Water Resources Institute
Annual Technical Report
FY 2011

Introduction

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

The Wisconsin WRI funds an average of 15 short-term research projects of either a fundamental or applied nature that typically involve about 50 faculty, staff and students at a half-dozen campuses around the state each year. By supporting short-term projects, the institute is able to quickly respond to issues as they emerge. WRI annually provides about 30 graduate and undergraduate students in the UW System with opportunities for training and financial support while they work toward their degrees. During the current reporting period a total of 38 students/trainees (16 undergraduates, 11 master's degree students, five Ph.D. students and six post-doctoral students) received WRI support from both Federal and non-Federal sources.

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

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

Research Program Introduction

As established by Wisconsin's Groundwater Law of 1984, the state provides $250,000 to $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 Safety & Professional Services, 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 350 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.

Our priorities for groundwater research are established annually by the Wisconsin Groundwater Research Advisory Council (GRAC) and 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 rigorous external peer review (coordinated by the WRI) and relevancy review by the Research Subcommittee of the state's Groundwater Coordinating Council.

Beginning in 2010, the annual 104(B) allocation was used to expand the scope of the joint solicitation to include research on the effects of climate change on Wisconsin's water resources. Priorities for climate change research were established through a partnership between the WRI and the Wisconsin Initiative on Climate Change Impacts (WICCI). Established in 2007, WICCI is a university-state partnership created to: (a) assess and anticipate the effects of climate change on specific Wisconsin natural resources, ecosystems and regions; (b) evaluate potential effects on industry, agriculture, tourism and other human activities; and (c) develop and recommend adaptation strategies that can be implemented by businesses, farmers, public health officials, municipalities, resource managers and other stakeholders.

We believe these partnerships with other state agencies provides WRI with the ability to fund highly relevant research and allows our limited funds for 104(B) to be leveraged to the fullest extent.

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:	3/1/2011
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Research Category:	Ground-water Flow and Transport
Focus Category:	Nitrate Contamination, Agriculture, Hydrogeochemistry
Descriptors:	
Principal Investigators:	Emily H. Stanley

Publications

1. Powers, S.M., R.A. Johnson, and E.H. Stanley. 2012. Nutrient retention and the problem of hydrologic disconnection in streams and wetlands. Ecosystems 15:435-449
2. Powers, Stephen Michael. 2012. River nutrient uptake and transport across extremