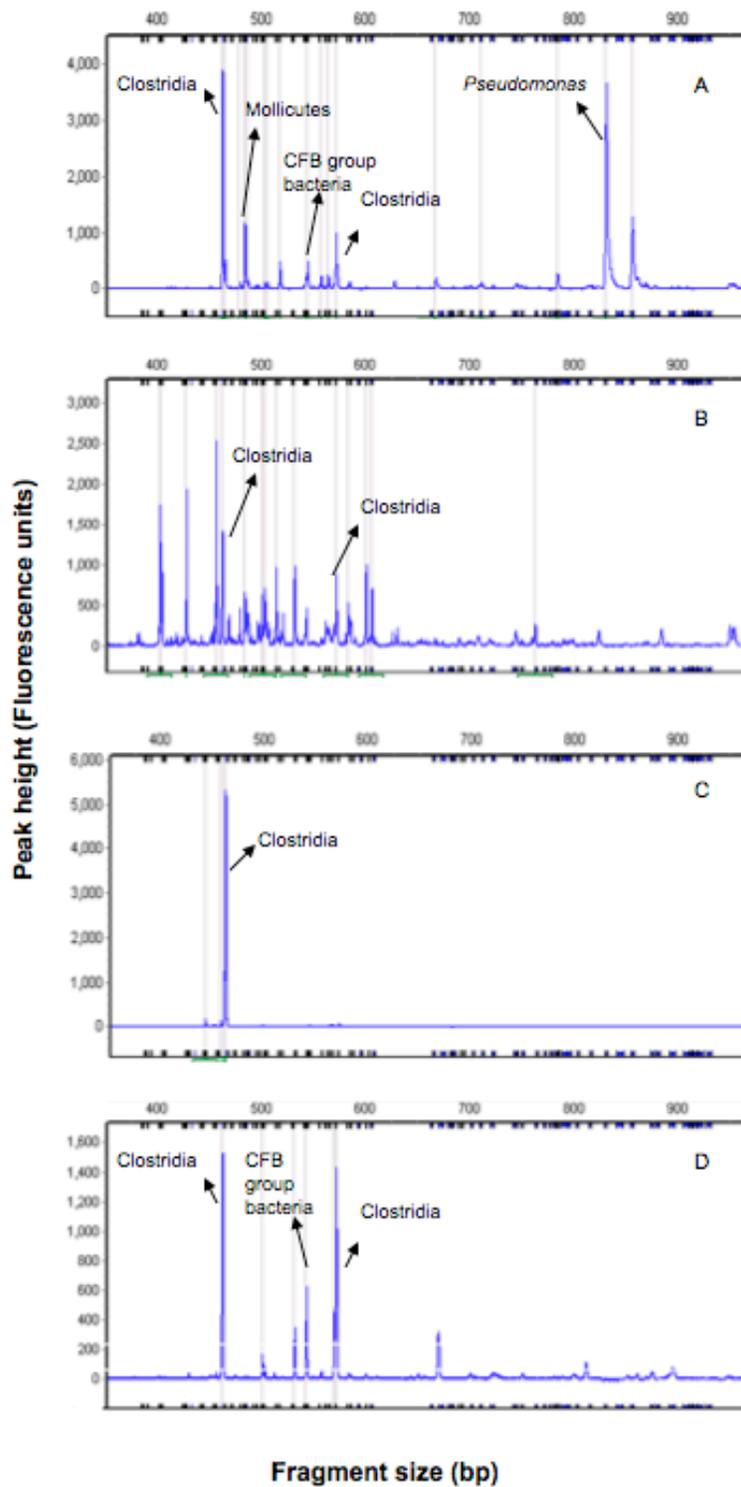


Figure 2. ARISA Profile of bacterial communities from Location 1. Data are from quarterly samples: Panel A., June 2007, B. November 2007, C. February 2008, D. May 2008.

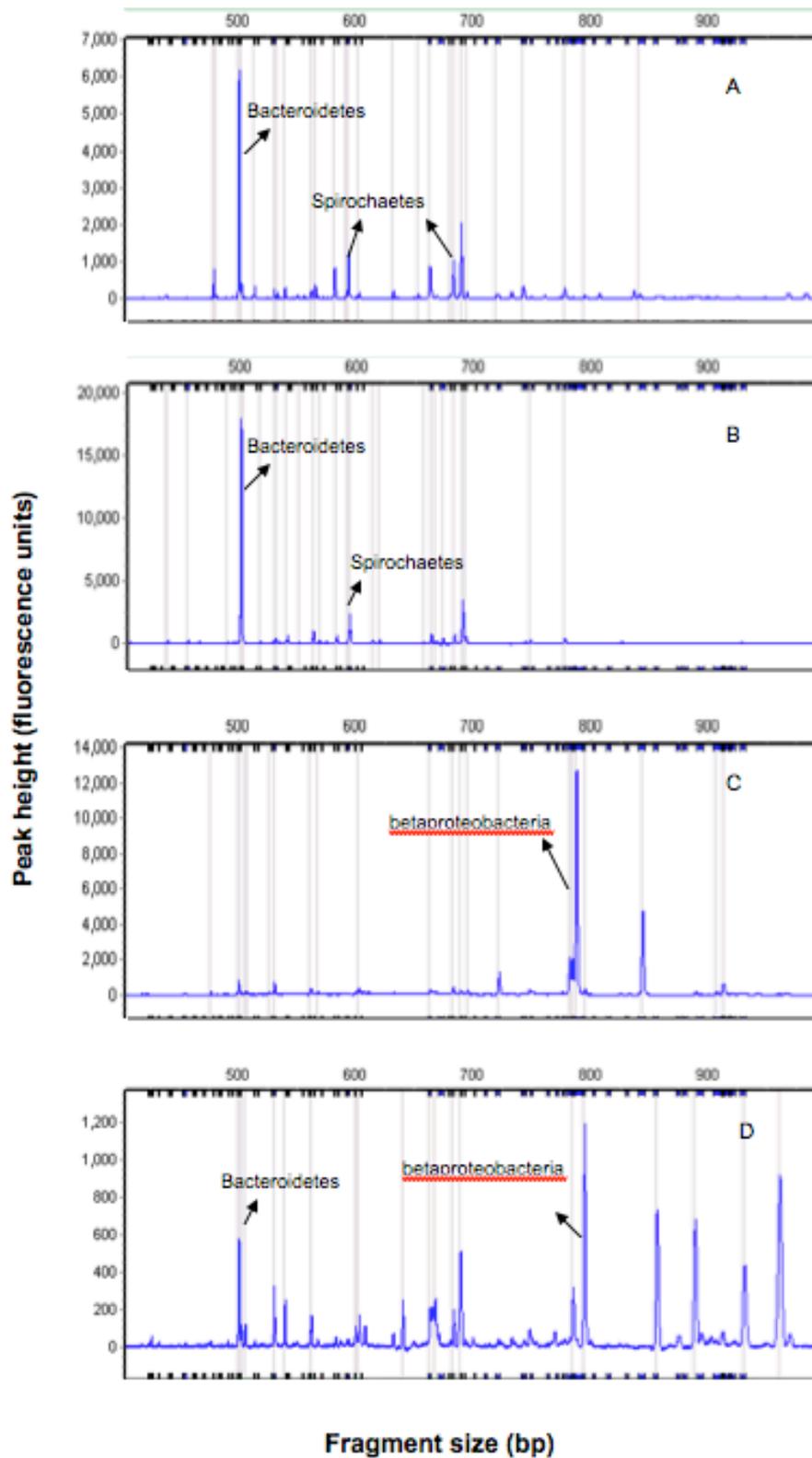


Figure 3. ARISA Profile of bacterial communities from Location 2. Data are from quarterly samples: Panel A., June 2007, B. November 2007, C. February 2008, D. May 2008.

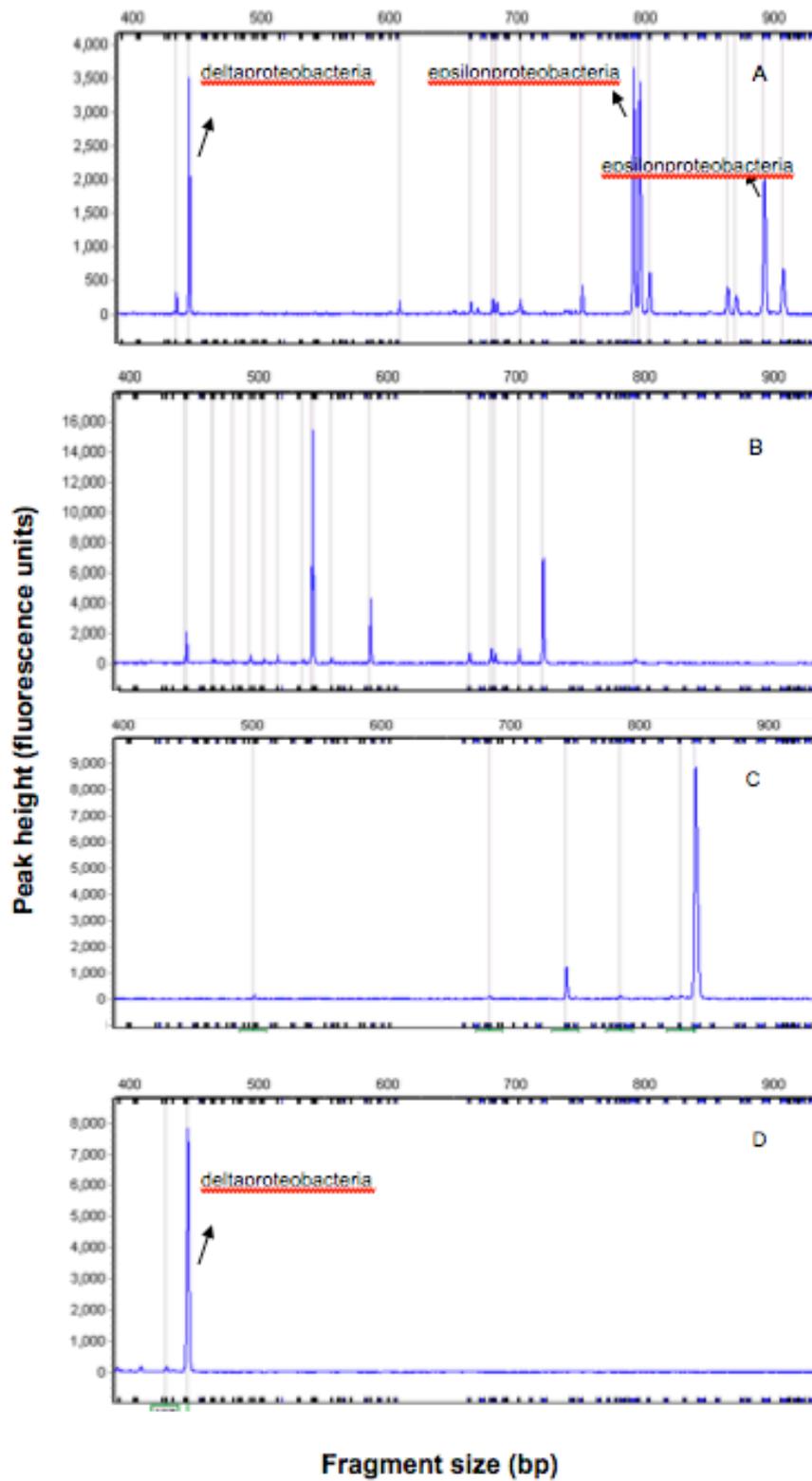


Figure 4. ARISA Profile of bacterial communities from Location 3. Data are from quarterly samples: Panel A., June 2007, B. November 2007, C. February 2008, D. May 2008.

Table 1. Estimated relative abundance of selected fragments in the bacterial community profiles for the three locations under study.

Location 1	Fragment size (bp)	Putative class/order	% identity	Mean Relative Intensity* \pm S.D. (Relative abundance)			
				June'07	Nov'07	Feb'08	May'08
	463	<i>Clostridia</i>	90%	16.55 \pm 2.05	6.79 \pm 1.14	74.77 \pm 0.39	19.25 \pm 14.29
	484	<i>Mollicutes</i>	92%	4.91 \pm 0.29	2.85 \pm 0.35	ND	ND
	544	<i>CFB group</i>	92%	2.05 \pm 0.49	ND	ND	12.32 \pm 1.81
	572	<i>Clostridia sp.</i>	98%	4.53 \pm 0.74	4.17 \pm 0.04	ND	36.25 \pm 0.42
	831	<i>Pseudomonas sp.</i>	97%	41.65 \pm 3.88	ND	ND	ND
Location 2							
	501	<i>Bacteroidetes</i>	90%	34 \pm 7.09	48.3 \pm 7.39	1.33 \pm 0.24	5.49 \pm 1.99
	594	<i>Spirochaetes</i>	87%	7.3 \pm 0.6	11.67 \pm 1.36	ND	ND
	690	<i>Spirochaetes</i>	88%	18.9 \pm 5.35	10.76 \pm 3.45	ND	8.26 \pm 2.38
	795	<i>Beta proteobacteria</i>	92%	ND	ND	47.59 \pm 1.67	16.28 \pm 3.78
Location 3							
	443	<i>Delta proteobacteria sp.</i>	97%	10.6 \pm 0.72	4.0 \pm 0.24	ND	88.04
	789/795	<i>Epsilon proteobacteria</i>	95%	21.8 \pm 0.11	ND	ND	ND
	891	<i>Epsilon proteobacteria</i>	91%	16.4 \pm 2.43	ND	91.92 \pm 0.88	ND

* Average of triplicate ARISA runs

ND – Peak not detected or below threshold of a peak area of 250 fluorescence units.

CONCLUSIONS – Distinct community profiles are associated with early and late stage of dechlorination. The species that are previously known to be affiliated with dechlorination sites are not observed in the location showing stalling of dechlorination at vinyl chloride. Late stage processes are preferred since it does not lead to the accumulation of toxic by-products. Therefore, understanding the difference in microbial communities stimulated in areas showing early and late stage processes is imperative. This study also gives an insight into populations other than dechlorinators in a field site undergoing ERD. A greater understanding of the role played by these species is needed for complete and successful ERD treatment.

ACKNOWLEDGMENTS – The authors are grateful to Dr. Frederick Payne (ARCADIS) for allowing access to samples from the site thus enabling this study, and to Wes May (ARCADIS) for his efforts in supplying groundwater samples for analysis.

REFERENCES -

1. Macbeth, T.W., et al., *Molecular characterization of a dechlorinating community resulting from in situ biostimulation in a trichloroethene-contaminated deep, fractured basalt aquifer and comparison to a derivative laboratory culture*. Applied and Environmental Microbiology, 2004. **70**(12): p. 7329-7341.
2. Nelson, D., F.C. Payne, and S.S. Suthersan, *Enhanced reductive dechlorination – A broader perspective*. Contaminated Soils, Sediments and Water 2003. **9**: p. 69-89.
3. Suthersan, S.S. and F.C. Payne, *Realities of enhanced reductive dechlorination*. Pollution Engineering, 2003. **April**: p. 42-49.
4. Cupples, A.M., A.M. Spormann, and P.L. McCarty, *Comparative evaluation of chloroethene dechlorination to ethene by Dehalococcoides-like microorganisms*. Environmental Science & Technology, 2004. **38**(18): p. 4768-4774.
5. Flynn, S.J., F.E. Löffler, and J.M. Tiedje, *Microbial community changes associated with a shift from reductive dechlorination of PCE to reductive dechlorination of cis-DCE and VC*. Environmental Science & Technology, 2000. **34**(6): p. 1056-1061.
6. Freeborn, R., et al., *Phylogenetic analysis of TCE-dechlorinating consortia enriched on a variety of electron donors*. Environ. Sci. Technol., 2005. **39**: p. 8358-8368
7. Magnuson, J.K., et al., *Trichloroethene reductive dehalogenase from Dehalococcoides ethenogenes: Sequence of tceA and substrate range characterization*. Applied and Environmental Microbiology, 2000. **66**(12): p. 5141-5147.
8. Krajmalnik-Brown, R., et al., *Genetic identification of a putative vinyl chloride reductase in Dehalococcoides sp strain BAV1*. Applied and Environmental Microbiology, 2004. **70**(10): p. 6347-6351.
9. Lowe, M., et al., *Geochemistry and microbial diversity of a trichloroethene-contaminated Superfund site undergoing intrinsic in situ reductive dechlorination*. Fems Microbiology Ecology, 2002. **40**(2): p. 123-134.
10. Fisher, M.M. and E.W. Triplett, *Automated approach for ribosomal intergenic spacer analysis of microbial diversity and its application to freshwater bacterial communities*. Applied and Environmental Microbiology, 1999. **65**(10): p. 4630-4636.
11. Brown, M.V., et al., *Coupling 16S-ITS rDNA clone libraries and automated ribosomal intergenic spacer analysis to show marine microbial diversity: development and application to a time series*. Environmental Microbiology, 2005. **7**(9): p. 1466-1479.
12. Weisburg, W.G., et al., *16s Ribosomal DNA Amplification for Phylogenetic Study*. Journal of Bacteriology, 1991. **173**(2): p. 697-703.

13. Grant, A. and L.A. Ogilvie, *Name that microbe: rapid identification of taxa responsible for individual fragments in fingerprints of microbial community structure*. Molecular Ecology Notes, 2004. **4**(1): p. 133-136.
14. Ingvorsen, K., A.J.B. Zehnder, and B.B. Jorgensen, *Kinetics of Sulfate and Acetate Uptake by Desulfobacter-Postgatei*. Applied and Environmental Microbiology, 1984. **47**(2): p. 403-408.
15. Richardson, R.E., et al., *Phylogenetic characterization of microbial communities that reductively dechlorinate TCE based upon a combination of molecular techniques*. Environmental Science & Technology, 2002. **36**(12): p. 2652-2662.

REFERENCES -

1. Macbeth, T.W., et al., *Molecular characterization of a dechlorinating community resulting from in situ biostimulation in a trichloroethene-contaminated deep, fractured basalt aquifer and comparison to a derivative laboratory culture*. Applied and Environmental Microbiology, 2004. **70**(12): p. 7329-7341.
2. Nelson, D., F.C. Payne, and S.S. Suthersan, *Enhanced reductive dechlorination – A broader perspective*. Contaminated Soils, Sediments and Water 2003. **9**: p. 69-89.
3. Suthersan, S.S. and F.C. Payne, *Realities of enhanced reductive dechlorination*. Pollution Engineering, 2003. **April**: p. 42-49.
4. Cupples, A.M., A.M. Spormann, and P.L. McCarty, *Comparative evaluation of chloroethene dechlorination to ethene by Dehalococcoides-like microorganisms*. Environmental Science & Technology, 2004. **38**(18): p. 4768-4774.
5. Flynn, S.J., F.E. Löffler, and J.M. Tiedje, *Microbial community changes associated with a shift from reductive dechlorination of PCE to reductive dechlorination of cis-DCE and VC*. Environmental Science & Technology, 2000. **34**(6): p. 1056-1061.
6. Freeborn, R., et al., *Phylogenetic analysis of TCE-dechlorinating consortia enriched on a variety of electron donors*. Environ. Sci. Technol., 2005. **39**: p. 8358-8368
7. Magnuson, J.K., et al., *Trichloroethene reductive dehalogenase from Dehalococcoides ethenogenes: Sequence of tceA and substrate range characterization*. Applied and Environmental Microbiology, 2000. **66**(12): p. 5141-5147.
8. Krajmalnik-Brown, R., et al., *Genetic identification of a putative vinyl chloride reductase in Dehalococcoides sp strain BAV1*. Applied and Environmental Microbiology, 2004. **70**(10): p. 6347-6351.
9. Lowe, M., et al., *Geochemistry and microbial diversity of a trichloroethene-contaminated Superfund site undergoing intrinsic in situ reductive dechlorination*. Fems Microbiology Ecology, 2002. **40**(2): p. 123-134.
10. Fisher, M.M. and E.W. Triplett, *Automated approach for ribosomal intergenic spacer analysis of microbial diversity and its application to freshwater bacterial communities*. Applied and Environmental Microbiology, 1999. **65**(10): p. 4630-4636.
11. Brown, M.V., et al., *Coupling 16S-ITS rDNA clone libraries and automated ribosomal intergenic spacer analysis to show marine microbial diversity: development and application to a time series*. Environmental Microbiology, 2005. **7**(9): p. 1466-1479.
12. Weisburg, W.G., et al., *16s Ribosomal DNA Amplification for Phylogenetic Study*. Journal of Bacteriology, 1991. **173**(2): p. 697-703.

13. Grant, A. and L.A. Ogilvie, *Name that microbe: rapid identification of taxa responsible for individual fragments in fingerprints of microbial community structure*. Molecular Ecology Notes, 2004. **4**(1): p. 133-136.
14. Ingvorsen, K., A.J.B. Zehnder, and B.B. Jorgensen, *Kinetics of Sulfate and Acetate Uptake by Desulfobacter-Postgatei*. Applied and Environmental Microbiology, 1984. **47**(2): p. 403-408.
15. Richardson, R.E., et al., *Phylogenetic characterization of microbial communities that reductively dechlorinate TCE based upon a combination of molecular techniques*. Environmental Science & Technology, 2002. **36**(12): p. 2652-2662.

Grant No. 08HQGR0001 Alternative Cover Guidance Document

Basic Information

Title:	Grant No. 08HQGR0001 Alternative Cover Guidance Document
Project Number:	2007WI199S
Start Date:	10/1/2007
End Date:	9/30/2008
Funding Source:	Supplemental
Congressional District:	02
Research Category:	Engineering
Focus Category:	Radioactive Substances, Groundwater, None
Descriptors:	
Principal Investigators:	Craig H Benson, Craig H Benson

Publication

1. none

Annual Progress Report

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

Submitted By: Jim Hurley

Submitted: 6/1/2009

Project Title

WR07R010: Alternative Cover Guidance Document

Project Investigators

Craig Benson, University of Wisconsin-Madison

Progress Statement

This project is focused on preparing a guidance document regarding design, construction, monitoring, and performance assessment of alternative covers for landfills. As of 29-Feb-08, we had prepared a detailed outline for the guidance document and have drafted some of the primary sections.

Principal Findings and Significance

Principal Findings and Significance

Description

This document is intended to provide engineers and scientists in the design and regulatory communities with the information s needed to effectively design, construct, monitor, and assess of alternative covers for landfills. When complete, this document will become the definitive source of information on the technology.

Interactions

Description

This project involves interaction with Region 8 of US EPA and state environmental regulators in Colorado, Wyoming, and Montana.

Event Date

Other Project Support

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

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

Publication

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 Multiple 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

.....

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

.....

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

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

Basic Information

Title:	Multi-Parameter, Remote Groundwater Monitoring with Referencing Using Crossed Optical Fiber Fluorescent Sensor Arrays.
Project Number:	2007WI2100
Start Date:	7/1/2007
End Date:	6/30/2009
Funding Source:	Other
Congressional District:	
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	, Peter Geissinger

Publication

1. Henning, Paul E., M. Veronica Rigo, and Peter Geissinger. 2007. Application of Microsphere Templating to Create Porous Optical Fiber Claddings for Crossed-Fiber Sensor Arrays. Proceedings of the American Chemical Society, 2007 National Meeting, Chicago, IL, U.S.A.
2. Geissinger, Peter and Alan W. Schwabacher. 2007. Fourier Transform Analysis for Linear, Periodic Arrays. Proceedings of the American Chemical Society, 2007 National Meeting, Chicago, IL, U.S.A.
3. Rigo, M.V. 2009. Plasmonic Optical Fiber Sensor for Oxygen Measurement. Ph.D. thesis, Department of Chemistry & Biochemistry, University of Wisconsin-Milwaukee.

FINAL PROJECT REPORT

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

Funded by:

State of Wisconsin Groundwater Research and Monitoring Program

Project ID: WR06R001

Submitted by:

Peter Geissinger
Associate Professor
Department of Chemistry & Biochemistry
University of Wisconsin-Milwaukee

TABLE OF CONTENTS

LIST OF FIGURES	3
PROJECT SUMMARY	4
MAIN SECTION	6
Introduction	6
Procedures and Methods	7
Optical Setup	7
Sensing Mechanisms	7
Sensor Fabrication	8
Results & Discussion	8
Leaching	8
Sensor Response Times	9
Calibration Curves	10
Sensor Reversibility, Repeatability, Longevity	12
Sensor Specificity	12
Ongoing Research and Future Work	13
Conclusions and Recommendations	15
References	15
APPENDIX A	16
Awards	16
Invited Talks	16
Contributed Talks	17
Poster Presentations	17

LIST OF FIGURES

Figure 1: <i>Optical time-of-flight detection</i>	6
Figure 2: <i>Fiber-fiber coupling scheme for improved spatial resolution</i>	7
Figure 3: <i>DO sensor fabrication scheme</i>	8
Figure 4: <i>DO sensor response time in N₂ and O₂ saturated media</i>	9
Figure 5: <i>Sensor response time to a pH-change from 4.0 to 6.4</i>	9
Figure 6: <i>Response of the pH-sensor in a microtemplated cladding</i>	9
Figure 7: <i>SEM image of a templated fiber junction</i>	9
Figure 8: <i>Referenced luminescence intensity and lifetime the DO sensor</i>	10
Figure 9: <i>Stern-Volmer plot of the referenced intensity and lifetime for the DO sensor</i>	10
Figure 10: <i>pH-sensor calibration curve</i>	11
Figure 11: <i>Fluorescein emission pulse shapes for different pH values</i>	11
Figure 12: <i>Reversibility of the DO sensor in the PEG-based hydrogel</i>	12
Figure 13: <i>DO sensor response after six months submerged in water</i>	12
Figure 14: <i>pH sensor repeatability</i>	12
Figure 15: <i>Effect of potential interferents on sensor performance</i>	13
Figure 16: <i>pH sensor calibration curves for two values of solution ionic strength</i>	13
Figure 17: <i>Polystyrene nanosphere templates</i>	13
Figure 18: <i>Fluorescein derivatives and their pK_a values</i>	14
Figure 19: <i>Luminescence enhancement factor η for RuPhen and silver nanorod.</i>	14

PROJECT SUMMARY

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

Project I.D.: WR06R001

Project Investigator: *Peter Geissinger*, Associate Professor, Department of Chemistry & Biochemistry, University of Wisconsin-Milwaukee

Research Assistants: *M. Veronica Rigo*, Graduate Student (Ph.D. program)

Paul E. Henning, Graduate Student (Ph.D. program)

Both: Department of Chemistry & Biochemistry, University of Wisconsin-Milwaukee

Period of Contract: July 1, 2006 – June 30, 2008

Background/Need: Real-time, in-situ measurements of general chemical and physical properties of groundwater are essential for studying the interactions of aquifers with surrounding soils and minerals. Furthermore, measuring contaminant concentrations continually over extended times and spatially resolved is at the heart of investigations regarding the sources of contamination of groundwater as well as the fate of these contaminants due to transport and chemical reactions. This project focused on the application of our recently developed (and patented) optical fiber sensor platform to groundwater monitoring issues.

Objectives: The goals of this project were to explore real-time, continuous measurement of pH and dissolved oxygen concentration as first sensing applications. For long-term deployment, sensor longevity, and ruggedness were important issues to be considered in the sensor design.

Methods: For measurement of the desired parameters at many locations using only a small number of optical fibers, we create many sensor regions along an optical fiber. At desired locations along the optical fiber, the fiber core is exposed by removing the original fiber cladding and suitable replacement claddings containing sensor molecules are attached. Sensing is based on changes of the fluorescence properties of sensor molecules. Light propagating inside of the fiber interacts with the sensor molecules outside of the fiber through evanescent fields. Fluorosensors located within the range of the evanescent fields are optically excited; subsequent fluorescence emission is captured by the fiber and guided to the detector at the fiber end(s). Spatially resolved readout is possible using pulsed-laser excitation and time-resolved detection; the arrival times of the fluorescence pulses from the respective sensor regions encode their locations. The spatial resolution improves dramatically by using two fibers that form orthogonal fiber-fiber junctions; sensor regions are located between the fibers at these junctions. One fiber carries the excitation light pulses, whereas the second fiber captures the fluorescence pulses and guides them to the detector. Sensor molecules are covalently attached to a porous gel, which replaces the original fiber cladding. This sensor active cladding is covalently attached to the core of the fiber, which is functionalized with a hydrophobic, self-assembled monolayer. In addition to providing attachment sites, this layer protects the fiber core from damage due to hydroxyl penetration. This array constitutes a general, high-spatial resolution sensing platform, whose functionality depends on the chosen sensor molecules.

Results & Discussion: A ruthenium complex was used to measure dissolved oxygen (DO) concentration. Sensing is based on the luminescence quenching due to the presence of oxygen. The dependence of the emission intensity on dissolved oxygen concentration is given by the Stern-Volmer equation. A second sensor region was employed as a reference region, recording

excitation laser pulse energies. Signal pulse energies were then divided by reference pulse energies to exclude source fluctuations effects. The sensor was capable of a detection limit of 0.18 ppm DO, which is well below the concentrations found in (most) streams and lakes. The sensor DO concentration resolution was 0.78 ppm at 4 ppm DO concentration and 0.82 ppm at 49 ppm DO concentration. The sensor was kept continuously submerged in (tap) water for more than six month; after this time period the sensor response was at 83% of the initial values, leading to a marginally poorer detection limit and resolution. We also monitored the dependence of the luminescence emission lifetimes on the DO concentration (also given by the Stern-Volmer equation). This measurement is advantageous because it is independent of pulse energies; however, the lifetime measurement is more complicated (signal pulse deconvolution is required for sensor molecules with lifetimes comparable to the excitation pulse widths). We found virtually identical detection limits and sensor resolutions, showing that the use of the sensor reference improves the quality of the pulse-energy-based measurement to that of the lifetime-based measurement.

To improve signal strengths either to allow for lower detection limits or for placing sensors at larger distances from light source and detector, we explored integrating metal nanoparticles into our sensors with the goal of exploiting the phenomenon of metal-enhanced luminescence, which is due to the surface plasmon resonance of the nanoparticles. Initial results using silver nanorods showed a fluorescence enhancement of a factor of 10 for DO measurement using a ruthenium complex as sensor dye.

The dye fluorescein encapsulated in a hydrogel was used for pH sensing. Again, a pulse energy reference sensor region was used to account for fluctuations of the pulse energies of the laser light source. A pH-resolution of better than 0.05 pH-units in the region of the sensor dye's pK_a -value was found. While this sensor performed successfully, the need for improvement of sensor response times (for pH sensing) became clear. We approached this issue by micro-templating the fiber cladding material, this created a porous cladding material that allowed for rapid analyte penetration and, consequently, for fast response times. Response times improved dramatically: 90% of the total signal change occurred within ~2s following a pH change.

Conclusions/Implications/Recommendations: We demonstrated that our fiber sensor platform is suitable for measurements in aqueous environments using pH- and DO-sensing as examples. These measurements were greatly improved by the capability of the platform of providing other sensor regions in close proximity to pH- and DO sensor regions for pulse energy referencing. A novel cladding containing engineered nanochannels improved sensor response times substantially. With these sensor arrays, these measurements can be carried out continuously, in real-time and at many locations!

Related Publications: M. Veronica Rigo, for research conducted within the framework of this project, was recognized with the "Best Oral Presentation Award" at the University of Wisconsin System Laboratory for Surface Studies Symposium (2008), the "Conference Poster Award" at the 2007 International Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, and a "Poster Prize" at the 2006 American Water Resources Association (Wisconsin Section) Annual Meeting.

Key Words: Remote sensing, optical fibers, fiber sensor arrays, pH, dissolved oxygen

Funding: This work is currently funded by the UW-Milwaukee Research Growth Initiative.

Introduction

The use of optical fiber sensors for monitoring groundwater contaminants was first suggested twenty years ago by T.E. Hirschfeld [1]. Hirschfeld listed a number of arguments in favor of optical fiber sensors for this purpose such as (1) that the insertion of fiber-optic probes into groundwater can be accomplished with small diameter boreholes; (2) that the measurements take place in-situ, avoiding sample contamination due to transport and delayed analysis; and (3) that the monitoring takes place in real time. Measuring contaminant concentrations continually over extended times and spatially resolved is at the heart of investigations regarding the sources of contamination of groundwater as well as the fate of these contaminants due to transport and chemical reactions.

In our optical fiber sensors (as in Hirschfeld's and other subsequent measurements (see e.g. [2])), sensing is based on changes of molecular fluorescence due to changes in the physical and chemical environment or due to the presence of specific chemical compounds. Fluorescence detection is an inherently sensitive technique, as (in principle) measurements can take place against zero background. Moreover, not only can a change in fluorescence intensity be used for sensing, but also changes in the maximum wavelength of fluorescence emission and changes in the fluorescence lifetime. To detect non-fluorescent compounds, the fibers could be functionalized with indicator molecules whose fluorescence properties change with binding of or interaction with the analyte.

In contrast to Hirschfeld's sensors, which are placed at the end of an optical fiber, we employ many discrete sensor regions along an optical fiber (i.e. quasi-distributed sensing) [3,4] for sensing. Sensor dyes are located in the fiber cladding in a suitable substance replacing the original cladding. The light propagating through the fiber core under total internal reflection conditions can interact with the sensor molecules *outside* of the fiber core through the evanescent fields of the core modes. If a fluorescent molecule is present within the range of the evanescent fields, it can be excited through the light in the fiber core; total internal reflection is attenuated in this case. Subsequently, the fluorescence emitted by this molecule can be captured by the fiber and propagate to the fiber ends *under guided conditions*! Spatially resolved readout is accomplished using pulsed laser excitation and time-resolved detection: a laser pulse is coupled into the fiber core and triggers a fluorescent pulse at a sensor region (see Figure 1). This fluorescence pulse, after being captured by the fiber, travels back to the front-end of the fiber; from the time delay τ_d between the exciting pulse and the fluorescence pulse the location L of the emitting fluorophore can be calculated according to $L = (c/2n_{co})\tau_d$, where c and n_{co} are the speed of light in vacuum and the refractive index of the fiber core, respectively. Each sensor region on the fiber returns fluorescence pulses with its own characteristic time delay: the measured signal

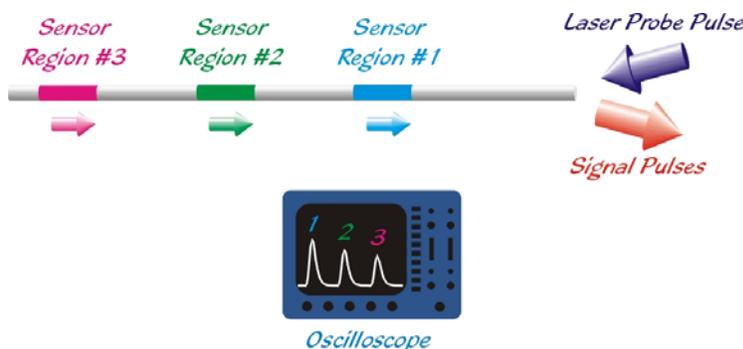


Figure 1: Optical time-of-flight detection for spatially resolved readout of many sensor regions supported by a single fiber. The time delay between excitation pulse and returning fluorescence pulse encodes the locating of the emitting sensor (see text).

is a pulse train that encodes the location of all emitting sensors. This technique is known as Optical Time Domain Reflectometry [5], or, more appropriately for fluorescence based measurements, Optical Time-of Flight Detection (OTOF) [6].

This project focused on the application of our recently developed (and patented) optical fiber sensor platform (see below for details) to groundwater monitoring issues. The goal was to implement two fairly standard measurement tasks, namely pH and dissolved oxygen concentration, which still are very relevant measurements given that on optical fibers the measurements can take place continuously, in real-time, and at many remote locations. Moreover, measurements in demanding environments such as groundwater are frequently plagued by biofouling, which is the deposition of organic matter on the submerged probes. This issue limits the time a sensor can be deployed. Therefore, we studied ways to protect the fiber sensor from fouling and from damage from hydroxyls entering the fiber core through microcracks (causing optical transmission losses to increase).

Procedures and Methods

Optical Setup: The spatial resolution, i.e. the minimum separation of adjacent sensor regions on a fiber, is determined by the fluorescence lifetimes of the sensor molecules. For standard sensor molecules, the spatial resolution is of the order of 2.5m or larger. To allow for point monitoring of multiple parameters, we developed an optical fiber sensor array [7-9], which is based on the evanescent coupling between two optical fibers forming orthogonal fiber-fiber junctions. The sensor molecules are placed at this fiber-fiber junction. A laser pulse traveling through the first fiber excites the sensor molecules at the junction through the evanescent fields; the subsequent

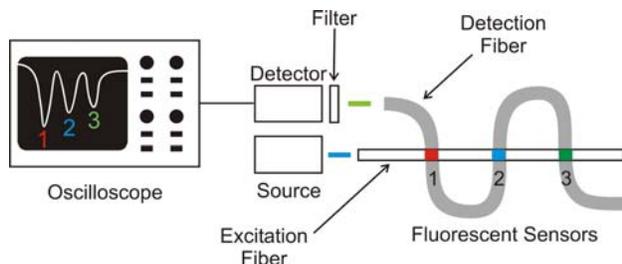


Figure 2: Fiber-fiber coupling scheme for improved spatial resolution (see text). Sensor regions are located at the fiber-fiber junctions.

fluorescence pulse is captured – again through evanescent fields – by the second fiber and guided to the detector. The merits are illustrated when multiple fiber-fiber junctions are considered (see Figure 2): along the excitation fiber, which carries the excitation laser pulse, the sensor regions may be spaced by as little as a few millimeters; however, the fluorescence pulses entering the second fiber are delayed with respect to each other on the way to the detector using delay coils, restoring full time- and, hence, spatial resolution.

A dye laser pumped by a pulsed nitrogen laser (pulse width 0.6 ns) was used to provide to excited the sensor molecules; various photomultiplier tubes (PMT) were used to detect their fluorescence. The PMT output was recorded by fast oscilloscope (bandwidth 1 GHz).

Sensing Mechanisms: Dissolved oxygen (DO) sensing is based on the luminescence quenching of a ruthenium complex. A collision of an oxygen molecule with the ruthenium complex while the latter is in its electronic excited state results in energy transfer from ruthenium to oxygen. Thus, the ruthenium complex returns to its electronic ground state non-radiatively, which results in a decrease of the luminescence signal. This process is described by the Stern-Volmer equation

$$\frac{\tilde{I}_0}{\tilde{I}} = 1 + K_{SV} DO,$$

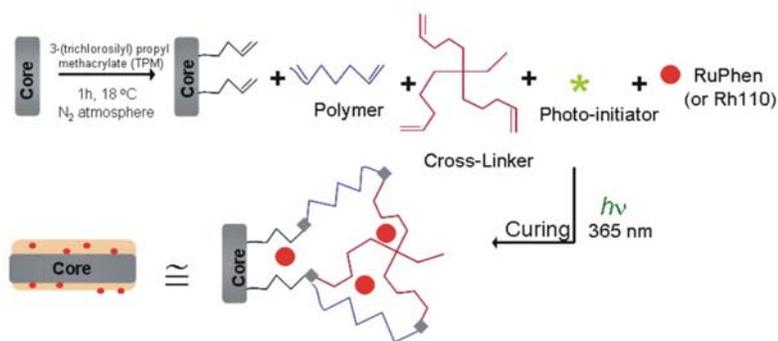
where \tilde{I}_0 and \tilde{I} are the integrated ruthenium luminescence intensities in absence and presence of O_2 , respectively, DO is the dissolved oxygen concentration, and K_{SV} is the Stern-Volmer quenching constant. In many cases, this equation also holds true for the luminescence lifetimes τ_0 and τ absence and presence of O_2 , i.e.

$$\frac{\tau_0}{\tau} = 1 + K_{SV} DO.$$

pH-sensing is based on the protonation/deprotonation reaction of a dye (in our case fluorescein) as the pH changes. Protonation/deprotonation changes the luminescence properties of the dye. pH-sensing is most sensitive in the pH-range about the pK_a -value (which indicates 50% protonation).

Sensor Fabrication: To create a sensor region, the fiber core has to be exposed. First the outer layers of commercially available fibers were removed with mechanical fiber strippers. The most effective way of removing the fiber cladding was by burning in a flame. Fiber core images recorded with a scanning electron microscope verified that most of the cladding is removed with the technique and that the fiber core is undamaged.

The next step is to functionalize the exposed fiber core with a self-assembled, hydrophobic monolayer. This layer protects the fiber core from hydroxyl penetration and creates a reactive surface that is used to covalently attach sensor-active fiber claddings. The latter encapsulate the sensor molecules. Alternatively, sensor molecules may be covalently attached to these claddings, as long as the attachment does not negatively affect their fluorescence properties. Figure 3 shows the steps for the fabrication of the DO sensor. Coating solutions were created by mixing the cladding material (poly(ethylene glycol) diacrylate 575 (PEG-DA)), a crosslinking agent and a photoinitiator. Separate solutions of dichlorotris (1, 10-phenanthroline) ruthenium (II) (RuPhen - the oxygen sensor dye) and Rhodamine 110 (Rh110 - the intensity reference dye,) in ethanol were made. Each fluorophore solution was added to the



PEG-DA 575 solution to make a 1:10 (v/v) mixture. Exposure to UV radiation (wavelength 365 nm) initiated crosslinking and attachment to the monolayer on the fiber core. The pH-sensor was created in a similar fashion. The commercially available dye fluorescein was derivatized to allow for covalent attachment to PEG-DA.

Figure 3: DO sensor fabrication scheme (for details see text).

Results & Discussion

Leaching: We tested the degree of encapsulation of RuPhen and Rh110 in the cladding material. Based on the molecular size of Rh110 and RuPhen the best matrix candidates are PEG-DA with a molecular weight of 575 or/and PEG-MA with a molecular weight of 1000. The higher the polymer molecular weight, the more hydrophobic and porous it becomes. The fiber was submerged in water and the degree of dye leakage out of the cladding was monitored by monitoring the change the fluorescence intensity every ten minutes for two days. We found that

an increase in the dye leaching occurs as the matrix molecular weight increases. This can be understood in terms of the increasing porosity and decreasing hydrophobicity of the matrix as the molecular weight increases. Addition of the crosslinker and photopolymerization greatly reduced the dye leakage; after an initial loss of dye of $\sim 20\%$, the fluorescence signal remained constant. However, as crosslinking decreases the matrix porosity, the sensor response times may be affected. Clearly, when possible, covalent attachment is preferable, as shown with the dye used for pH sensing.

Sensor Response Times: Figure 4 shows the response of the DO sensor to repeated changes between a nitrogen and oxygen environment by bubbling nitrogen through the water in the cell containing the fiber sensors. The calculated transition times are of the order of 5 seconds; however we believe that the actual sensor response times are shorter, because changing between oxygenated and deoxygenated environments is not instantaneous due to the filling times of the attached tubing and due to the time required for the diffusion of oxygen to and away from the sensor sites. Thus, the given response times constitute an upper limit.

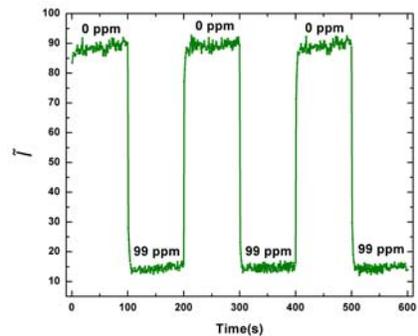


Figure 4: DO sensor response time in N_2 and O_2 saturated media.

The response times of the pH-sensor, however, were disappointing: upon change of pH from 4.0 to 6.4, the fluorescence signal increased only gradually; for full equilibration, two hours were required in a static solution (i.e. no stirring - see Figure 5)! A different approach was required to dramatically improve the sensor response times: we decided to employ a nano/microsphere templating approach to engineer nano/microscale channels into the cladding material for improved analyte penetration. Polystyrene spheres (diameter 950 nm) were mixed with the matrix polymer, crosslinking agent, and photoinitiator. This slurry was placed onto the fiber core. After brief exposure to UV radiation, the slurry hardened. Subsequently, the polystyrene beads were removed with toluene, leaving behind a network of micro- and nanoscale channels (see Figure 7), which allow for easy analyte penetration to the sensor molecules. Figure 6 shows the response of the pH-sensor in a nano/microtemplated cladding to a series of pH-changes. It can be seen that there is now an initial fast response to pH-changes; most of the total signal change occurs during this time period! Full equilibration is reached after 15 minutes.

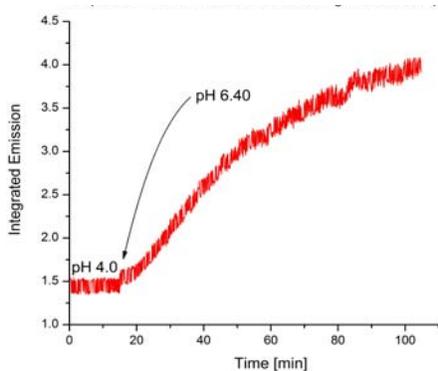


Figure 5: Sensor response time to a pH-change from 4.0 to 6.4.

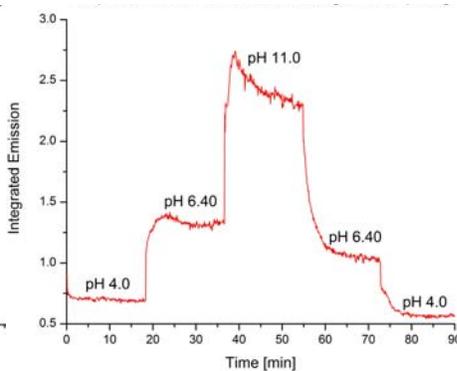


Figure 6: Response of the pH-sensor in a microtemplated cladding.

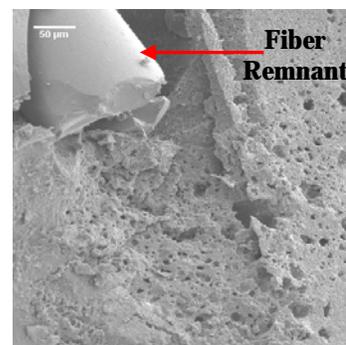


Figure 7: SEM image of a templated fiber junction.

Calibration Curves: The sensor response to a series of DO concentrations was determined from the ratio of the fluorescence intensity of RuPhen to that of Rh110; this ratio is denoted \tilde{I} . The total sensor sensitivity can be expressed by the overall quenching response to dissolved oxygen (Q_{DO}) given by

$$Q_{DO} = \frac{\tilde{I}_{N_2} - \tilde{I}_{O_2}}{\tilde{I}_{N_2}} \times 100\% ,$$

where \tilde{I}_{N_2} and \tilde{I}_{O_2} represent referenced intensities in fully deoxygenated and fully oxygenated water, respectively. The higher the Q_{DO} -value, the better is the sensor sensitivity. For sensor molecules encapsulated and/or attached to polymers, the Q_{DO} -value is dependent on the polymer material composition. While hydrogel films demonstrated a good performance for sensing oxygen gas, their performance for DO sensing was expected to be different. Oxygen has a relatively low solubility in water (0.00425 g in 100 g of water at 21° C, 1 atm), which implies that there is a reduced number of oxygen molecules in air-equilibrated water compared with air under ambient conditions. Tailoring the matrix composition alleviates this problem and increases Q_{DO} . The chemical fabrication of the PEG-DA hydrogels allows for manipulating the physicochemical properties of this material by varying the amount or type of reactant used in its synthesis. A less hydrophilic film should enhance the DO sensing process by reducing water solubility in the matrix, causing the partitioning of oxygen out of the solution to the matrix, thus increasing the accessibility of oxygen molecules to RuPhen sensor molecules. In particular, addition of the crosslinker increases the hydrophobicity of the PEG-DA 575 hydrogel film, which leads to an enhancement in the quenching response, resulting in a value of $Q_{DO} = 83\%$ (see Figure 8). It is important to mention that the addition of the crosslinker increases the refractive index of the hydrogel cladding. Thus, there is a limit to the amount of crosslinker that may be added, because the refractive index of the hydrogel clad n_{clad} has to remain smaller than that of the core, i.e. $n_{clad} < n_{core}$, to preserve the guiding conditions of the optical fiber.

Figure 8 shows the referenced RuPhen luminescence intensity and excited state lifetime vs. DO concentration (the sensor and reference were submerged in water). Both quantities decrease with increasing oxygen concentration in accordance with the Stern-Volmer equation. To better illustrate this, both quantities were plotted as $\tilde{I}_0/\tilde{I} - 1$ and $\tau_0/\tau - 1$ vs. DO concentration in accordance with the Stern-Volmer equation (see Figure 9). The dash-dotted line represents the best linear fit generated by the least-squared method. The sensor has a good linearity over the whole range of DO concentration tested, which may indicate negligible matrix heterogeneity effects. The good

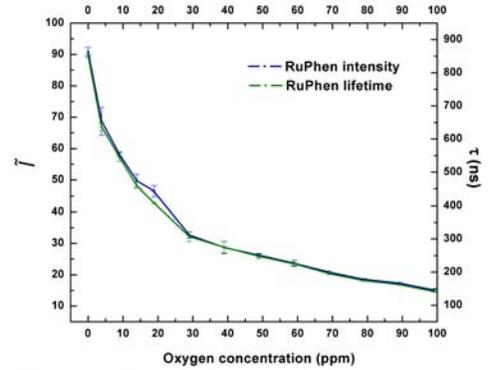


Figure 8: Referenced luminescence intensity (blue, left axis) and lifetime (green, right axis) of the RuPhen sensor for different DO concentrations [ppm].

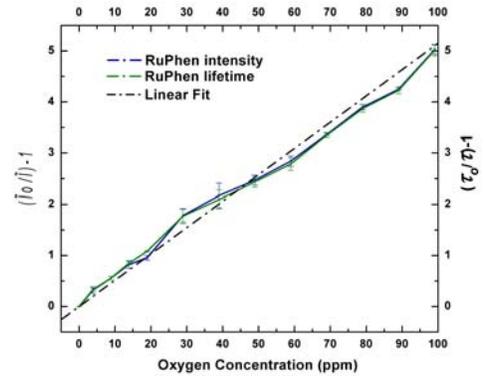


Figure 9: Stern-Volmer plot of the referenced intensity and lifetime for the DO sensor in the aqueous phase.

Q_{DO} value and the linearity in the Stern-Volmer plot may result from the structure and hydrophobic nature of the film used in the sensor preparation.

The sensor sensitivity, i.e. the change of the luminescence intensity per unit DO concentration change, depends on DO concentration; as the Stern-Volmer equation shows, the sensor luminescence intensity I depends on DO concentration as DO^{-1} . Thus, the sensor resolution, R , which is the smallest measurable DO concentration change, also depends on DO concentration. It is important to note that the sensor sensitivity and resolution increase with decreasing DO concentration. Therefore, the sensor performs best at the lowest DO concentrations. We found at 4 ppm DO concentration a resolution of $R= 0.78$ ppm, whereas at 49 ppm DO concentration the resolution was $R= 0.82$ ppm. The DO detection limit was found to be 0.18 ppm.

The calibration curve for the pH sensor in a nano/microtemplated cladding was established by placing the fiber-fiber junctions into a series of buffer solutions. Although the emission intensity of the fluorescein sensor dye was usually stable, the use of an intensity reference improved the sensor accuracy. In this case, the reference signal was detected by directing part of the laser pulses towards a photodiode detector, before the laser pulses were coupled in the fiber. Figure 10 shows the calibration curve (emission intensity divided reference intensity vs. pH) with a sigmoidal fit curve, which also allowed for the extraction of the pK_a value, which was found to be $pK_a = 7.07 \pm 0.04$. Hysteresis effects were small, i.e. there were minor signal differences for measurement sequences from low to high pH vs. sequences from high to low pH.

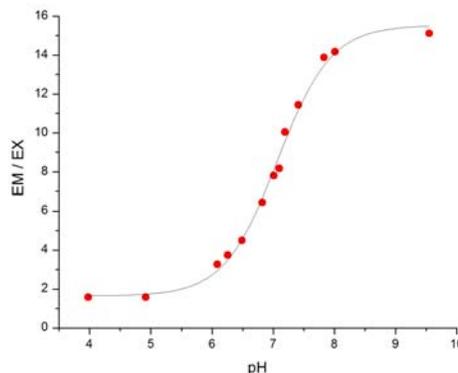


Figure 10: *pH-sensor calibration curve (see text for details).*

From the calibration curve (Figure 10), it is obvious that the sensor is most sensitive (i.e. has the largest signal change for a unit pH change) in the pH region around the pK_a value. Consequently, the pH resolution is highest in this pH region as well; we determined a pH resolution of 0.03 pH units within the range of $pK_a \pm 0.5$ and a pH resolution of 0.07 pH units within the range of $pK_a \pm 1.0$.

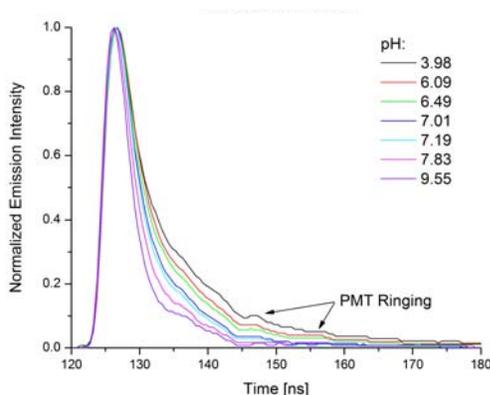


Figure 11: *Fluorescein emission pulse shapes for different pH values.*

In addition to emission intensity changes, fluorescein also exhibits a decrease of the fluorescence lifetimes with increasing pH. Figure 11 shows a series of signal pulses vs. time for different pH values, showing that fluorescence lifetime measurements can serve as alternative, intensity-independent measurement method for pH. As the fluorescence lifetimes (~ 10 ns) – which are much shorter than those of RuPhen – are close to the laser pulse width, deconvolution of the measured signal pulse shapes is required to extract the correct fluorescence lifetimes. This is complicated by the PMT ringing (see Figure 11) at the tails of the emission pulses. PMT ringing is an artifact inherent in PMTs. However, we are

currently implementing time-correlated single photon counting measurements, which are insensitive to this artifact and allow for detection of the lowest light levels.

Sensor Reversibility, Repeatability, Longevity: We used the cycle-purging method to check the reversibility of RuPhen DO sensor physically entrapped in the PEG-DA 575 hydrogel matrix. The referenced sensor intensity \tilde{I} was plotted during several oxygenation/deoxygenation cycles (Figure 12). Upon switching from nitrogen-saturated to oxygen-saturated solution, the referenced intensity \tilde{I} decreased with an increase of DO concentration as expected. This process was repeated multiples times with no significant change in \tilde{I} between the initial nitrogen-saturated solution, indicating complete reversibility and repeatability of the sensor.

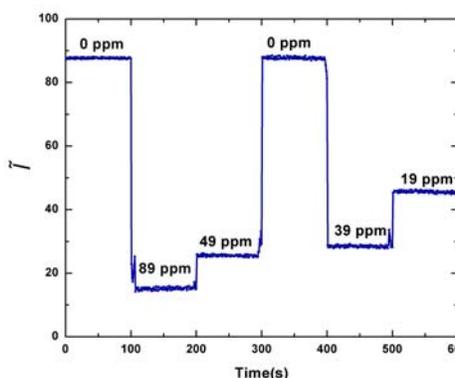


Figure 12: Reversibility of the DO sensor in the PEG-based hydrogel for alternating DO concentrations.

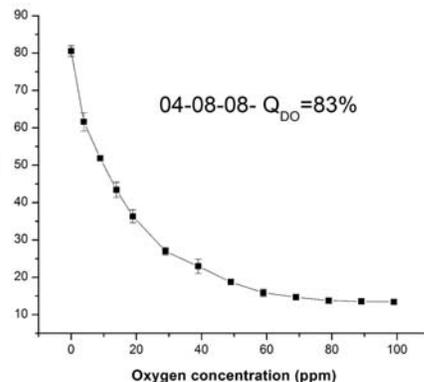


Figure 13: DO sensor - referenced intensities vs. DO concentration after six months submerged in water.

The DO sensor was submerged continuously in (laboratory) water for more than six months. Figure 13 shows the referenced emission intensities vs. DO concentrations after this time period. There was no performance degradation, as shown by the unchanged Q_{DO} -value of 83%!

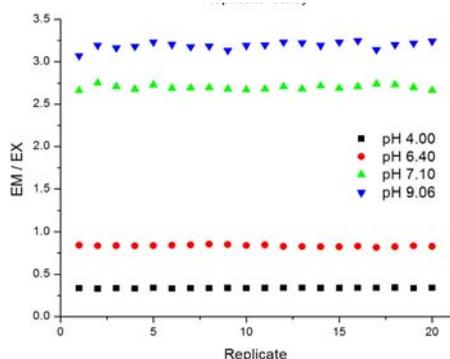


Figure 14: pH sensor repeatability. Referenced emission intensity vs. number of replicate measurements.

The pH-sensor was also tested for repeatability. Twenty replicate measurements were made for four different pH-values (see Figure 14). The sensor proved to produce stable results. The dye fluorescein is known for being photolabile, that is, it tends to decompose after prolonged exposure to resonant light. While most energy relaxation takes place via photon emission (which provide our sensor signal), the occasional non-radiative relaxation does occur, which means that excitation energy is released as heat. We observed this effect in earlier measurements with physically entrapped fluorescein molecules, which have to store this energy internally, which in turn could lead to decomposition. Covalent attachment of fluorescein to the hydrogel matrix, however, appears to improve the photostability of fluorescein; the excitation energy absorbed by fluorescein when optically excited can be released as heat to the hydrogel matrix through the attachment bond. Further measurements are needed to quantify the improvement of the sensor stability due to the covalent attachment.

Sensor Specificity: The DO response sensor was tested in present of different anions, cations reducing and oxidizing agents as well as in the presence of proteins to determine the possible interferences to the DO measurement. The results are shown in Figure 15. The DO sensor

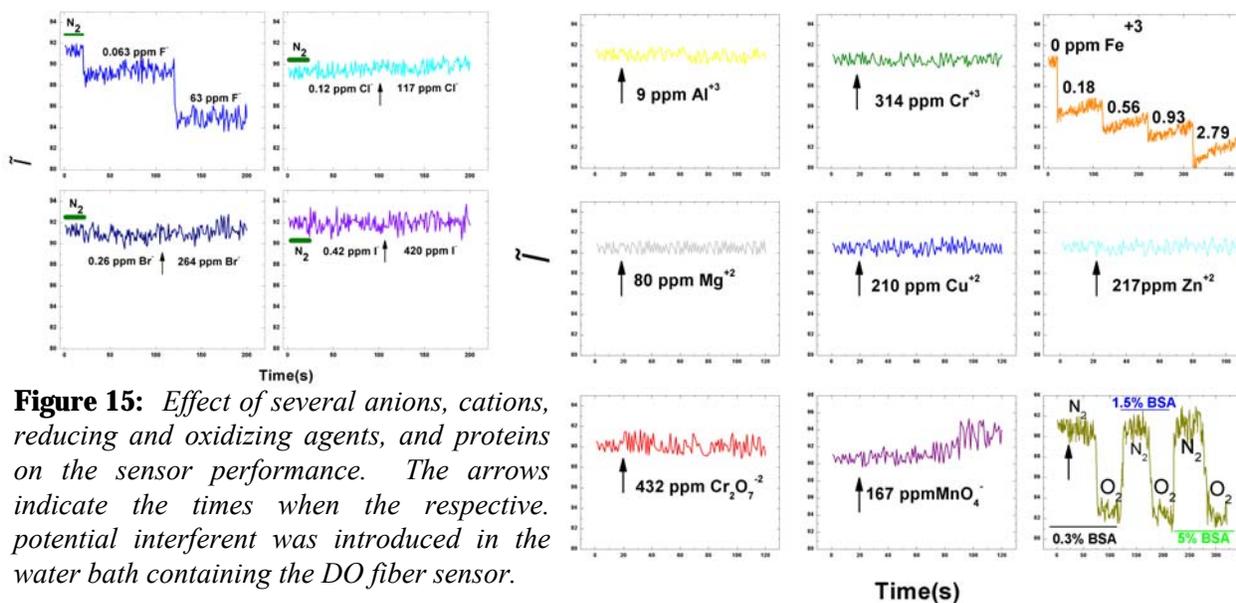


Figure 15: Effect of several anions, cations, reducing and oxidizing agents, and proteins on the sensor performance. The arrows indicate the times when the respective potential interferent was introduced in the water bath containing the DO fiber sensor.

response was affected by the presence of F^- and Fe^{+3} . Non-covalent interactions between the fluorescent sensor and native proteins (Bovine Serum Albumin) were investigated, which is important in cellular environments. These plots also show that the encapsulation of RuPhen in a biocompatible material reduces dye toxicity and minimizes biofouling.

The response of the pH sensor was tested for a possible dependence on the ionic strength of the surrounding aqueous solution. Calibration curves for two different ionic strengths were obtained (see Figure 16). We found that the pH measurement is in fact independent of ionic strength. Thus, the pH measurement does not have to be corrected for ionic strength; future arrays will contain separate sensor regions for measuring ionic strength.

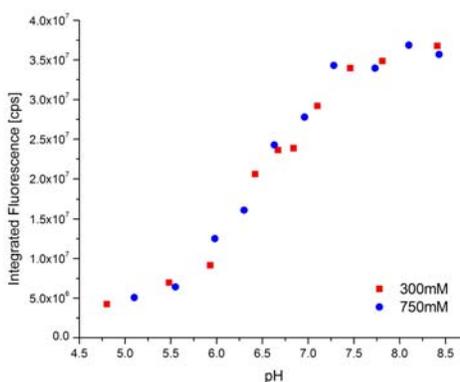


Figure 16: pH sensor calibration curves for two values of solution ionic strength. No effect can be seen.

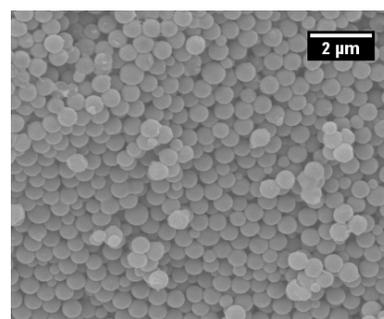


Figure 17: Polystyrene nanosphere templates synthesized in our lab for sensor cladding fabrication with nanochannels.

Ongoing Research and Future Work:

(a) Cladding materials with engineered channels for rapid analyte penetration

Because of the dramatic improvements in the sensor response times when using a cladding with engineered micro- and nanochannels, we will continue to improve the templating strategy. Starting point are the polystyrene spheres. While the first set was acquired commercially, we have begun to synthesize our own spheres (see Figure 17). This allows us to systematically vary sphere diameter and also sphere diameter distributions. It is anticipated that a broader distribution of bead diameters leads to more continuous channel networks, thus improving

analyte penetration and, consequently, sensor response times. We will also use different polymers to form the cladding “scaffold” once the spheres have been removed. Moreover, we will develop strategies for covalently attaching other fluorescent sensor dyes to the walls of the nanochannels for improved analyte access, and, consequently, for improved sensor responses.

(b) pH-sensor improvement

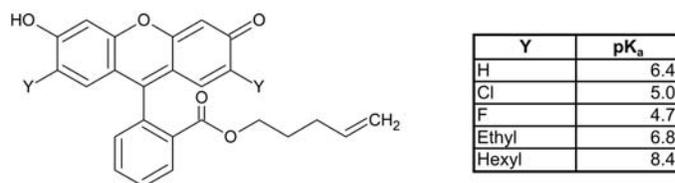


Figure 18: Fluorescein derivatives and their pK_a values.

regions (which is easily accomplished within our fiber sensor platform), a significantly wider pH range may be probed. All of these derivatives can be covalently attached to avoid dye leaching and to increase photostability.

(c) Dissolved oxygen sensor improvement

The oxygen-quenching process – i.e. the mechanism used for oxygen sensing – is temperature dependent. Thus, the sensor response must be corrected for temperature effects to allow for quantitative remote DO concentration measurements in environments experiencing wide temperature variations. We recently began testing a fluorescent dye as temperature sensor. The dye is enclosed in an oxygen impermeable polymer nanoparticle to exclude any effect of oxygen on this sensor. The temperature sensor will be added to our fiber sensor arrays. Furthermore, we are planning to add sensor regions that monitor the concentration of substances that were identified as interferents of the DO measurement. With these sensor responses, the DO response can be corrected for increased accuracy.

Finally, using the DO sensor as example, we began implementing a strategy of increasing the luminescence of sensor dyes. This is accomplished by adding to sensor regions metal nanoparticles at well-defined distances (~ 8-10 nm) from the sensor dyes. When the free electrons of the metal nanoparticles are excited at their surface plasmon resonance frequency, the electromagnetic field at the sensor dyes is enhanced. This leads to enhanced absorption and/or enhanced emission of a dye molecule, if the nanoparticle sizes are chosen appropriately. We constructed a DO sensor fiber-fiber junction that meets these requirements; we found that silver nanorods separated by four spacer layers from RuPhen (the thickness of one spacer layer is 2 nm), produced an almost ten-fold luminescence enhancement of RuPhen! This is shown in more detail in Figure 19, where the luminescence enhancement factor η is plotted vs. the number of spacer layers; for four spacer layers there is a clear maximum (blue curve) in the luminescent enhancement. This emission enhancement should translate into lower detection limits and/or the ability of placing sensor farther along the fiber from the light source and detector. We will continue this promising line of

To extend the range of pH values that can be measured with our fiber sensor arrays, we have begun synthesizing derivatives of fluorescein with different pK_a values. This is accomplished by varying one single side group (see Figure 18). Thus, by creating several sensors

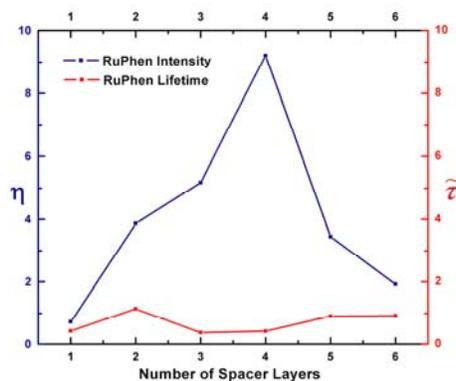


Figure 19: Luminescence enhancement factor η (blue) for RuPhen vs. number of spacer layers between RuPhen and silver nanorods.

investigation with the goal of further improving the enhancement factor for different nanoparticles shapes and sizes and for other sensor dyes.

(d) Sensor platform improvement

We will continue to develop the fiber sensor platform for sensing of many parameters in aqueous environments. The next steps are the addition of sensor regions for temperature and ionic strength measurements (see above). Furthermore, we are currently assembling a highly sensitive detection scheme (time correlated single photon counting) that allows for detection single photon and precisely measure their arrival times at the detector. This promises much improved detection limits and precise determination of luminescence lifetimes.

Conclusions and Recommendations

We demonstrated the suitability of our fiber sensor platform for use in aqueous environments. The performance of a dissolved oxygen sensor and a pH sensor were carefully evaluated with regard to detection limits, resolution, interferences, repeatability, and longevity. The response time of the pH sensor was improved dramatically using engineered cladding materials containing nano- and microscale channels for improved analyte penetration. The “scaffold” material around these channels was optimized for longevity in aqueous environments; the dissolved oxygen fiber sensor was submerged continuously in water for six months and showed not performance degradation. These are very promising results for future long-term deployment of fiber sensor arrays into ground and surface waters. Further improvement of our sensor platform is ongoing.

References

- [1] T. E. Hirschfeld, *Feasibility of Using Fiber Optics for Monitoring Groundwater Contaminants*, *Opt. Eng.*, **22**, 527-531 (1984)
- [2] J. E. Kenny, G. B. Jarvis, W. A. Chudyk, and K. O. Pohlig, *Remote Laser-Induced Fluorescence Monitoring of Groundwater Contaminants: Prototype Field Instrument*, *Anal. Instr.*, **16**, 423-445 (1987)
- [3] J. P. Dakin, *Distributed Optical Fiber Sensors*; Proceedings of the Conference on Distributed and Multiplexed Fiber Optic Sensors II, pp 76-108, Boston, MA, U.S.A., 1992.
- [4] C. A. Browne, D. H. Tarrant, M. S. Olteanu, J. W. Mullens, and E. L. Chronister, *Intrinsic Sol-Gel Clad Fiber-Optic Sensors with Time-Resolved Detection*, *Anal. Chem.*, **68**, 2289-2295 (1996)
- [5] Y. Ueno and M. Shimizu, *Optical Fiber Fault Location Method*, *Appl. Opt.*, **15**, 1385-1388 (1976)
- [6] R. A. Potyrailo and G. M. Hieftje, *Spatially Resolved Analyte Mapping with Time-of-Flight Optical Sensors*, *Trends Anal. Chem.*, **17**, 593-604 (1998)
- [7] B. J. Prince, A. W. Schwabacher, and P. Geissinger, *A Readout Scheme for Closely Packed Fluorescent Chemosensors on Optical Fibers*, *Anal. Chem.*, **73**, 1007-1015 (2001)
- [8] B. J. Prince, A. W. Schwabacher, and P. Geissinger, *Fluorescent Fiber-Optic Sensor Arrays Probed Utilizing Evanescent Fiber-Fiber Coupling*, *Appl. Spectrosc.*, **55**, 1018-1024 (2001)
- [9] P. E. Henning, A. Benko, R. J. Olsson, A. W. Schwabacher, and P. Geissinger, *Apparatus and Methods for Optical Time-of-Flight Discrimination in Combinatorial Library Analysis*, *Rev. Sci. Instr.*, **76**, 062220 (2005)

APPENDIX A:

AWARDS

M. Veronica Rigo, for research conducted within the framework of this project, was recognized with the “Best Oral Presentation Award” at the University of Wisconsin System Laboratory for Surface Studies Symposium (2008), the “Conference Poster Award” at the 2007 International Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, and a “Poster Prize” at the 2006 American Water Resources Association (Wisconsin Section) Annual Meeting.

PRESENTATIONS

Invited Talks

Department of Chemistry Colloquium
University of Wisconsin-Oshkosh
Oshkosh, WI, U.S.A., November 2, 2007
The “Lighter” Side of Remote Sensing: Distributed Optical Fiber Sensing using Fiber-Grid Arrays and Metal-Enhancement Effects
Peter Geissinger

Science and Math Student Club
University of Wisconsin-Washington County
West Bend, WI, U.S.A., October 24, 2007
The “Lighter” Side of Communication: Connecting the World with Optical Fibers
Peter Geissinger

Research Seminar
Intelligent Optical Systems, Inc.
Torrance, CA, U.S.A., June 19, 2007
High Spatial Resolution Optical Fiber Sensor Arrays
Peter Geissinger

Department of Chemistry Colloquium
University of Wisconsin-Whitewater
Whitewater, WI, U.S.A., February 23, 2007
The “Lighter” Side of Remote Sensing: Distributed Optical Fiber Sensing using Fiber-Grid Arrays and Metal-Enhancement Effects
Peter Geissinger

The Science Bag Public Lecture Series
University of Wisconsin-Milwaukee
Milwaukee, WI, U.S.A., January 5, 12, 14, 19, 26, 2007
The “Lighter” Side of Communication: Connecting the World with Optical Fibers
Peter Geissinger and Robert J. Olsson

Department of Chemistry Colloquium
University of Missouri – Columbia
Columbia, MO, U.S.A., October 6, 2006

The “Lighter” Side of Remote Sensing: Distributed Optical Fiber Sensing using Fiber-Grid Arrays, Metal-Enhancement Effects, and ... Combinatorial Chemistry?

Peter Geissinger

Contributed Talks

FACSS 2008: 35th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies

Federation of Analytical Chemistry and Spectroscopy Societies

Reno, NV, U.S.A., September 28-October 2, 2008

Fabrication of Functional Plasmonic Nanoparticles through Layer-by-Layer Assembly on Optical Fiber for Real-Time and Spatially-Resolved Oxygen Measurement

M. Veronica Rigo and Peter Geissinger

Laboratory for Surface Studies Summer Symposium

University of Wisconsin-Milwaukee

Milwaukee, WI, U.S.A., August 21, 2008

Plasmonic Optical Fiber Sensors

M. Veronica Rigo and Peter Geissinger

FACSS 2007: 34th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies

Federation of Analytical Chemistry and Spectroscopy Societies

Memphis, TN, U.S.A., October 9-13, 2007

Fabrication of Porous Optical Fiber Claddings for Crossed-Fiber Sensor Arrays Using Microsphere Templating

Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

American Water Resources Association – Wisconsin Section Annual Meeting

Wisconsin Dells, WI, U.S.A., March 1-2, 2007

Optical Sensing of Dissolved Oxygen and Temperature in Aqueous Environments

M. Veronica Rigo, Robert J. Olsson, and Peter Geissinger

Poster Presentations

FACSS 2008: 35th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies

Federation of Analytical Chemistry and Spectroscopy Societies

Reno, NV, U.S.A., September 28-October 2, 2008

Fabrication of Porous Cladding Materials for Remote Sensing with Crossed-Fiber Sensor Arrays Using Microsphere Templating

Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

Laboratory for Surface Studies Summer Symposium

University of Wisconsin-Milwaukee

Milwaukee, WI, U.S.A., August 21, 2008

Absorptivity of a Dye-Doped Hydrogel Matrix for Optical Fiber Sensor Applications

Megan Schultz and Peter Geissinger

Laboratory for Surface Studies Summer Symposium
University of Wisconsin-Milwaukee
Milwaukee, WI, U.S.A., August 21, 2008
Fabrication of Porous Cladding Materials Using Microsphere Templating for Remote Sensing with Crossed-Fiber Sensor Arrays
Paul E. Henning and Peter Geissinger

Chicago/Wisconsin/Central Illinois Rubber Group Meeting
American Chemical Society- Rubber Division
Lake Geneva, WI, U.S.A., May 13, 2008
Plasmon-Controlled Fluorescent Optical-Fiber Sensor for Ultrasensitive and Real Time Detection of Oxygen in Gas and Aqueous Media
M. Veronica Rigo and Peter Geissinger

Chicago/Wisconsin/Central Illinois Rubber Group Meeting
American Chemical Society- Rubber Division
Lake Geneva, WI, U.S.A., May 13, 2008
Fabrication of Porous Cladding Materials for Crossed-Fiber Sensor Arrays Using Microsphere Templating
Paul E. Henning and Peter Geissinger

University of Wisconsin-Milwaukee
Department of Chemistry Student Award Day Research Poster Session
Milwaukee, WI, U.S.A., May 8, 2008
Plasmon-Controlled Fluorescent Optical-Fiber Sensor for Ultrasensitive and Real Time Detection of Oxygen in Gas and Aqueous Media
M. Veronica Rigo and Peter Geissinger

University of Wisconsin-Milwaukee
Department of Chemistry Student Award Day Research Poster Session
Milwaukee, WI, U.S.A., May 8, 2008
Fabrication of Porous Cladding Materials for Crossed-Fiber Sensor Arrays Using Microsphere Templating
Paul E. Henning and Peter Geissinger

American Water Resources Association – Wisconsin Section Annual Meeting
Brookfield, WI, U.S.A., March 6-7, 2008
Optical Fiber Sensors for Real-Time, Remote, and Spatially Resolved Oxygen Sensing
M. Veronica Rigo and Peter Geissinger

American Water Resources Association – Wisconsin Section Annual Meeting
Brookfield, WI, U.S.A., March 6-7, 2008
Rugged, Highly-Porous Fiber Claddings for Remote Sensing in Aqueous Environments
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

Pittcon 2008 – 59th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
New Orleans, LA, U.S.A., March 2-7, 2008
Fabrication of Porous Cladding Materials for Crossed-Fiber Sensor Arrays Using Microsphere Templating
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

Pittcon 2008 – 59th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
New Orleans, LA, U.S.A., March 2-7, 2008
Metal-Enhanced Fluorescent Optical Fiber Platform for Real-Time Oxygen Sensing
M. Veronica Rigo and Peter Geissinger

Pittcon 2008 – 59th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
New Orleans, LA, U.S.A., March 2-7, 2008
Multi-Fluorophore Optical Fiber Sensors for Real Time Oxygen Measurement
M. Veronica Rigo, Robert J. Olsson, and Peter Geissinger

SETAC 2007 28th Annual North American Meeting
Society of Environmental Toxicology and Chemistry
Milwaukee, WI, U.S.A., November 11-15, 2007
Optical Fiber Platform for Real-Time, Remote, and Spatially Resolved Sensing of Oxygen
M. Veronica Rigo and Peter Geissinger

SETAC 2007: 28th Annual North American Meeting
Society of Environmental Toxicology and Chemistry
Milwaukee, WI, U.S.A., November 11-15, 2007
Optical Fiber Sensors with Microsphere-Templated, Porous Fiber Claddings for Remote Measurement in Aqueous Environments
Paul E. Henning, M. Veronica Rigo and Peter Geissinger

University of Wisconsin System Chemistry Faculties Meeting
University of Wisconsin-Green Bay
Green Bay, WI, U.S.A., October 20-21, 2007
Using Microsphere Templating to Create Porous Optical Fiber Claddings for Crossed-Fiber Sensor Arrays
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

FACSS 2007: 34th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies
Federation of Analytical Chemistry and Spectroscopy Societies
Memphis, TN, U.S.A., October 9-13, 2007
Surface Plasmon Resonance Optical Fiber Platform for Real-Time Oxygen Sensing
M. Veronica Rigo and Peter Geissinger

Laboratory for Surface Studies Summer Symposium
University of Wisconsin-Milwaukee
Milwaukee, WI, U.S.A., August 28, 2007
Using Microsphere Templating to Create Porous Optical Fiber Claddings for Crossed-Fiber Sensor Arrays
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

Laboratory for Surface Studies Summer Symposium
University of Wisconsin-Milwaukee
Milwaukee, WI, U.S.A., August 28, 2007
Localized Surface Plasmon Resonance of Nanostructures for Sensor Applications
M. Veronica Rigo and Peter Geissinger

University of Wisconsin-Milwaukee
Department of Chemistry Student Award Day Research Poster Session
Milwaukee, WI, U.S.A., May 3, 2007
Metal-Enhanced-Fluorescence Optical Fiber Oxygen Sensor Using Silver Nanostructures
M. Veronica Rigo and Peter Geissinger

University of Wisconsin-Milwaukee
Department of Chemistry Student Award Day Research Poster Session
Milwaukee, WI, U.S.A., May 3, 2007
Development of Porous Fiber Claddings by Microsphere Templating
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

2007 National Meeting
American Chemical Society
Chicago, IL, U.S.A., March 25-29, 2007
Fourier Transform Analysis for Linear, Periodic Arrays
Peter Geissinger and Alan W. Schwabacher

2007 National Meeting
American Chemical Society
Chicago, IL, U.S.A., March 25-29, 2007
Application of Microsphere Templating to Create Porous Optical Fiber Claddings for Crossed-Fiber Sensor Arrays
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

American Water Resources Association – Wisconsin Section Annual Meeting
Wisconsin Dells, WI, U.S.A., March 1-2, 2007
Optical Fiber Sensors with Microsphere-Templated, Porous Fiber Claddings for Remote Measurement in Aqueous Environments
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

Pittcon 2007 – 58th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
Chicago, IL, U.S.A., February 25 – March 2, 2007
Application of Microsphere Templating to Create Porous Optical Fiber Claddings for Crossed-Fiber Sensor Arrays
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

Pittcon 2007 – 58th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
Chicago, IL, U.S.A., February 25 – March 2, 2007
Fiber Optic Surface Plasmon Resonance Sensor for Oxygen Measurement
M. Veronica Rigo and Peter Geissinger

41st Midwest Regional Meeting
American Chemical Society
Quincy, IL, U.S.A., October 25-27, 2006
Nanosphere Templating for Rigid, Porous Optical Fiber Claddings for Use in Large Crossed-Fiber Sensor Arrays
Paul E. Henning, M. Veronica Rigo, and Peter Geissinger

41st Midwest Regional Meeting
American Chemical Society
Quincy, IL, U.S.A., October 25-27, 2006
*Improving Detection Limits in Optical Fiber Sensor Arrays through Metal Enhanced
Fluorescence*
M. Veronica Rigo and Peter Geissinger

Laboratory for Surface Studies Summer Symposium
University of Wisconsin-Milwaukee
Milwaukee, WI, U.S.A., August 18, 2006
*Ratiometric Sensing Using Dual-Emissive Dyes and Dye Mixtures in a High-Spatial Resolution
Optical Fiber Sensor Array*
Paul E. Henning, Robert J. Olsson, and Peter Geissinger

Laboratory for Surface Studies Summer Symposium
University of Wisconsin-Milwaukee
Milwaukee, WI, U.S.A., August 18, 2006
Fiber Optic Sensor for Oxygen Measurement in Gas and Aqueous Phase
M. Veronica Rigo, Robert J. Olsson, and Peter Geissinger

Geochemical Characterization of Sulfide Mineralization in Eastern Wisconsin Carbonate Rocks

Basic Information

Title:	Geochemical Characterization of Sulfide Mineralization in Eastern Wisconsin Carbonate Rocks
Project Number:	2007WI213O
Start Date:	7/1/2007
End Date:	6/30/2008
Funding Source:	Other
Congressional District:	
Research Category:	Not Applicable
Focus Category:	Geochemical Processes, Groundwater, Water Quality
Descriptors:	
Principal Investigators:	

Publication

**GEOCHEMICAL CHARACTERIZATION OF SULFIDE MINERALIZATION IN EASTERN
WISCONSIN CARBONATE ROCKS**

A final report prepared for the University of Wisconsin Water Resources Institute

J. A. Luczaj
Department of Natural & Applied Sciences
University of Wisconsin – Green Bay

M. J. McIntire
Department of Natural & Applied Sciences
University of Wisconsin – Green Bay

October 6, 2008

TABLE OF CONTENTS

List of Tables and Figures 1
Project Summary 2
Introduction 4
Procedures and Methods 6
Results and Discussion 6
 Field and Core Observations 6
 Scanning Electron Microscopy..... 7
 ICP-AES Analytical Results 8
 Discussion 9
 Comparison With Existing Research Results 10
Conclusions and Recommendations 12
Acknowledgements 12
References 13
Appendix A 14
Appendix B 15

LIST OF FIGURES AND TABLES

- Figure 1a. Generalized stratigraphic column for northeastern Wisconsin.**
- Figure 1b. Map showing the locations of samples analyzed in this study.**
- Figure 2. Scanning electron microscope images of polished sections and vug-filling cements.**
- Figure 3. Scatter plots of selected metal concentrations from ICP-AEX analyses.**
- Table 1. Minimum and maximum concentration values for iron and trace metals.**
- Appendix B1. Table showing sample numbers, locations, and ICP-AES analytical results.**

PROJECT SUMMARY (Two pages maximum):

Title: Geochemical characterization of sulfide mineralization in eastern Wisconsin carbonate rocks

Project I.D.: University of Wisconsin System (UWS) Project number WR07R004

Investigators:

Principal Investigators:

Dr. John Luczaj, Assistant Professor; Dr. Michael McIntire, Assistant Professor
Department of Natural & Applied Sciences
University of Wisconsin – Green Bay
Green Bay, WI 54311

Undergraduate Research Assistants:

Andrew Steffel, Research Assistant; Andrea Duca, Research Assistant
Earth Science Majors
Department of Natural & Applied Sciences
University of Wisconsin – Green Bay
Green Bay, WI 54311

Period of Contract: 7/1/2007 – 6/30/2008

Background/Need:

Characterization of geologic factors affecting groundwater movement, contamination, and aquifer recharge was a stated research priority by the University of Wisconsin System in the Joint Solicitation for Groundwater Research & Monitoring Proposals document for fiscal year 2008.

The chemistry of groundwater systems is controlled in part by the composition of the host rock. Groundwater in eastern Wisconsin carbonate rocks has the potential to be in direct contact with significant quantities of sulfide minerals because of their petrographic location in the host rocks. Sulfide minerals are often found coating the walls of joints, faults, and interconnected vugs in these dolostones. Oxidation of these sulfide minerals has been shown to be the major source of arsenic and other metals of concern in eastern Wisconsin (e.g., Thornburg and Sahai, 2004; Johnson and Riewe, 2006). Because interconnected fractures and bedding planes are important groundwater conduits in carbonate aquifers, the composition of minerals coating these fractures is an important control on groundwater quality.

Objectives:

The objective of the project was to characterize the trace metal composition of the carbonate (and other) rocks from outcrops, quarries, and drill cores in northeastern Wisconsin to gain a better understanding of potential sources of arsenic and other metals of concern.

This information will improve our understanding of the regional, stratigraphic, and petrographic distribution of these elements in the different Paleozoic strata of eastern Wisconsin. These activities will help to create a baseline for follow-up studies and help determine future impacts of arsenic and other metals in Wisconsin's groundwater.

Methods:

Samples were obtained by field work in quarries and at outcrops, from several drill cores, and from existing collections held by the principal investigator. Most field work was performed in Summer 2007, although additional sampling was performed in early Summer 2008. Drill cores that became available in Spring 2008 also benefited the study. The majority of samples used in the study were from various

localities in Marinette, Oconto, Brown, and Shawano counties. Additional samples from several other eastern Wisconsin counties supplemented the study.

Both biased and unbiased sampling methods were used to collect samples for chemical analysis. Samples that were representative of the stratigraphic horizon or those that were taken at random are labeled as “Bulk” specimens. In contrast, sampling that was deliberately biased in an attempt to analyze the most metals-rich materials are labeled as “Concentrate”. Samples were submitted to ALS-Chemex in Thunder Bay, Ontario, Canada for Conventional 35-element ICP-AES Analysis after Aqua Regia Digestion to obtain metal concentrations. Petrographic investigations in May 2008 using a Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopic (EDS) capabilities allowed further characterization of the petrographic distribution of trace metals in the rocks.

Results and Discussion:

Three principal observations have been made during this research. First, it is apparent that the sulfide mineralization observed in Winnebago and Outagamie counties does indeed extend northward into Brown, Shawano, Oconto, and Marinette counties. This mineralization contains metals of concern similar to those in Winnebago and Outagamie counties.

Second, in all of the samples examined in the SEM, none displayed separate mineral phases for arsenic, such as arsenopyrite. However, in one sample, a nickel-iron sulfide phase was identified, suggesting that the distribution of at least some metals of concern is not restricted entirely to the occurrence of pyrite or marcasite (FeS₂).

Third, the distribution of sulfide minerals in the host sedimentary rocks of the region is heterogeneous, but stratigraphically predictable in the region. In addition to the well-documented Sulfide Cement Horizon (SCH) below the base of the Platteville Dolomite, other stratigraphic horizons display a predictable occurrence of sulfides, especially the base of the Silurian Mayville Dolomite and the top of the Maquoketa Shale or Neda Formation.

Conclusions/Implications/Recommendations:

This study provides two major conclusions, both of which can be applied to better understand the water quality in the region. First, the sulfide mineralization observed in Winnebago and Outagamie counties does indeed extend northward into Brown, Shawano, Oconto, and Marinette counties. In addition, abundant quantities of sulfides appear near the contact between the Silurian Mayville Formation and the underlying Maquoketa and/or Neda formations east of the Niagara escarpment. While most water quality issues in wells east of the escarpment are the result of bacteria and nitrate contamination, the possibility of metals contamination might exist for wells that reach a total depth near or at this stratigraphic horizon.

Future water quality studies should focus on these two mineralized stratigraphic horizons, as it seems likely that similar water quality problems should exist near the outcrop belts of these rocks.

Related Publications: None at present (Poster is planned for 2009 Wisconsin Section of AWRA, with peer-reviewed journal manuscript to be submitted at a later date).

Key Words: arsenic, nickel, iron, metals, sulfide, pyrite, stratigraphic, northeast Wisconsin, carbonate, sulfide cement horizon, Neda Formation, Sinipee Group, Prairie du Chien Group, Silurian, Ordovician

Funding: University of Wisconsin System (UWS) Project number WR07R004

INTRODUCTION

Much attention has been given to the problem of arsenic contamination in groundwater from northeastern Wisconsin. The focus of previous research (e.g., Pelczar, 1996; Johnson and Riewe, 2006; Burkel and Stoll, 1999; Schreiber et al., 2000; Schreiber et al., 2003; Gotkowitz et al., 2003; Thornburg and Sahai, 2004) has been to characterize the distribution of arsenic in well waters and aquifer rocks, primarily in parts of Winnebago and Outagamie Counties. Little information is known about the trace element signature of the carbonates in those two counties that also host these sulfide minerals (pyrite, marcasite, galena, sphalerite, and others). Even less is known about the potential for arsenic and other metals contamination in Paleozoic rocks from other areas, such as those along the northern part of this outcrop belt in Marinette, Oconto, and Shawano Counties. With parts of northeastern Wisconsin expecting significant population growth over the next 25 years (Egan-Robertson et al., 2004), a better understanding of potential sources of groundwater contamination is needed, especially in rural areas where domestic well supplies are prevalent. It is apparent from existing well data that arsenic contamination exists in areas outside of Winnebago and Outagamie Counties, even in areas away from the St. Peter Sandstone outcrop belt (e.g., Johnson and Riewe, 2006). However, because of fewer wells and more limited screening for arsenic and other metals of concern in these areas, it is unclear whether the potential for arsenic and other metals contamination differs from the well-studied area in Winnebago and Outagamie Counties.

Luczaj (2000, 2006) characterized the ancient hydrothermal groundwater flow system responsible for water-rock interaction in eastern Wisconsin Paleozoic rocks. This ancient system was responsible for precipitation and replacement of a suite of Mississippi Valley-type (MVT) sulfide minerals that includes pyrite, marcasite, galena, sphalerite, millerite, and chalcopyrite. It is this hydrothermal system that precipitated the arsenic and nickel-bearing sulfide minerals in the region, including those in the uppermost meter of the St. Peter Sandstone.

Field, petrographic, and geochemical evidence suggests a link between the late-stage dolomite, trace MVT minerals, and authigenic potassium (K)-silicate minerals in eastern Wisconsin rocks, which preserve a regional hydrothermal signature. Constraints placed on the conditions of water-rock interaction using fluid-inclusion techniques indicate replacement and precipitation of dolomite, quartz, and sphalerite between 65 and 120°C in the presence of dense brines with salinities between 13 and 28 weight %, NaCl equivalent (Luczaj, 2000, 2006).

The chemistry of a groundwater system is controlled in part by the composition of the host rock. Groundwater in eastern Wisconsin carbonate rocks has the potential to be in direct contact with significant quantities of sulfide minerals, depending upon their abundance and spatial distribution in the host rocks. Sulfide minerals are often found coating the walls of joints, faults, and interconnected vugs in these dolostones. Oxidation of these sulfide minerals has been shown to be the major source of arsenic and other metals of concern in eastern Wisconsin (e.g., Gotkowitz et al., 1996; Thornburg and Sahai, 2004; Johnson and Riewe, 2006). Because interconnected fractures are important groundwater conduits in carbonate aquifers, the composition of minerals coating these fractures is an important contributing component of groundwater quality.

This study had three principal objectives. The first objective was to examine the stratigraphic and regional distribution of sulfide mineralization in Paleozoic rocks throughout northeastern Wisconsin (Figure 1). While the carbonate portions of the section received the most attention, sampling of sandstones, shales, and iron formation (Neda) was also conducted. The primary sources of rock samples were quarries and outcrops. This effort was supplemented by examination of numerous drill cores from throughout the region that became available after the project funding was awarded. Additional samples from an existing collection held by principal investigator Luczaj were also incorporated, where appropriate. The rocks examined and analyzed ranged in age from Cambrian through Silurian, representing most of the stratigraphic range of Paleozoic sedimentary rocks in the region.

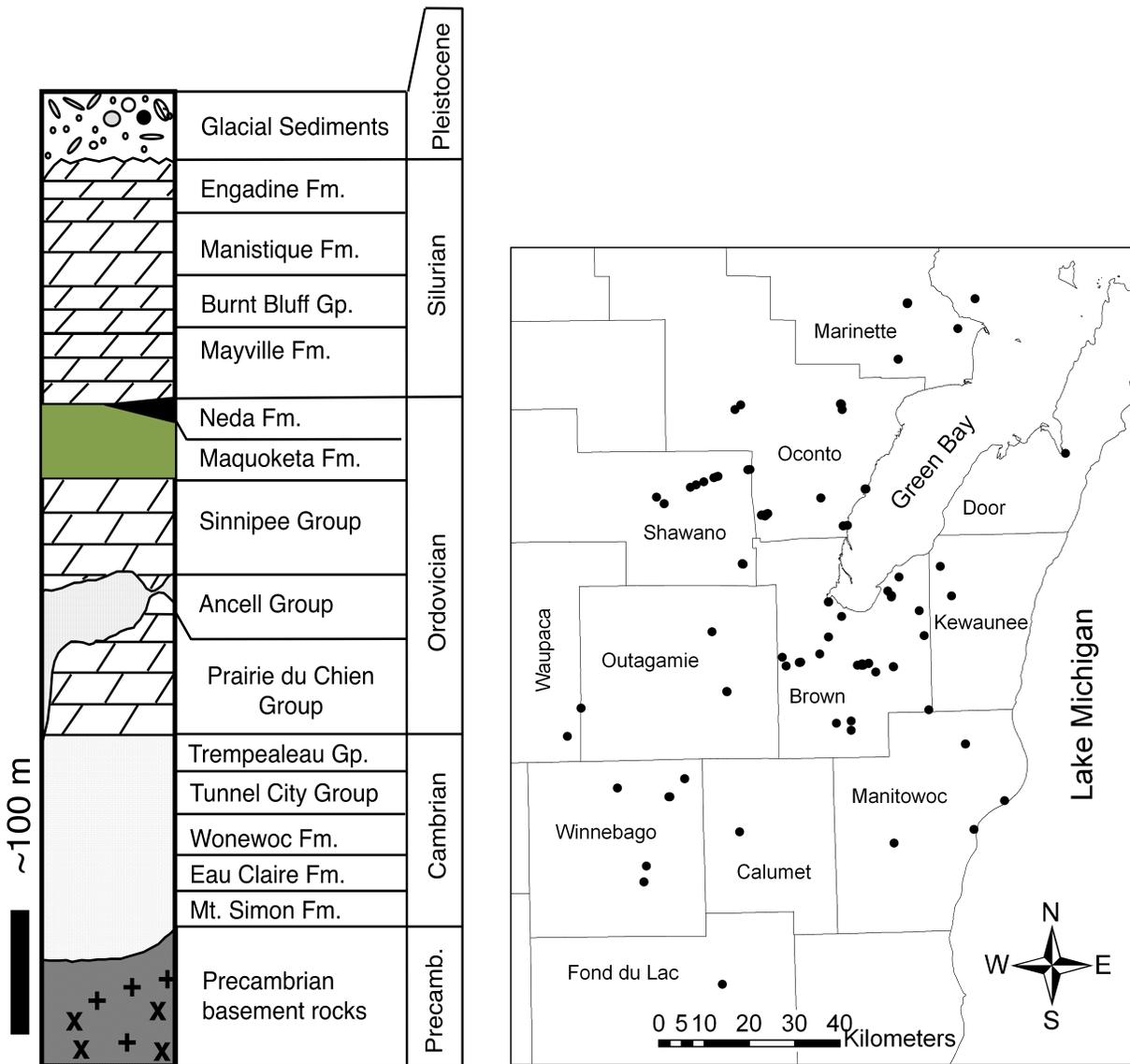


Figure 1. A (left). Generalized Stratigraphic column for northeastern Wisconsin (modified after Luczaj, 2006). B (right). Map showing the locations of samples analyzed in this study.

The second objective included Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). This technique was used to explore the chemistry and petrographic distribution of metal sulfide minerals and associated minerals in 18 selected samples.

The third objective was to characterize the bulk geochemistry of both representative and non-representative (sulfide-rich or otherwise visually biased) samples. In total, 212 samples were submitted for 35 Element Aqua Regia ICP-AES analysis by ALS Chemex in Thunder Bay, Ontario. Unanticipated delays occurred due to negotiation with a major corporation to obtain core samples and locations. In addition, the final round of analytical results was not received until September 2008 due to unexpected laboratory delays.

PROCEDURES AND METHODS

Design of a sampling strategy was affected by two major limitations. First, the distribution of outcrop and core samples is not random in either the stratigraphic or the regional sense. Outcrops in the region are more common near either the Silurian or the Ordovician escarpments. Quarry locations also tend to be preferentially distributed near the base of the Silurian Mayville Formation, near the base of the Platteville Formation, and near the base of the Prairie du Chien Group carbonates. This outcrop distribution leads to a biased stratigraphic sampling. A second limitation is that physical access to samples near quarry high walls is often restricted for safety reasons related to MSHA regulations. We made reasonable attempts to sample multiple stratigraphic levels where possible.

We collected and processed two principal types of samples. Samples that were representative of the stratigraphic horizon or those that were taken at random are labeled as “Bulk” specimens (See Appendix B1). In contrast, sampling that was deliberately biased in an attempt to analyze the most metals-rich materials are labeled as “Concentrate”. Bulk samples collected were typically 1-2 kilograms, except for drill cores, which had a mass of at least 0.25 kilogram. Specimens labeled as “Concentrate” were as large as possible, but generally were at least 0.2 kilogram.

Two methods were employed to investigate the chemical composition of the rocks:

1. Digestion of whole-rock samples was performed by ALS Chemex of Thunder Bay, Ontario using Conventional 35-element ICP-AES Analysis after Aqua Regia Digestion. The results of these analyses yielded concentrations for 35 different elements, including arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), molybdenum (Mo), and vanadium (V). This suite of elements was chosen because it is part of a standard ICP-AES analysis package supplied by commercial labs. Additional “overlimit” analyses, conducted with standard laboratory methods, were required for certain samples in which sulfur (S), iron (Fe), and phosphorous (P) exceeded instrument limits. Results for all analytical work are available in Appendix B.
2. Selected polished rock sections and crystal-lined vugs were analyzed with a Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) available at UW Green Bay. This technique was used to explore the chemistry and petrographic distribution of metal sulfide minerals and associated minerals in 18 selected samples. While the instrument available had X-ray mapping capability, the specimens for which this was attempted did not show significant concentrations of trace elements.

RESULTS AND DISCUSSION

The Paleozoic stratigraphic section (Figure 1) was divided into six principal stratigraphic units for this study. They are the Cambrian sandstones, the Prairie du Chien Group (PDC) carbonates, the Ancell Group sandstones and shales, the Sinnipee Group carbonates, the Maquoketa Shale/Neda Ironstone, and the Silurian carbonates. Multiple samples from each of these stratigraphic units were included in the study, with an emphasis on the carbonate portions of the section.

Field and Core Observations

Observations made at quarries and outcrops clearly indicate that the trend of sulfide mineralization observed in Winnebago and Outagamie counties definitely extends northward into Brown, Shawano, Oconto, and Marinette Counties. The sulfide mineralization was dominated by pyrite or marcasite (FeS_2 polymorphs), but sphalerite (ZnS), chalcopyrite (CuFeS_2), and galena (PbS) were also observed in hand specimens.

The distribution of sulfide minerals in the host sedimentary rocks of the region is heterogeneous, but stratigraphically predictable in the region. Regionally, the unit with the most sulfide mineralization was

the top of the Ordovician Ancell Group (St. Peter and Glenwood formations). This zone of concentrated iron sulfide mineralization, known as the Sulfide Cement Horizon (SCH), is exposed on the floor or in sump trenches in several quarries in Shawano, Oconto, and Marinette counties. Nodules and intergranular cements of FeS_2 are abundant where this group of rocks is exposed. A thin (~10-50 cm) layer of dark brown shale above the St. Peter Sandstone is interpreted to be the Glenwood Shale. It contains abundant fine-grained sulfides, including pyritized arthropod and bryozoan fossils in some quarries.

The next most mineralized zone is the contact between the Silurian Mayville Dolomite and the underlying Ordovician Maquoketa Shale and Neda Formations. Where present, the Upper Ordovician Neda Ironstone and related strata appear to have sulfides associated with the upper extent of those units. In places, the mass of sulfides is striking, with large (10-40 cm thick) accumulations of pyrite easily identified. This sulfide mineralization often extends in to the lower few meters of the Silurian Mayville Dolomite. In at least one case, a local quarry operator has problems with the “aesthetic” quality of aggregate materials due to rust stains from weathering of pyrite fragments in asphalt and concrete products. This interval is best exposed in quarries and natural outcrops along Scray Hill in the towns of Ledgeview and Glenmore, southeast of Green Bay. Significant, but lesser amounts of pyrite are present at this contact and within the upper part of the Maquoketa Formation where the Neda Formation is missing.

The Ordovician Sinnipee Group carbonates contained significant quantities of metal sulfides, even at stratigraphic intervals farther away from the SCH in the Ancell Group. Sulfide mineralization was abundant along hardgrounds (a carbonate depositional surface), in vertical fractures and joints, and as vug fillings and intercrystalline cements (Figure 2). The mineralization was recognized throughout the Sinnipee Group, and some vertical fractures were mineralized by pyrite and calcite cements throughout 50+ feet of vertical exposure.

The carbonate units with the least amount of mineralization are the Silurian dolostones and the Prairie du Chien Group (PDC) dolostones. Some minor mineralization was identified in the PDC Group, especially in an outcrop and quarry south of New London on Highway 45. Chalcopyrite, pyrite, and galena were observed at this location along with a number of other non-sulfide minerals. Cores and outcrops of the Silurian dolostones indicate that most sulfides are restricted to the lower few meters of the Mayville Formation.

Scanning Electron Microscopy

Eighteen samples of polished rock slabs or crystal-lined vugs were carbon coated before analysis in an SEM with EDS capabilities at UW Green Bay. The main focus of the SEM work was to identify whether or not separate mineral phases could be identified for metals of concern or if FeS_2 phases (pyrite or marcasite) were the likely host materials for certain metals.

Separate mineral phases containing Zn, Pb, Ni and Cu were identified in a few samples (Figure 2). As expected, pyrite and marcasite (FeS_2) were the dominant sulfide phases present in most specimens. Zn and Pb sulfide phases were sphalerite and galena, respectively. The crystal morphology and EDS spectrum of the Cu-bearing phase suggests that it is chalcopyrite (CuFeS_2), but the Ni-bearing phase is less obvious. In one sample, an apparently cubic nickel-iron sulfide phase was identified, suggesting that the distribution of at least some Ni is not restricted entirely to the occurrence of pyrite or marcasite (FeS_2). The Ni-bearing phase contained significant amounts of Fe, and because of its cubic shape, the mineral pentlandite ($(\text{Fe, Ni})_9\text{S}_8$) is a possibility. The identified Ni-phase was microscopic, so it was not possible to use X-ray powder diffraction to identify the mineral.

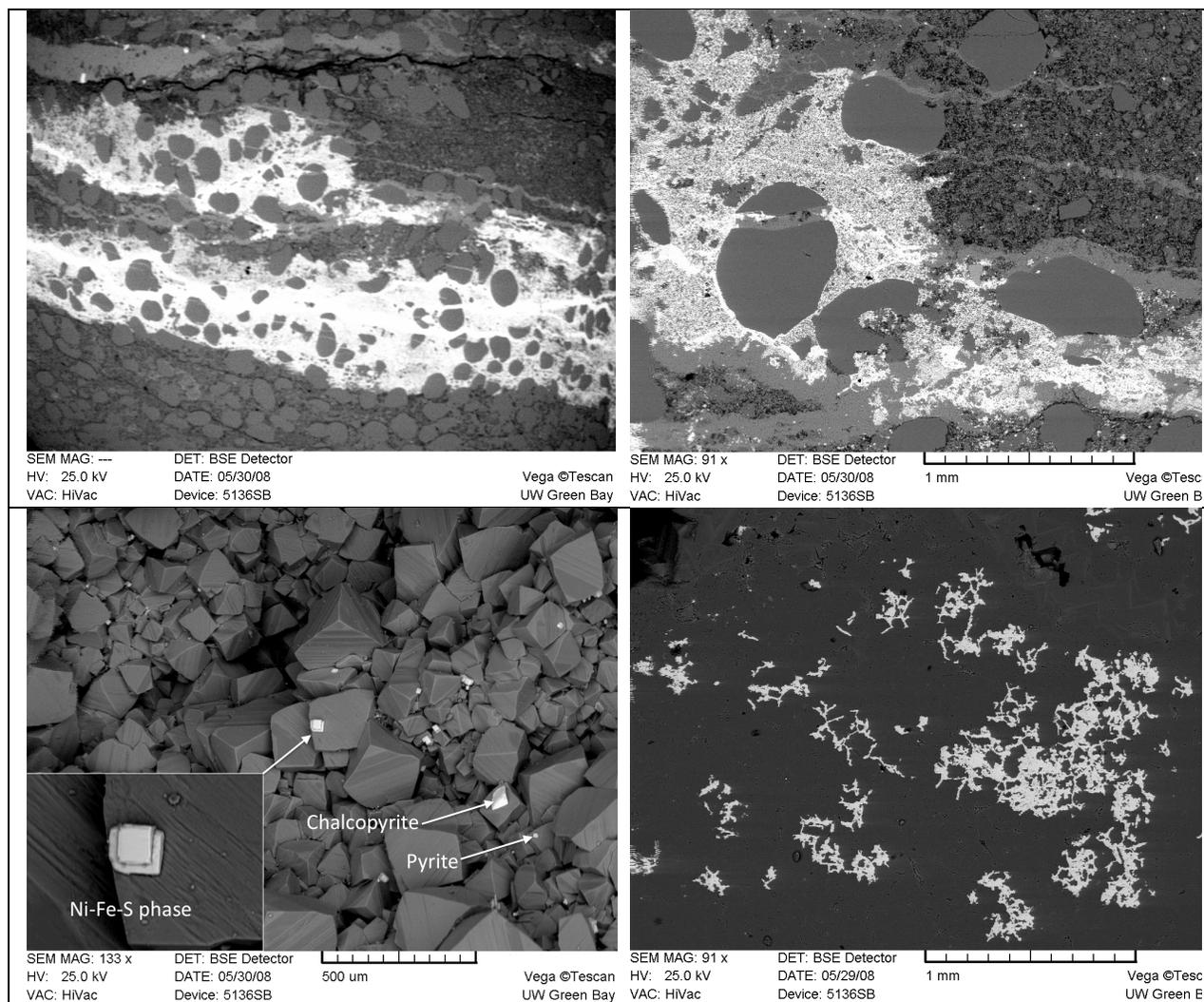


Figure 2. Scanning electron microscope images of polished sections and vug filling cements illustrating the character of sulfide mineralization in the region. A and B. (upper left and upper right) Sample 07-MT-FP-2 (Marinette County) from a quartz sandstone layer in lower Platteville Formation with fracture-filling cements. Round grains are quartz sand. Bright white areas in fracture are FeS_2 cements, whereas gray cements are calcite. Gray spotted areas in B are crystals of an unknown K-Al-Silicate mineral cement, possibly illite or K-feldspar. C. (lower left) Sample 07-OCO-MTV-2 (Oconto County) showing euhedral vug-filling dolomite crystals with associated pyrite, chalcopyrite, and cubic Ni-Fe-sulfide crystals from the Sinnipee Group dolostone. Inset shows the $\sim 40\mu\text{m}$ crystal that is possibly pentlandite. D. (lower right) Sample 07-BN-LQ-1 (Brown County) exhibiting partial replacement and filling of intercrystalline pore spaces between dolomite crystals in the Sinnipee Group dolostone.

In contrast to the above metals, none of the samples examined with the SEM displayed separate mineral phases for arsenic (As), such as arsenopyrite. While the presence of arsenopyrite cannot be ruled out in these rocks, it seems likely that As is substituting for Fe as a trace element in the iron sulfides as has been suggested by others (e.g., Thornburg and Sahai, 2004).

ICP-AES Analytical Results

Analytical results for all 212 samples are presented in Appendix B. Nearly all specimens were obtained

from northeastern Wisconsin, but four samples (96-RA-1.1, 97-RA-2, Stop 2 Rohl, 07-UWGB-TS-1.1) were from other parts of the state and were used for comparison purposes only.

The main purpose for analyzing the metals content of these rocks was to look for regional and stratigraphic trends in the character of the mineralization. We examined the concentrations of these metals and made certain comparisons between Fe, La, Mo, V, and the 8 metals of concern (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn).

Table 1 presents the range of metals concentrations for all samples in the study (Bulk and Concentrate). Averages were not calculated because an unbiased sampling strategy is not possible for the region across all stratigraphic intervals.

Table 1. Minimum and maximum concentration values for iron and trace metals in Paleozoic rocks of northeastern Wisconsin. Concentrations for Fe are in %, while all other concentrations are in parts per million (ppm).

	<u>Fe (%)</u>	<u>As</u>	<u>Cd</u>	<u>Co</u>	<u>Cr</u>	<u>Cu</u>	<u>Mo</u>	<u>Ni</u>	<u>Pb</u>	<u>V</u>	<u>Zn</u>
Minimum	0.06	< 2	< 0.5	< 1	< 2	< 1	< 2				
Maximum	28.4	499	4.2	133	38	1620	25	1110	1660	353	25200

Discussion

Various graphing methods were employed to determine possible correlations between the different metals. Many of these correlations were best expressed when plotted as separate stratigraphic populations. The most obvious trends include a correlation between As and Ni, As and Co, and between Cr and V. Weak correlations may exist between As and Cu, and Co and Ni. The Sinipee Group samples showed a particularly good correlation between As and Co, as well as between As and Ni.

After graphical analysis of all data, it is apparent that three stratigraphic horizons showed the most significant mineralization. These were the top of the Ansell Group, the Ordovician – Silurian contact, and the Sinipee Group dolostones. All three of these zones showed the potential for relatively high As concentrations (Figure 3a).

Positive correlations were found between several of the metals of concern. Some of these correlations hold for all stratigraphic intervals, whereas others are stronger for some units than for others. For example, while a general correlation exists for V and Cr over all stratigraphic intervals, the mineralized zone near the Ordovician-Silurian contact showed a particularly unexpected and interesting relationship due to enrichment of V relative to Cr (Figure 3b). While some scatter exists on As vs. Co plots, there is a well-defined positive linear correlation for samples hosted by Sinipee Group dolostone (Figure 3c).

Ni vs. Fe plots show a weak correlation, if any. One stratigraphic difference noted is that FeS₂-rich samples from the Maquoketa/Neda contact and the Silurian dolostones just above this contact are depleted in Ni, relative to samples from the Ansell and Sinipee groups (Figure 3d). Samples near the Ordovician-Silurian contact are also depleted in Ni, but appear to be enriched in V and La (lanthanum) (see Figure 3b and Appendix B1).

Some variations appear to be regional in nature. For example, Mo appeared to vary in a significant way regionally, with higher concentrations found in samples from Oconto County. The As vs. Ni plot (Figure

3e) shows a positive correlation for two distinct populations. Samples from all stratigraphic intervals fall into only one of these populations, except for the Ancell Group samples, which are split between the two populations. The population branch that shows significantly elevated Ni concentrations, relative to As, is represented by some Ancell Group samples from three Oconto County quarries (Duame Quarry, Chase Quarry, and Montevideo Quarry). An enlargement of the As vs. Ni plot shows that a similar split might occur for samples from the Sinnipee Group (Figure 3f).

We think that metals such as As, Fe, and Co correlate well with each other because As and Co are likely substituting for Fe in pyrite or marcasite. The reasons for a correlation between Cr and V are unknown, and most samples with appreciable quantities of these materials are located near the contact between the Silurian dolostones and the Ordovician Neda Ironstone. Poor correlation between Fe and Zn, Pb, and Cu are probably because those metals precipitate in separate phases, such as sphalerite, galena, and chalcopyrite, and are independent of the presence of pyrite or marcasite in any particular sample.

Rocks near the Ordovician-Silurian contact were somewhat deficient in Ni relative to Fe, as compared to the Ancell and Sinnipee Groups. These differences are likely due to the source of metals in the hydrothermal fluids that passed through the rocks. The Maquoketa Shale is a regional confining unit that likely isolated the Silurian dolostone units above it from the Ordovician sandstones and carbonates below it during the mineralization period in the Paleozoic.

Assuming that in FeS₂-rich samples, all As is hosted by pyrite or marcasite, then an estimate of the range in concentrations of As in pure FeS₂ can be made. The estimated concentration of As in FeS₂ varies from low values (~25 ppm) to a maximum of about 1,400 ppm.

Comparison With Existing Research Results

Results of the whole-rock analyses from this study were compared with published concentrations for metals in the St. Peter Sandstone of Winnebago and Outagamie Counties and other localities in northeastern Wisconsin (Pelczar, 1996, CH2M Hill, 2000; Gotkowitz et al., 2003). This procedure allowed generalized comparisons to be made between rocks in the Oshkosh to Green Bay corridor versus those in the Green Bay to Marinette corridor. It is worth mentioning that most previous work was limited to a smaller number of samples because those studies were mostly focused on detailed water quality research in a few locations. We compared our results with previously reported values, but those data tables and graphs are not presented here due to space constraints.

Arsenic concentrations relative to iron in this study were compared to those from the studies mentioned above. In general, whole-rock arsenic concentrations varied between 0 ppm and 500 ppm for all studies. However, three samples from Winnebago and Outagamie counties reported in previous studies had As concentrations that ranged between 500 and 743 ppm. While a few samples reported by Gotkowitz et al. (2003) had higher maximum Co concentrations than those in this study, a comparison of As vs. Co data also shows general overlap between the studies.

There were, however, some differences noted between the studies. First, the Cr concentrations in all samples in this study were below 40 ppm (Table 1). In contrast, 18 of 21 samples analyzed in previous studies (Simo et al., 1996; Gotkowitz et al., 2003) were reported to have Cr concentrations between 100 and 764 ppm, regardless of location, with most concentrations above 200 ppm. Because the locations of some of these data overlap those in our study, these high Cr values seem anomalous. One value reported by Gotkowitz et al. (2003) for an unmineralized sample of St. Peter Sandstone had a Cr concentration above 500 ppm, even though the sample had no sulfur and less than 1% Fe. Because of this anomalous behavior of Cr, we did not attempt to draw any conclusions about the difference in Cr between our studies and previous studies as they relate to rock geochemistry. It might be possible, however, that samples in

the previous studies were submitted to a laboratory that crushed the samples with high Cr-steel, which is an alloy known for its toughness and which would be a suitable material for crushing rocks.

A comparison of As vs. Ni shows general agreement between most samples analyzed in our study and those of Gotkowitz et al. (2003) and Pelczar (1996), except for a few samples of Anzell Group sulfides from Oconto County (Figures 3e and f).

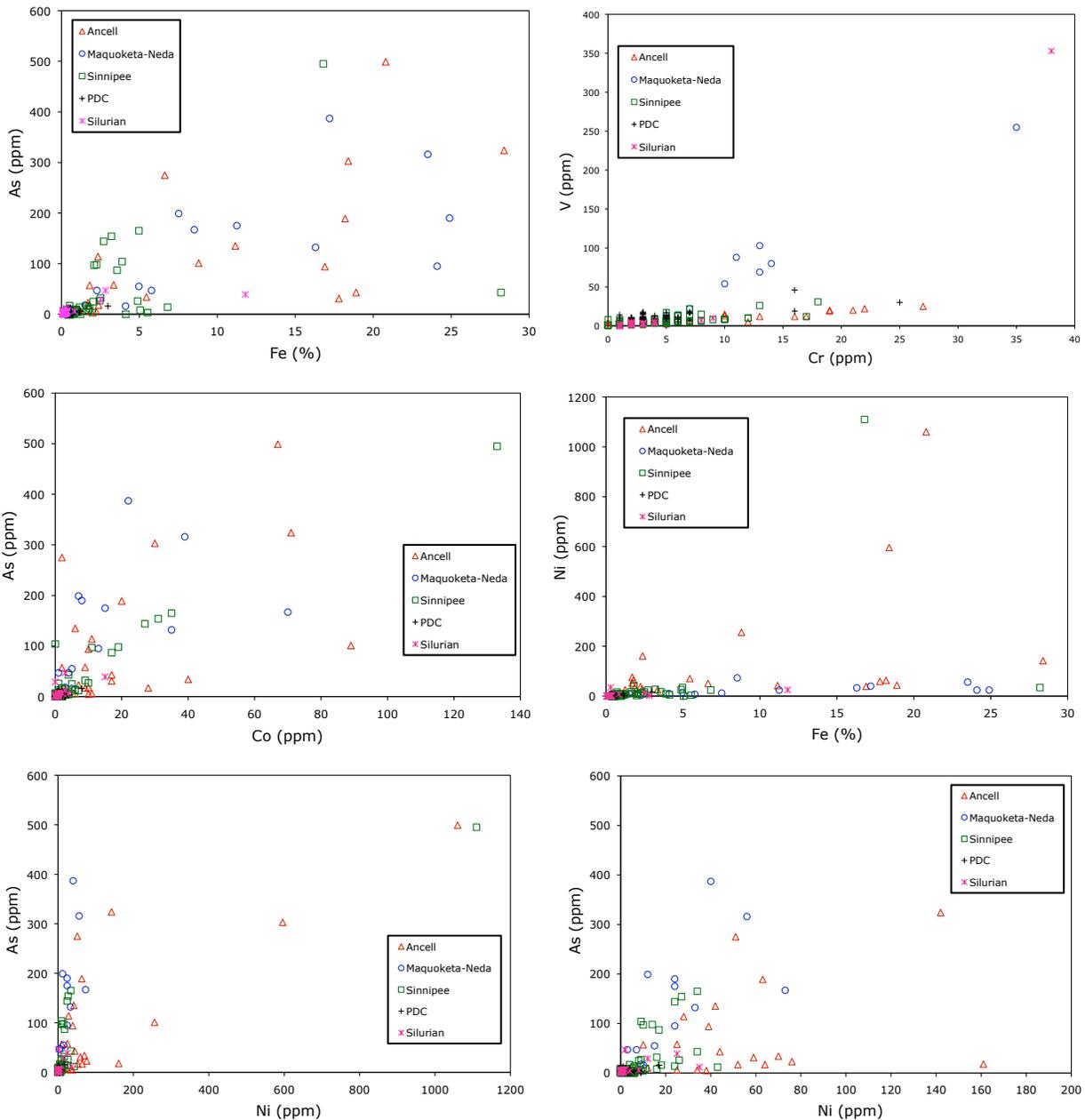


Figure 3. Scatter plots of selected metal concentrations from ICP-AES analyses on rock specimens from this study. Reported values for metals are in parts per million (ppm), except for iron, which is in percent (%). Legends in each graph indicate the particular stratigraphic unit sampled. A. (upper left) Arsenic (As) vs. iron (Fe). B. (upper right) Vanadium (V) vs. chromium (Cr). C. (middle left) Arsenic (As) vs. cobalt (Co). D. (middle right) Nickel (Ni) vs. iron (Fe). E. (lower left) Arsenic (As) vs. nickel (Ni). F. (lower right) Expanded view of E for arsenic (As) vs. nickel (Ni).

It is important to consider the potential impact of this mineralization on groundwater quality in the region north of Winnebago and Outagamie Counties. While the upper Ancell Group is likely to be the most significant source of metals due to the abundance of sulfides and the fact that porous media flow dominates, water quality in the Sinnipee Group should also be studied more carefully in the future. Because the distribution of sulfide minerals is very heterogeneous, their locations along fractures, faults, bedding planes, and in vugs is important. Fracture and bedding plane dominated flow are likely to greatly amplify the interaction between groundwater and sulfide minerals under the right redox conditions. In addition, certain stratigraphic zones of dolostone with high intercrystalline porosity, such as one about 20 feet above the base of the Platteville Formation, also contain abundant Fe-sulfides. For these reasons, the “average” concentration of metals within the Sinnipee Group as a whole are probably not so important – rather, the complex distribution of sulfide minerals and fluid flow pathways likely has a much larger influence on water quality in the carbonate units.

Because receipt of some analytical results was delayed by the contracted laboratory, some results were received in September 2008. Intensive analysis of all data is ongoing, and we will present further details and interpretations in a future publication.

CONCLUSIONS AND RECOMMENDATIONS

This study provides two major conclusions, both of which can be applied to better understand the water quality in the region. First, the sulfide mineralization observed in Winnebago and Outagamie counties definitely extends northward into Brown, Shawano, Oconto, and Marinette counties. This includes both the highly concentrated SCH at the top of the St. Peter Formation, as well as the disseminated iron and other metal sulfides in other parts of the section.

Abundant quantities of sulfides also appear near the contact between the Silurian Mayville Formation and the underlying Maquoketa and/or Neda formations east of the Niagara escarpment. While most water quality concerns in these wells has been focused on bacteria and nitrate contamination, the possibility of metals contamination might exist for wells that reach a total depth near or at this stratigraphic horizon.

Future water quality studies should focus on these two mineralized stratigraphic horizons, as it seems likely that similar water quality problems would exist at and near the outcrop belts of these rocks. However, the dominance of bedding plane and fracture flow pathways throughout the Sinnipee Group means that groundwater impact from metals could occur throughout this unit. We recommend that a detailed domestic well sampling program for all metals of concern be considered for areas near and east of the SCH in Marinette, Oconto, Shawano and western Brown counties.

ACKNOWLEDGEMENTS

We would like to thank the numerous quarry operators and private citizens who granted us property access, without which this study would not have been possible. Quarry operators that granted access during this study included Daanen & Janssen, Inc., McKeefry & Sons, Inc., Peters Concrete Company, Jackie Foster, Inc., Northeast Asphalt, Inc., Scott Construction Company, Michels Materials, and Murphy Concrete & Construction. Drill cores were made available by the City of Green Bay, STS Consultants, and the American Transmission Corporation. Dave Johnston (DNR) and Bruce Brown (WGNHS) also provided helpful discussions and ideas. John Lyon (UW Green Bay) provided helpful training on necessary SEM equipment. Todd Kostman (UW-Oshkosh) was kind enough to allow use of a carbon coater to prepare SEM samples.

REFERENCES

- Burkel, R. S. and Stoll, R. C., 1999, Naturally Occurring Arsenic in Sandstone Aquifer Water Supply Wells of Northeastern Wisconsin. *Groundwater Monitoring and Remediation*, v. 19, p. 114-121.
- CH2M Hill, 2000, Green Bay ASR Phase IIA Mineralogical and Water Quality Testing and Results. Technical Memorandum prepared for Green Bay (Wisconsin) Water Utility August 24, 2000, 23 pages plus appendices.
- Egan-Robertson, D., Harrier, D., and Kale, B., 2004, Wisconsin Population – 2030: A Report on Projected State, County and Municipal Populations and Households for the Period 2000-2030. Wisconsin Demographic Services Center - Department of Administration, 24 pages.
- Gotkowitz, M. B., Simo, J. A., and Schreiber, M., 2003, Geologic and geochemical controls on arsenic in groundwater in northeastern Wisconsin. Wisconsin Geological and Natural History Survey Open-File Report, no. 2003-1, 60 pages.
- Johnson, D. M. and Riewe, T., 2006, Arsenic and Northeastern Wisconsin. *Water Well Journal*, v. 60, p. 26-31.
- Luczaj, J. A., 2006, Evidence against the Dorag (Mixing-Zone) model for dolomitization along the Wisconsin arch – A case for hydrothermal diagenesis. *AAPG Bulletin*, v. 90, p. 1719-1738.
- Luczaj, J. A., 2000, Epigenetic dolomitization and sulfide mineralization in Paleozoic rocks of eastern Wisconsin: Implications for fluid flow out of the Michigan Basin, U.S.A. Ph.D. Dissertation, Johns Hopkins University, 445 pages.
- Paull, R. A., and Emerick, J. A., 1991, Genesis of the Upper Ordovician Neda Formation in eastern Wisconsin. *Geoscience Wisconsin*, v. 14, p. 23-52.
- Pelczar, J. S., 1996, Groundwater chemistry of wells exhibiting natural arsenic contamination in east-central Wisconsin. M.S. Thesis, University of Wisconsin – Green Bay, 206 pages.
- Schreiber, M. E., Gotkowitz, M. B., Simo, J. A., and Freiberg, P. G., 2003, Mechanisms of arsenic release to ground water from naturally occurring sources, eastern Wisconsin. In, A. Welch and K. Stollenwerk eds., *Arsenic in Ground Water*, Kluwer Academic Publishers, Boston, p. 259-280.
- Schreiber, M. E., Simo, J. A., and Freiberg, P. G., 2000, Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, eastern Wisconsin, USA. *Hydrogeology Journal*, v. 8, no. 2, p. 161-176.
- Thornburg, K. and Sahai, N., 2004, Arsenic Occurrence, Mobility, and Retardation in Sandstone and Dolomite Formations of the Fox River Valley, Eastern Wisconsin. *Environmental Science and Technology*, v. 38, p. 5087-5094.

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

There are no finished publications or manuscripts at this time. We are planning to present this work at the March 2009 Wisconsin Section of AWRA, with submittal of a peer-reviewed publication during the summer of 2009.

APPENDIX B:

Appendix B1 (Pages 1-18)

Summaries of sample numbers, locations, descriptions, and analytical results.

Appendix B2 (11 reports, 8 shipments and 3 overlimit analyses)

35 Element ICP-AES results from ALS Chemex.

Occurrence and Generation of Nitrite in Ground and Surface Waters in an Agricultural Watershed

Basic Information

Title:	Occurrence and Generation of Nitrite in Ground and Surface Waters in an Agricultural Watershed
Project Number:	2008WI191B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	2
Research Category:	Ground-water Flow and Transport
Focus Category:	Nitrate Contamination, Agriculture, Hydrogeochemistry
Descriptors:	None
Principal Investigators:	Emily H. Stanley

Publication

Annual Progress Report

Selected Reporting Period: 7/1/2008 - 6/30/2009

Submitted By: Emily Stanley

Submitted: 5/20/2009

Project Title

WR07R003: Occurrence and Generation of Nitrite in Ground and Surface Waters in an Agricultural Watershed

Project Investigators

Emily Stanley, University of Wisconsin-Madison

Progress Statement

The overarching goal of this research project is to better understand the extent of nitrite (NO₂⁻) occurrence in groundwater, and the conditions that promote the accumulation of this potentially toxic form of nitrogen in both ground- and surface waters of agriculturally-dominated catchments. This goal is being addressed by (1) examining temporal patterns of groundwater and surface water chemistry and NO₂⁻ occurrence along four upland-to-stream transects, (2) measuring NO₂⁻ generation in a series of controlled laboratory experiments to quantify rates and likely pathways of NO₂⁻ formation; and (3) conducting a survey of groundwater chemistry to determine if NO₂⁻ is present in groundwater at diverse locations in Wisconsin.

Activities during Year 1 emphasized Objectives (1) and (2). Wells were installed at two sites in the East Branch Pecatonica River (EBP) valley in partnership with researchers interested in the hydrologic consequences of stream restoration. Monthly groundwater monitoring began in August 2007 and ground and surface water samples were analyzed for all forms of nitrogen. We have been able to take advantage of infrastructure and ongoing hydrologic research at this site, which should be of great assistance for data interpretation. Water chemistry monitoring is ongoing, and will continue through summer 2009. We have started the proposed laboratory experiments to determine the pathway and site of NO₂⁻ formation (Objective 2), and have also conducted a similar whole-ecosystem field based study to quantify in-stream rates of NO₂⁻ uptake and identify the pathway of NO₂⁻ formation as well.

Principal Findings and Significance

Principal Findings and Significance

Description

Well sampling at the EBP site has revealed that both absolute and relative concentrations of NO₂⁻ in groundwater in the stream valley are substantially lower than in surface water. Indeed, nitrite was often near or below detection limits in sampling wells. From a drinking water perspective, this is a 'good news' result, given the toxicity potential of NO₂⁻. We also have not observed any consistent differences in the form or amount of nitrogen in groundwater between the recently restored and unrestored sites used in this study. The generality of the low groundwater nitrite condition is currently being examined by sampling groundwater wells elsewhere in the state. Initial surveys in other sites have also revealed low NO₂⁻ levels. Additional well sampling will occur in summer 2009 (Objective 3, to be addressed in Year 2). This result also suggests that NO₂⁻ is formed either during groundwater

discharge into the stream, or as a result of surface water exchange with hyporheic sediments within the channel. Laboratory sediment assays clearly demonstrated that NO₂⁻ is generated during the reduction of NO₃⁻ (i.e, via denitrification or dissimilatory nitrate reduction to ammonium) in stream bed sediments, rather than as a result of oxidation of NH₄⁺ (nitrification). Further, fine, silty sediments are particularly active sites of NO₂⁻ generation, suggesting that practices that reduce such inputs of fine sediments might also reduce NO₂⁻ presence in streams.

Interactions

Description

This project is being done with the assistance of the Wisconsin Chapter of The Nature Conservancy (TNC), who owns the properties being used in this study. Further, TNC is partnering with the Wisconsin Department of Natural Resources (WDNR) to restore both study reaches in the East Branch of the Pecatonica (one reach was restored prior to the start of this study; the second reach will be restored this fall). Consequently, we have interacted regularly with representatives from both TNC and WDNR, as both groups are facilitating the research activities and are keenly interested in learning about our research results. This is an ongoing interaction.

Event Date

7/1/2007

.....

Description

Following a presentation of Year 1 results, I had a series of discussions with Jeffrey Frey, a hydrologist with the USGS Indiana District. We have had preliminary discussions about the distribution of NO₂⁻ in Indiana streams. He has done a preliminary investigation of Indiana's NAWQA data base and found NO₂⁻ concentrations equal to, and often in excess of those observed in Wisconsin streams. Interestingly, his preliminary analysis suggests that surface water concentrations peak in the spring, compared to a mid-summer peak in Wisconsin. This may suggest a distinct mechanism of NO₂⁻ formation among the different locations that may be worth additional future study.

Event Date

6/9/2008

Partners

Name/Organization

Steven Loheide

Affiliation

University of Wisconsin- Madison

Affiliation Type

Academic Institutions

Email

loheide@cae.wisc.edu

Description

Dr. Loheide is also engaged in research at the East Branch of the Pecatonica River, and is similarly interested in the environmental consequences of stream restoration. He has a Ph.D. student studying the hydrologic changes associated with restoration of this site. As such, his group's work is being done in coordination with our work on surface and groundwater chemistry, and we expect that these parallel efforts will be mutually informative.

Presentations & Public Appearances

Title

Potential sources of nitrite in southern Wisconsin agricultural streams

Presenter(s) Emily H. Stanley
Presentation Type Professional meeting
Event Name Annual summer meeting- American Society of Limnology and Oceanography
Event Location St. John's, Newfoundland
Event Date 6/9/2008
Target Audience Scientific audience
Audience Size 50
Description This talk was part of an organized special session entitled: "Agricultural streams: Ecosystem function in headwater systems draining highly productive agricultural regions." The audience was composed of a mix of researchers from universities and federal agencies in the U.S. and Canada.

.....

Title On the receiving end: nitrogen in Wisconsin streams
Presenter(s) Emily H. Stanley
Presentation Type Seminar
Event Name University Program in Ecology Seminar
Event Location Duke University, Durham, NC
Event Date 2/15/2008
Target Audience
Audience Size 40
Description This was an invited seminar for the Ecology group at Duke University.

.....

Title Terrestrial and aquatic controls of inter-annual variability in river phosphorus yields
Presenter(s) Powers, S.M. and E.H. Stanley
Presentation Type Professional meeting
Event Name Annual meeting of the North American Benthological Society
Event Location Grand Rapids, MI
Event Date 5/20/2009
Target Audience Scientific audience
Audience Size 50
Description This is a presentation at a scientific society

Students & Post-Docs Supported

Student Name Stephen Powers
Campus University of Wisconsin-Madison

Advisor Name Emily Stanley
Advisor Campus University of Wisconsin-Madison

Degree

PhD
Graduation Month May
Graduation Year 2012
Department Center for Limnology
Program Limnology and Marine Science
Thesis Title Ecosystem Geometry, Catchment Composition, and the Cycling of Nutrients through Rivers
Thesis Abstract

Undergraduate Students Supported

New Students: **2**

Continuing Students: **1**

A Thermal Remote Sensing Tool for Mapping Spring and Diffuse Groundwater Discharge to Streams

Basic Information

Title:	A Thermal Remote Sensing Tool for Mapping Spring and Diffuse Groundwater Discharge to Streams
Project Number:	2008WI192B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	2
Research Category:	Ground-water Flow and Transport
Focus Category:	Management and Planning, Methods, Water Supply
Descriptors:	None
Principal Investigators:	Steven Loheide

Publication

1. Deitchman, R and S. Loheide. 2009. Ground-based thermal imaging of groundwater flow process at the seepage face. Accepted for publication, Geophysical Research Letters.

Annual Progress Report

Selected Reporting Period: 7/1/2007 - 6/30/2008

Submitted By: Richard Deitchman

Submitted: 5/27/2009

Project Title

WR07R005: A Thermal Remote Sensing Tool for Mapping Spring and Diffuse Groundwater Discharge to Streams

Project Investigators

Steven Loheide, University of Wisconsin-Madison

Progress Statement

The first research objective of this project is the use of thermal remote sensing data, collected from both a single-engine airplane and an unmanned aerial vehicle (UAV), for mapping of spring and diffuse groundwater discharge to streams in Wisconsin. The temperature of groundwater is relatively constant, whereas surface water temperature varies on seasonal and diurnal cycles. As a result of this thermal signature, it is possible to locate groundwater discharge using thermal imaging. Progress towards this research objective during the reporting period (3/1/2008-2/29/2009) includes:

- Completion of four separate thermal imaging flights over the East Branch Pecatonica River field site (7 AM, 11 AM, 3 PM and 7 15 PM) to assess large-scale stream temperature dynamics. [7/2008]
- Field data collection, including in-stream data logger installation and stream gaging, for comparison to remotely-sensed data and for stream temperature modeling [3/2008-2/2009]
- Processing of thermal infrared data to develop longitudinal profiles of stream temperature [7/2008-12/2008]
- Development and completion of a one-dimensional stream temperature model using data from the July 2008 thermal imaging flights and from in-stream data loggers as validation. We used Heat Source, distributed by the Oregon Department of Environmental Quality, for our simulations. [3/1/2008 - 2/29/2009]
- Field testing of the UAV system at the East Branch Pecatonica River (near Barneveld, WI) and Allen Creek (near Ft. Atkinson, WI) [3/2008-2/2009]
- Assessment of the policy and legal implications of thermal remote sensing from both a single-engine airplane and UAV for the State of Wisconsin [8/2008-2/2009]
- Preparation of manuscript titled, " Simulating the impacts of climate change on the temperature of a Driftless Area trout stream using remotely sensed thermographic profiles and in-stream temperature histories" [3/2008 - current]

A second research objective of this work is to use thermal remote sensing to distinguish between focused and diffuse groundwater discharge. In 3/2008, thermal imagery revealed fine-scale (centimeter) variability in groundwater discharge through seepage faces that could best be investigated using ground-based thermography. In conjunction with an ongoing study on the effects of current and future stormwater management practices on the hydroecology of West Wingra Marsh in the University of Wisconsin Arboretum, ground-based thermal remote sensing was employed at a stream bank seepage face in order to characterize the nature of groundwater flux. No method exists to image groundwater processes along seepage faces, which are external boundaries of the saturated zone. The purpose of this field study was to evaluate the use of ground-based, centimeter-scale thermal infrared imaging for characterizing groundwater flow at the stream bank. Seepage faces are often poorly understood, although they may exert a significant influence on the eco-hydrology of riparian areas. The imagery provides a method to visualize point and diffuse discharge at the centimeter scale and characterize the degree of heterogeneity of the

hydraulic properties of the sediment. Progress towards this research objective during the reporting period (3/1/2008-2/29/2009) includes:

- Reconnaissance collection of thermal imagery of seepage faces at a drainage ditch in West Wingra Marsh to compare longitudinal variation in the height of the groundwater seepage face, seepage face intensity and the nature of groundwater flow (focused vs. diffuse discharge). [3/2008-6/2008]
- Collection of imagery on both sides of the seepage face to characterize processes at the stream reach scale [6/2008]
- Collection of 24 hours of continuous thermal imagery at one location along the Wingra Marsh drainage ditch to assess diurnal variation in seepage face temperature. Observed differences in thermal inertia allow detection of water table position, regimes of higher groundwater flux, and variation in soil moisture in the vadose zone [7/2008]
- Collection of winter thermal imagery for comparison to the summer data set [2/2009]
- Collection of three, 8" diameter soil cores and permeameter testing to assess hydraulic conductivity of the stream bank sediments [2/2009]
- Statistical analysis and image processing of seepage face data [3/2008-2/2009]
- Presentation by Deitchman at American Water Resources Association - Wisconsin Section 2009 Annual Meeting [3/5/2009 - won "Best Student Platform" presentation award]
- Preparation of manuscript for Geophysical Research Letters, titled "Ground-based thermal imaging of groundwater flow processes at the seepage face" [submitted 3/2009, accepted pending minor revisions on 5/11/2009]

Principal Findings and Significance

Principal Findings and Significance

Description

This research project demonstrates that thermal remote sensing: (1) provides a method to observe the water table and groundwater discharge processes at the seepage face, (2) provides ultra-high resolution imagery of stream temperature, (3) provides strong validation data for stream temperature modeling, (4) can be used in conjunction with stream temperature modeling to quantify groundwater discharge to stream and (5) may assist the State of Wisconsin in promoting sustainable use of groundwater and protecting spring resources.

This research involved data collection at three different sites in Wisconsin: (1) East Branch Pecatonica River, (2) Allen Creek and (3) The University of Wisconsin-Madison Arboretum. Thermal imagery collected from both an unmanned aerial vehicle (UAV) and from a small-airplane at the East Branch Pecatonica River, was used to validate a stream temperature model which was used for forecasting potential changes in stream temperature as a consequence of climate change (Figure 1). The model simulates stream temperature change with three air temperature/groundwater temperature increase scenarios (1, 3 and 5°C) and changes in stream flow (-30% baseflow and +30% baseflow) (Figure 2). The data reveal that in the more extreme climate change scenarios (e.g. increase in air and groundwater temperature of 5°C and thirty percent less baseflow), native brook trout and non-native brown trout populations may experience mortality due to exceedance of acceptable thermal regimes. Without the remotely-sensed thermal data, a sub-reach with higher groundwater discharge that serves as a thermal refuge even in climate change scenarios would not have been located. This finding is particularly important in the Driftless Area because the region benefits with greater than \$1 billion in annual expenditures on recreational trout angling (Trout Unlimited, 2008).

In addition to small airplane work at the East Branch Pecatonica River, UAV flights at the site indicated that thermal resolution of stream temperature maps can be up to three times greater than the resolution of imagery collected from small airplanes at greater flight altitudes (Figure 3). The data showed that UAVs are a valuable alternative to small airplanes and may be employed to study finer scale processes (e.g. smaller springs). However, regulations by the Federal Aviation Administration (FAA) limit UAV operation to pre-approved sites, with flight range restricted to the operators line of sight. Figure 4 shows thermal imagery collected from a single-engine airplane and highlights the use of thermal imaging for spring identification.

Ground-based thermal imaging of groundwater in the University of Wisconsin Arboretum provides a method to (1) identify water table position using thermal imagery, (2) enhance conceptual models of geologic heterogeneity and (3) distinguish between focused and diffuse groundwater discharge to the

surface. Thermal imagery collected on both sides of a stream bank seepage face showed groundwater flow as a both locally discrete and locally diffuse process. Additionally, twenty four hours of time-lapse thermal imagery demonstrated that during the summer months, peak air temperature, when the difference between air and groundwater temperature is greatest, is the ideal time window to collect thermal imagery of groundwater (Figure 5). Hydraulic conductivity measurements, obtained with a falling-head permeameter, validated the data interpretation by revealing a positive correlation between remotely-sensed seepage intensity and hydraulic conductivity seeps (Figure 6). Wisconsin water managers and policy makers would benefit from the use of thermal remote sensing. However, there are numerous regulatory hurdles, including Federal Aviation Administration regulations and technical deficiencies, that will limit the implementation of unmanned aerial vehicle thermal remote sensing for spring management in the state. Overcoming or complying with these requirements, thermal remote sensing from small airplanes and ground-based efforts will assist in groundwater supply management efforts and help protect valuable spring resources and ecosystems.

Description

Figure Captions:

Figure 1a:

Comparison of remotely-sensed (RS), in-stream (In) and simulated (Sim) temperatures on July 24, 2008 for the East Branch Pecatonica River. The profile moves downstream left to right (0 km is upstream, 10.47 km is downstream). Remotely-sensed temperatures were sampled using a thermal infrared camera. In-stream records at 2.75 km, 7.3 km and 7.75 km were recorded using HOBO loggers. Simulated temperatures were modeled using Heat Source V.8.0.4 software.

Fig 1b:

Longitudinal profile of groundwater discharge to the stream estimated through stream temperature modeling.

Figure 2:

Maximum daily temperature for model simulations of the base case (no change in air/groundwater temperature or recharge), the base case plus 1°C, the base case plus 3°C and the base case plus 5°C at 7.75 km [top]. Maximum daily temperature for model simulations of the base case (no change in air/groundwater temperature or recharge), the base case -30% recharge and the base case +30% recharge at 7.75 km [bottom]. A decrease in recharge decreases the volume of stream flow allowing the stream to warm more readily.

Figure 3:

Thermal imagery collected from the unmanned aerial vehicle at the East Branch Pecatonica 2006 restoration site in July 2008. The straight, left-right trending feature in panel A is a road, which appears warm relative to its surroundings in the thermal image. The imagery was collected in the afternoon on a warm summer day, and the stream is very cool relative to the land surface.

Figure 4:

Thermal imagery of spring flow into Lake Wingra (south shore), Madison, Wisconsin collected from a fixed-wing aircraft. The imagery was collected in November 2008. The groundwater temperature is warmer than the surface in winter (November in Wisconsin) consequently the springs appear as the warm locations in the thermal imagery (approximately 2-6°C). The top frame displays a large spring whereas the bottom frame is a much smaller spring.

Figure 5:

Twenty-four hours of continuous thermal data collected at one stream bank: A) Thermal image showing two regions of interest (SAT – saturated zone, UNSAT – unsaturated zone). B) Standard deviation of the twenty-four hour time lapse data, which exhibits the lower thermal inertia of the

unsaturated zone. C) Twelve thermal images at two-hour intervals D) Twenty-four hour average temperature history of two regions of interest (SAT and UNSAT) E) Vertical soil moisture profile (5 cm increments) from the stream to the top of the stream bank.

Figure 6:

Winter thermal imagery and location of soil cores with hydraulic conductivity measurements: A) Winter visible image of seepage face with soil core locations annotated. B) Winter thermal imagery of seepage face with soil core locations and hydraulic conductivity values (K) [A= high intensity seepage, B= moderate intensity seepage, C= low intensity seepage]. Note: snow cover prevents interpretation of the thermal image above the seepage zone.

*note - figures are provided on iPro (My Activities Files --> Supporting Figures) and are labeled Figure 1-6

Interactions

Description

Organization/Agency: The Nature Conservancy

Category: Non-governmental organizations

Contact Name: Steve Richter

Contact Email: srichter@tnc.org

Description: Landowners of East Branch Pecatonica field site; provide site support and permissions; conduct quarterly science meetings to discuss research findings and implications for ongoing restoration activities at the site.

Event Date

.....

Description

Organization/Agency: Wisconsin Department of Natural Resources

Category: Local and State

Contact Name: Bob Hansis

Contact Email: Robert.Hansis@Wisconsin.gov

Description: Advice for field activities near East Branch Pecatonica field site, assistance with single-engine airplane flights through the use of DNR pilots and state of Wisconsin aircraft, conduct quarterly science meetings to discuss research findings and implications for ongoing restoration activities at the site.

Event Date

.....

Description

Organization/Agency: Friends of Allen Creek Watershed (FACW)

Category: Local

Contact Name: Andy Selle

Contact Email: aselle@interfluve.com

Description: Coordination of addition of Allen Creek to project study sites and assistance with completion of FAA permitting. FACW will use the spring inventory we develop for the watershed to plan restoration and conservation efforts. We plan to conduct field work in late summer 2008 and winter 2008.

Event Date

.....

Description

Organization/Agency: Friends of Cherokee Marsh (FOCM)
Category: Local
Contact Name: Jon Becker
Contact Email: Jonbecker@aol.com
Description: Preliminary interaction regarding future mapping of springs in Cherokee Marsh (Madison, WI) using single-engine airplane. They seek a better understanding of the location of springs in the marsh and impact of those springs on the hydroecology of the wetland. Ultimately, we would like to work with FOCM to use this information to guide restoration of the wetland and protection of recharge areas feeding the springs and fens of Cherokee Marsh.

Event Date

.....

Description

We worked closely with the unmanned aircraft division of the Federal Aviation Administration in order to obtain a Certification of Authorization (COA) for use of the unmanned aerial vehicle. Due to the nature of our work, the FAA classifies our vehicle as a "public" aircraft. Consequently, the FAA required us to obtain a COA. The COA permits unmanned aircraft on the basis of air worthiness, planned flight locations and other factors. The process took 6-months and is now complete.
Event Date: August 2007 – February 2008
Permit Identification: 2007-AHQ-46

Event Date

.....

Description

Description: We obtained a permit from the Federal Communications Commission for use of the unmanned aerial vehicle transmitter.
Event Date: January 2008 – April 2008
Permit Identification: Federal Communications Commission Experimental Radio Station Construction Permit and License # 0049-EX-PL-2008 (WE2XOK Call Sign)

Event Date

.....

Description

Description: We worked with a local flight school to obtain a ground-school private pilot certificate in order to have clearance for use of our unmanned aerial vehicle.
Event Date: February and March 2008
Permit Identification: Completion of FAA Private Pilot written exam and clearance for a third class private pilot medical certification

Event Date

Journal Articles & Other Publications

Publication Type

Peer-Reviewed Journal Article/Book Chapter

Title

Ground-based thermal imaging of groundwater flow processes at the seepage face

Author(s) Richard S. Deitchman, Steven P. Loheide II
Publication/Publisher Geophysical Research Letters
Year Published
Volume & Number
Number of Pages
Description Accepted pending minor revisions on 5/11/2009
Any Additional Citation Information

.....

Publication Type Newsletter/Periodical
Title UW research taking a birds-eye view of groundwater discharge
Author(s) UW-Madison News
Publication/Publisher UW-Madison
Year Published 2007
Volume & Number
Number of Pages
Description Online UW News Article on project and other WRI-funded projects (8/14/2007)
Any Additional Citation Information

.....

Publication Type
Title Simulating the impacts of climate change on the temperature of a Driftless Area trout stream using remotely sensed thermographic profiles and in-stream temperature histories
Author(s) Richard S. Deitchman, Steven P. Loheide II
Publication/Publisher
Year Published
Volume & Number
Number of Pages
Description in preparation
Any Additional Citation Information

Other Project Support

Source College of Engineering Start Up Funds; Wisconsin Alumni Research Foundation
Dollar Value \$22,000
Description Financial support for thermal infrared camera, single-engine airplane flight time, unmanned aerial vehicle construction (parts and student labor), HOBO in-stream temperature loggers at East Branch Pecatonica field sites, installation and downloading of HOBO loggers by a student not involved in the project (summer 2007).
Start Date 7/1/2007
End Date 8/1/2008

Partners

Name/Organization	Eric Booth
Affiliation	East Branch Pecatonica River Restoration Observatory
Affiliation Type	Other
Email	egbooth@wisc.edu
Description	Multi-disciplinary team of researchers investigating hydrology, ecology, geomorphology, biogeochemistry and engineering at two restoration sites on the East Branch Pecatonica River. Researchers: -Eric Booth, Ph.D. Student, Center for Limnology/Civil and Environmental Engineering -Prof. Steve Loheide, Civil and Environmental Engineering -Prof. Emily Stanley, Center for Limnology -Prof. Jim Knox, Department of Geography Land Managers: -Steve Richter, The Nature Conservancy -Bob Hansis, Wisconsin Department of Natural Resources -Katie Abbott, Military Ridge Prairie Heritage Area Website: http://hydroecology.cee.wisc.edu/EBP/index.htm

Presentations & Public Appearances

Title	The use of an unmanned aerial vehicle for mapping spring and diffuse groundwater discharge to streams
Presenter(s)	Richard S. Deitchman
Presentation Type	Seminar
Event Name	Department of Civil and Environmental Engineering Water Resources Engineering and Environmental Fluid Mechanics Seminar
Event Location	Engineering Hall, Madison, WI
Event Date	12/13/2007
Target Audience	University students
Audience Size	20
Description	45 minute talk to Water Resources Engineering group on the project methodology.

.....

Title	Thermal remote sensing detection of groundwater discharge to streams
Presenter(s)	Steven P. Loheide II
Presentation Type	Professional meeting
Event Name	Geological Society of America (GSA) 2007 Annual Meeting
Event Location	Denver, Colorado
Event Date	10/29/2007

Target Audience Scientific audience
Audience Size 120
Description Invited presentation for session titled "Innovation and New Technologies for Measuring and Characterizing Groundwater-Surface Water Interaction"

.....

Title Thermal remote sensing of stream temperature - a tool for mapping springs
Presenter(s) Richard S. Deitchman, Steven P. Loheide II
Presentation Type Other
Event Name Friends of Allen Creek Watershed monthly meeting
Event Location Koshkonong Town Hall, Ft. Atkinson, Wisconsin
Event Date 9/9/2008
Target Audience Public
Audience Size 20
Description Public presentation on thermal remote sensing research and planned UAV flights at Allen Creek site

.....

Title Using thermal remote sensing in Wisconsin - a way to help administer 2003 WI Act 310?
Presenter(s) Richard S. Deitchman
Presentation Type Other
Event Name Meeting with WDNR representatives from the Water Use Section
Event Location WDNR, S. Webster Street, Madison, Wisconsin
Event Date 11/12/2008
Target Audience State government agency
Audience Size 7
Description Presentation to representatives from the Wisconsin DNR on the methodology and how thermal remote sensing may be used for statewide spring inventories

.....

Title The use of thermal remote sensing for mapping spring and diffuse groundwater discharge: applications to Wisconsin groundwater law and management
Presenter(s) Richard S. Deitchman
Presentation Type Seminar
Event Name University of Wisconsin - Madison Department of Urban and Regional Planning
Event Location Music Hall, Madison, Wisconsin
Event Date 12/11/2008
Target Audience University students
Audience Size 25
Description Presentation to students in a water policy course on the policy implications of the methodology

.....

Title	Characterization of groundwater flux using ground-based thermal remote sensing at the seepage face
Presenter(s)	Richard S. Deitchman, Steven P. Loheide II
Presentation Type	Professional meeting
Event Name	American Water Resources Association - Wisconsin Section 2009 Annual Meeting
Event Location	Stevens Point, Wisconsin
Event Date	3/5/2009
Target Audience	Mixed
Audience Size	50
Description	Presentation on ground-based thermal remote sensing work at the 2009 AWRA meeting; won "Best Student Platform" presentation award

Students & Post-Docs Supported

Student Name	Richard Deitchman
Campus	University of Wisconsin-Madison

Advisor Name	Steven Loheide
Advisor Campus	University of Wisconsin-Madison

Degree	Masters
Graduation Month	May
Graduation Year	2009
Department	Gaylord Nelson Institute for Environmental Studies
Program	Environment and Resources
Thesis Title	Thermal remote sensing of stream temperature – applications to hydrogeology and water resources policy in Wisconsin
Thesis Abstract	<p>Thermal remote sensing is increasingly utilized as a tool in hydrology because it is easily-transferable, can provide high-resolution, synoptic views of water resource issues and may provide answers to difficult research questions. Thermal infrared radiation is generally considered to have a wavelength between 3.5-20 μm. Commercial thermal infrared sensors typically detect radiation in the 7.5-13 μm wavebands. The reduced cost of thermal imaging cameras now provides a cost-effective method for imaging to be used for stream temperature and groundwater discharge analysis (Cardenas et al. 2008, Loheide and Gorelick 2006, Torgerson et al. 1999).</p> <p>The temperature of groundwater is relatively constant through time whereas surface water temperature varies on seasonal and diurnal cycles. This thermal signature allows groundwater discharge to be located at the surface with thermal imaging. The purpose of this research is to investigate the use of thermal remote sensing for water resources science and policy in the State of Wisconsin. Science-based management is essential to the future of Wisconsin's water resources. Wisconsin is very progressive nationally in water resources policy; Wisconsin Act 310 (2003), a groundwater quantity protection law, is one of the first pieces of legislation to recognize the interaction of groundwater and surface water. This project includes three case studies on the use of thermal remote sensing along with a chapter detailing the policy implications of the new methodologies for the State of Wisconsin.</p> <p>There is no existing method to image groundwater processes along a seepage face. Thus, it is often difficult to quantify the magnitude and spatial variability of groundwater flux across this interface. Ground-based thermal imaging was employed in the University of Wisconsin-Arboretum as a new, transferable, non-invasive method that uses heat as a natural tracer to image spatially-variable</p>

groundwater flow processes and distinguish between focused and diffuse groundwater discharge to the surface. For the first time, the work demonstrates that thermal remote sensing of groundwater at the seepage face provides indirect imaging of both the saturated zone-unsaturated zone transition and groundwater flux at the centimeter scale, offering further insight into flow heterogeneity. Airborne thermal remote sensing from a single-engine airplane was used to collect thermal infrared data that validated a one-dimensional stream temperature model of the East Branch Pecatonica River. Model simulations of various climate change scenarios suggest that stream temperatures may reach critical thresholds of mortality for brook trout (*Salvelinus fontinalis*) and brown trout (*Salmo trutta*). The work uses an existing, freely-available one-dimensional stream temperature model calibrated with longitudinal profiles of stream temperature created from four thermal imaging flights and data from in-stream loggers. It demonstrates that thermal infrared data can greatly assist stream temperature model validation due to its high spatial resolution, can be used to pinpoint spatial heterogeneity in groundwater inflow to streams and that stream temperature models considering climate change are important for fisheries management. Data collected from an unmanned aerial vehicle is used to show the potential use of thermal remote sensing for administration of 2003 Wisconsin Act 310. Among other measures, Act 310 regulates the influence of high-capacity pumping wells on springs. Springs are defined as "[areas] of concentrated groundwater discharge occurring at the surface of the land that result in a flow of at least one cubic foot per second at least 80 percent of the time." Currently, information about the location and flow of springs is limited on a statewide basis. Unmanned aerial vehicles may be employed to collect thermal imagery for the mapping of springs. However, numerous technical and regulatory barriers curtail the use of unmanned aerial vehicles for data collection on a statewide basis. This thesis highlights the value of unmanned aerial vehicles and discusses the policy, regulatory and technical barriers to implementation.

Other Activities

Description

Badger Ridge Middle School science education program. 6th grade students come to the department to learn about careers in environmental engineering. Loheide and Deitchman present an inquiry-based unit on groundwater and its importance in the state.

Event Date

5/27/2008

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
Project Number:	2008WI244S
Start Date:	9/15/2008
End Date:	9/14/2013
Funding Source:	Supplemental
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

Publication

NOTE: Your report is not complete until you click on the **Submit Report** button.

[<< Back](#)[Submit Report](#)

Annual Progress Report

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

Submitted By: Jim Hurley

Submitted: 6/11/2009

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

The project team continues to make good progress towards understanding the sources and cycling of mercury in airsheds and watersheds. During the past year we conducted studies in two coastally situated settings: Weeks Bay, Alabama, and Cape Romaine, South Carolina. In addition, to add to the interpretation of our results, our project has begun development of a generally applicable dry-phase mercury deposition model that will facilitate estimates of ionic and elemental mercury to surfaces. The model is calibrated by the use of atmospheric mercury speciation measurements made in the field.

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 deposition 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.

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	

NOTE: Your report is not complete until you click on the **Submit Report** button.

[<< Back](#)[Submit Report](#)

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:	2008WI195B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Stephen Wittman, Jim Hurley

Publication

1. Betz, Carolyn. 2009. Nitrate in Groundwater fact sheet. Madison: University of Wisconsin Water Resources Institute. 2 pages.
2. Betz, Carolyn. 2009. Arsenic in Groundwater fact sheet. Madison: University of Wisconsin Water Resources Institute. 2 pages.
3. Kline, Kathleen Schmitt. 2009. Wisconsin's Changing Water Resources: 33rd Annual Meeting Program and Abstracts. American Water Resources Association-Wisconsin Section and Water Resources Institute, University of Wisconsin, Madison, Wis. 76 pages.
4. White, Elizabeth, ed. 2008. Aquatic Sciences Chronicle, Summer issue. Madison: University of Wisconsin Aquatic Sciences Center. 8 pages.
5. White, Elizabeth, ed. 2008. Aquatic Sciences Chronicle, Fall issue. Madison: University of Wisconsin Aquatic Sciences Center. 8 pages.
6. White, Elizabeth, ed. 2009. Aquatic Sciences Chronicle, Winter issue. Madison: University of Wisconsin Aquatic Sciences Center. 8 pages.
7. White, Elizabeth, ed. 2009. Aquatic Sciences Chronicle, Spring issue. Madison: University of Wisconsin Aquatic Sciences Center. 8 pages.

INFORMATION AND OUTREACH ACTIVITIES

In 2007, the UW-Madison Water Resources Institute Web site (www.wri.wisc.edu) was rebuilt from ground(water) up to make it easier and faster for visitors to find information about WRI research projects and publications. Construction of the new site was a yearlong team effort led by James Hurley, assistant director for research & outreach, and his assistant Liz Albertson, a recent graduate from the UW-Madison Water Resources Management program. One of the goals of the Web site redesign was to provide the public with a real-time link to information about current research. To that end, the site was integrated with the UW Aquatic Sciences Center's interactive Project Reporting Online (iPRO) system, an online tool that allows principal investigators to report on the progress of their projects. The new site features a fresh design with better readability and vivid photography. The redesigned WRI Web site went online February 15, 2008, and to date it has logged **19,080** page views and **3,289** unique visitors.

WISCONSIN WATER RESOURCES INSTITUTE PUBLICATIONS

In 2007, the UW Water Resources Institute published a 20-page illustrated pamphlet and two-page executive summary describing the activities of Groundwater Coordinating Council (GCC) since its creation 20 years ago. The pamphlet, entitled *Protecting Wisconsin's Buried Treasure*, documents the accomplishments, impacts and benefits of the Groundwater Research & Monitoring Program. Drawing on some of the most important issues identified in the pamphlet, two fact sheets were published in 2009: *Nitrate in Groundwater* and *Arsenic in Groundwater*. Two more fact sheets are in preparation on *Water Quantity and Groundwater Drawdown* and *Pathogens in Groundwater*. These publications will provide a complementary packet of information with long-term usefulness to all GCC member agencies. Coordinated by the GCC Education Subcommittee, this project represents a truly collaborative effort involving all GCC members. All but six of the **235** copies of the pamphlet printed have been distributed, and a free electronic copy of the pamphlet in the ASC's online Publications Store has been downloaded **819** times between the date it was posted (11/1/07) and the end of May 2009.

In February 2006, WRI and the UW-Madison Department of Civil & Environmental Engineering published *Design Guidelines for Stormwater Bioretention Facilities* by Dustin Atchison, Ken Potter and Linda Severson. This manual provides design guidelines and a numerical model (RECARGA) that can be used for creating bioretention facilities for small-scale stormwater management that promotes infiltration of storm water in order to reduce its volume, improve its quality and increase groundwater recharge. This document continues to be extremely popular at the ASC Publications Store. Since its publication, a total of **490** print copies have been distributed and **21,321** downloads of the online PDF have been logged.

WATER RESOURCES RESEARCH HIGHLIGHTED IN NEWSLETTER

During 2008-09, WRI research and activities were featured in all four issues of the UW Aquatic Sciences Center's quarterly newsletter, *Aquatic Sciences Chronicle*, which is distributed statewide and nationally to more than **2,500** subscribers, including UW System faculty and students, local and state water management agencies, water-related NGOs, news media and WRIs in other states. Newsletter stories included the results of a WRI-funded study that sampled a subdivision's septic systems, groundwater monitoring wells and home water taps for

the presence of bacteria resistant to tetracycline antibiotic; highlights of the AWRA-Wisconsin Section's 2009 annual meeting, and the launch of the WRI Library's "Aqualog" blog.

"WATER MATTERS" LECTURE SERIES

The WRI cosponsored "Water Matters: A Lecture Series" as part of the public programming accompanying the October 2008–January 2009 "Mami Wata: Arts for Water Spirits in Africa and its Diasporas" exhibition at the UW-Madison Chazen Museum of Art. Besides the Chazen and WRI, other major partners in this project were the UW Sea Grant Institute and the UW-Madison Department of Art History. Designed to enhance public awareness and understanding of water resources issues in the context of a changing climate, the series of five lectures featured presentations by the WRI director (Anders Andren) and faculty members from the UW-Madison American Indian Studies Program, Center for Limnology, Zoology Department and Life Sciences Communications; Northland College Department of Biology, and UC-Berkeley.

The series attracted a total of **295** attendees, and evaluations were submitted by 116 (39%). Evaluation data indicate 52% of the lecture attendees were adult campus visitors (the primary target audience), 48% were students (the secondary target audience), and 48% had no prior awareness of the WRI. Seventy one percent reported that they gained new insights as a result of the lecture they attended, and on a scale of 1 to 5 (5 = excellent), 89% gave the presentations a rating of 4 or 5. In addition, the "Water Matters" Web site, which featured audio of the American Indian "MadTown Singers" group, attracted 514 visits and 827 page views over a one-month period. One of the presenters, UW-Madison Center for Limnology Director James Kitchell, was featured on the October 19, 2008, "University of the Air," a Wisconsin Public Radio program that typically attracts more than **300,000** listeners.

REGIONAL CLIMATE CHANGE SEMINAR SERIES

The WRI helped support "Climate Change in the Great Lakes Region: Starting a Public Discussion," a seminar series sponsored by the UW Sea Grant Institute and Wisconsin Coastal Management Program. From March through September 2007, eight climate-effects experts spoke at seven sites around Wisconsin to discuss what is known, what is predicted and what can be done to adapt to a changing climate. To continue and expand public discussion of what climate change means for the Great Lakes region, an 80-page summary report and a DVD featuring video and the PowerPoint® presentations from all eight seminars were published in 2008, either of which may be purchased or downloaded free of charge from the UW Aquatic Science Center's online Publications Store (aqua.wisc.edu/publications). To date, **760** copies of the printed summary report and **50** copies of the DVD have been distributed, and the online PDF of the report has been downloaded **2,129** times. A written summary and video of each seminar PowerPoint® presentation are also available for free download from the "The Seminars" section of the project Web site (www.seagrants.wisc.edu/ClimateChange), which has logged **1,471** page views in **762** visits by **657** unique visitors.

GROUNDWATER AWARENESS WEEK 2009

The WRI again contributed to a series of seven news releases for the annual "Groundwater Awareness Week" in March 2009 that were distributed via the UW-Madison WRI's statewide

media mailing list and the UW-Extension network. Phone calls from media looking for more information indicate at least some of the information made it into several Wisconsin newspapers and on radio and television. The WRI also arranged for Stephen Ales, drinking and groundwater team supervisor for the Wisconsin Department of Natural Resources, and Kevin Masarik, outreach specialist for the UW-Stevens Point Center for Watershed Science and Education, to be guests on the March 25 broadcast of Wisconsin Public Radio's popular "Larry Meiller Show," a 45-minute live call-in talk show with a regular statewide audience numbering in the **hundreds of thousands**. Aired on WPR stations statewide, the program attracted a dozen callers from throughout the state, mainly with questions related to well water contaminants and testing issues. Program producers have said the number of calls show strong enough statewide interest in the topic to merit additional programs on groundwater topics in the future. This was reinforced by the strong follow-up interest in this topic as evidenced by more than **27** WPR member downloads of the MP3 video file of the program and **76** "plays" of the RealMedia streaming audio archive of the program on the WPR Web site.

A.W.R.A. 2009 ANNUAL CONFERENCE

The WRI once again cosponsored the American Water Resources Association-Wisconsin Section's annual conference, "Wisconsin's Changing Water Resources," held March 5-6, 2009, in Stevens Point, Wis. Other sponsors included 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. About **170** water managers and scientists from throughout Wisconsin attended the conference, which featured more than 60 oral and poster presentations on a wide range of water resources topics. Plenary session topics included global effects of climate change, effects of climate change on Wisconsin lakes and future implications of climate change to Wisconsin. During the conference, the AWRA Wisconsin Section presented its "**Distinguished Service Award**" to WRI Assistant Director for Research and Outreach **James Hurley** in recognition of his exceptional contributions to water resources education, significant scientific contributions towards improving the water resources of Wisconsin and dedicated service to the AWRA organization.

WISCONSIN'S WATER LIBRARY OUTREACH ACTIVITIES

During the past year, Wisconsin's Water Library has continued its involvement in outreach efforts while providing a full range of library services to faculty, staff and students of the University of Wisconsin System. The library provided outreach by providing in depth reference assistance on a wide range of water-related topics. Some examples of reference queries answered included the history of dredging of the Baraboo River; research on statistics relating to Lake Michigan weather and water conditions; thorough inventory of periodical literature on water since the beginning of the 20th century; locating references on the safety of eating fish caught in Lake Mendota; research on temperature tolerance and preference and dissolved oxygen tolerance and preference for certain fish species; and a literature search on climate change effects (or varying water level change effects) on port, harbor or marina operations.

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 UWS as well as across the nation and the world.

Library staff continued to be involved in the Allied Drive Story Hours outreach program. Allied Drive is a neighborhood of Madison where many of the families live in poverty. The program is a partnership of eight specialized UW-Madison campus libraries, the UW-Madison School of Library and Information Studies, and the Madison School and Community Recreation Safe Haven Childcare Program in which each month a different campus library hosts a reading hour with themes relating to its specialized subject area. During the past year, the story hour was expanded to serve second and third graders in addition to first graders and kindergarteners.

LIBRARY WEB SITES

The main outreach tool for the library is the newly redesigned and launched library Web site (aqua.wisc.edu/waterlibrary). During 2008-09, the library combined the three previous sites into one, seamless resource. For UWS faculty, staff and students, the Web site introduces services and resources tailored to them. An important part of this redesign was the update of the research tool, the Water Research Guide (<http://researchguides.library.wisc.edu/waterresearchguide>). The research guide contains books, journals, databases and other resources on water, science and the Great Lakes.

For Wisconsin residents, the library Web site is an outreach site for those who want to learn more about our state's water resources. It makes books and other materials in the library accessible to any Wisconsin resident. During the past year, library staff produced six bimonthly lists of *Recent Acquisitions* and added several special features or annotated reading lists on such popular topics as "Flooding in Wisconsin," "Understanding and Protecting Groundwater—Recommended Reading," and "Readings on Aquaculture." The most popular pages on the site are "Water Facts", a special feature page on Native Americans and the environment, and a reading list on Landscaping & Ponds.

Wisconsin's Water Library also includes the "Water Library for Kids" Web site (www.aqua.wisc.edu/waterlibrary/kids). This site features children's books with aquatic themes that have won awards or appeared on best books lists. Most books are for preschool through second grade children, although there are also materials for older kids. Besides fiction and nonfiction books, the Web site also provides ideas and resources for story hours. Users can browse recommended reading lists by topic (frogs, fish and fishing, Great Lakes, water

pollution, etc.) and by age group. Any adult Wisconsin resident can check out books online and pick them up at their local public library.

During the past year, the library initiated a new Web 2.0 service, AquaLog (aqualog2.blogspot.com), using Blog technology to provide daily, up-to-date, water-related news, publications and resources about Wisconsin and the Great Lakes region. AquaLog's posts are searchable by topic and a monthly archive is available. A researcher or a member of the public can receive notices of updates to the blog using an RSS feed.

The popularity of the all the library Web sites continues to grow. From June 1, 2008 through May 31, 2009, the WRI Library received **20,614** visits by **18,997** unique visitors who logged **39,382** page views.

OTHER W.R.I. WEB SITES

WRI maintains several other Web sites in addition those described above. The UW Water Resources Institute Web Site (<http://wri.wisc.edu>) introduces users to the Wisconsin program and includes a variety of information for those interested in water-related issues and research. The project listing, project reports, groundwater research database, funding opportunities and conference information sections of the Web site are updated annually.

The ASC Publications Store (www.aqua.wisc.edu/publications) features publications from both the Water Resources and Sea Grant Institutes. WRI fact sheets on arsenic in groundwater (197 downloads), groundwater drawdown (716 downloads) and Wisconsin's groundwater resources (155 downloads) continue to be popular. **Forty two** WRI print publications and **3,480** downloads of the online copies of these publications were logged by the Publications Store from 7/1/08 through 6/18/09.

STUDENT SUPPORTED

<i>Name:</i>	Jennifer Champoux
<i>Campus:</i>	UW-Madison
<i>Advisor:</i>	Ethelene Whitmire
<i>Advisor Campus:</i>	UW-Madison
<i>Degree/Training:</i>	Master of Arts
<i>Graduation:</i>	May 17, 2008
<i>Department:</i>	Library and Information Studies
<i>Program of Degree:</i>	Library and Information Studies
<i>Thesis Title:</i>	n/a
<i>Thesis Abstract:</i>	n/a

USGS Summer Intern Program

None.

Notable Awards and Achievements

During its 2009 annual conference, the American Water Resources Association-Wisconsin Section presented its Distinguished Service Award to University of Wisconsin WRI Assistant Director for Research & Outreach James Hurley in recognition of his exceptional contributions to water resources education, significant scientific contributions towards improving the water resources of Wisconsin and dedicated service to the AWRA organization.

Publications from Prior Years

1. 2004WI82G ("Groundwater sustainability in a humid climate: Groundwater pumping, groundwater consumption, and land use change. ") - Water Resources Research Institute Reports - Gotkowitz, M. 2008. Groundwater Sustainability in a Humid Climate: Groundwater Pumping, Groundwater Consumption, and Land-Use Change. Water Resources Institute, University of Wisconsin, Madison. 19p. plus appendices.
2. 2005WI158O ("Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer") - Articles in Refereed Scientific Journals - Browne, B.A., G.J. Kraft, W.D. DeVita, and D.J. Mechenich. 2008. Collateral Geochemical Impacts of Agricultural N Enrichment from 1963 to 1985: A Southern Wisconsin Groundwater Depth Profile. *J. of Env. Quality* 37:1456-1467.
3. 2007WI202O ("Controls on Methylation of Groundwater Hg(II) in Hyporheic Zones of Wetlands. ") - Articles in Refereed Scientific Journals - Creswell, J. E., Kerr, S. C., Meyer, M. H., Babiarz, C. L., Shafer, M. M., Armstrong, D. E., Roden, E. E. 2009. 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
4. 2007WI203O ("Influence of Wetland Hydrodynamics on Subsurface Microbial Redox Transformations of Nitrate and Iron.") - Articles in Refereed Scientific Journals - Gorski, P.R., Armstrong, D.E., Hurley, J.P., Krabbenhoft, D.P. 2008. The influence of natural dissolved organic carbon on the bioavailability of mercury to a freshwater alga. *Environmental Pollution* 154:116-123.
5. 2005WI158O ("Nitrate and Pesticide Penetration into a Northern Mississippi Valley Loess Hills Aquifer") - Articles in Refereed Scientific Journals - Kraft, G.J., B.A. Browne, W.D. DeVita, and D.J. Mechenich. 2008. Agricultural Pollutant Penetration and Steady-State in Thick Aquifers. *Ground Water Journal* 46(1):41-50.
6. 2007WI212O ("Transport and Survival of Pathogenic Bacteria Associated With Dairy Manure in Soil and Groundwater. ") - Dissertations - Jablonski, M. 2009. Comparison of the Role of Ionic Strength and Surface Charge Heterogeneity on the Initial Adhesion, Distribution, and Detachment of Two *Escherichia coli* Strains. Master's thesis, Department of Civil Engineering and Mechanics, University of Wisconsin-Milwaukee.
7. 2007WI204O ("Monitoring Septic Effluent Transport and Attenuation using Geophysical Methods") - Other Publications - Summitt, A., Hart, D. J., Masarik, K., and Fratta, D. 2009. Imaging the Fate of Septic Tank Effluent using Multiple Geophysical Techniques. *Journal of Environmental and Engineering Geophysics* (in preparation for publication - draft completed).
8. 2005WI161O ("Evaluation of On-Site Wastewater Treatment as a Source of Antibiotic Resistance Genes in Groundwater") - 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.
9. 2004WI79B ("Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics in Subsurface Environments") - Articles in Refereed Scientific Journals - Gu, C.; Karthikeyan, K.G.; Sibley, S.D.; Pedersen, J.A. 2007. Complexation of the antibiotic tetracycline with humic acid. *Chemosphere*, 66, 1494-1501. doi: 10.1016/j.chemosphere.2006.08.028.
10. 2005WI152B ("Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation") - Articles in Refereed Scientific Journals - Li, Z., Beachner*, R., McManama*, Z., Hong, H. 2007. Sorption of Arsenic by Surfactant-Modified Zeolite and Kaolinite. *Micropor. Mesopor. Mater.*, 105, 291-297. <http://dx.doi.org/10.1016/j.micromeso.2007.03.038>
11. 2005WI152B ("Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation") - Articles in Refereed Scientific Journals - Li, Z., Jones, H. K., Zhang, P., Bowman, R., S. 2007. Chromate Transport through Columns Packed with Surfactant-Modified

- Zeolite/Zero Valent Iron Pellets, *Chemosphere*, 68(10), 1861-1866.
doi:10.1016/j.chemosphere.2007.03.011.
12. 2004WI1310 ("A Comparison of USEPA-Approved Enzyme-Based Total Coliform/E. coli Tests for Microbiological Groundwater Monitoring and Laboratory Consultation") - Articles in Refereed Scientific Journals - Olstadt, J., J. Schauer, J. Standridge and S. Kluender. 2007. A comparison of ten USEPA approved total coliform/E. coli tests. *Journal Water and Health*. 05.2, 267-282.
 13. 2005WI1530 ("A Combined Hydrogeologic/Geochemical Investigation of Groundwater Conditions in Waukesha County, Wisconsin") - Articles in Refereed Scientific Journals - Klump, S., Grundl, T., Purtschert, R. and Kipfer, R. 2008. Groundwater and climate dynamics derived from noble gas, ¹⁴C and stable isotope data. *Geology* 36(5): 395-398.
 14. 2005WI152B ("Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation") - Articles in Refereed Scientific Journals - Li, Z., Du, Y., Hong, H. 2008. Transport of Micelles of Cationic Surfactants through Clinoptilolite Zeolite. *Micropor. Mesopor. Mater.*, 116, 473-477. <http://dx.doi.org/10.1016/j.micromeso.2008.05.006>.
 15. 2005WI152B ("Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation") - Articles in Refereed Scientific Journals - Li, Z., Hong, H. 2008. Combination of Surfactant Solubilization with Permanganate Oxidation for DNAPL Remediation. *Water Res.*, 42, 605-614. <http://dx.doi.org/10.1016/j.watres.2007.08.010>
 16. 2004WI79B ("Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics in Subsurface Environments") - Articles in Refereed Scientific Journals - Sibley, S.D.; Pedersen, J.A. 2008. Interaction of the macrolide antimicrobial clarithromycin with dissolved humic acid. *Environ. Sci. Technol.* 42, 422-428. doi: 10.1021/es071467d
 17. 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.* (in press) <http://dx.doi.org/10.1016/j.jhazmat.2009.05.073>
 18. 2004WI79B ("Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics in Subsurface Environments") - Articles in Refereed Scientific Journals - Gao, J.; Pedersen, J.A. 2009. Sorption of sulfonamide antimicrobial agents to humic-clay complexes. *J. Environ. Qual.* (in press)
 19. 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>
 20. 2007WI2120 ("Transport and Survival of Pathogenic Bacteria Associated With Dairy Manure in Soil and Groundwater. ") - 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.
 21. 2007WI2130 ("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.
 22. 2004WI79B ("Fate of Representative Fluoroquinolone, Macrolide, Sulfonamide and Tetracycline Antibiotics in Subsurface Environments") - 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.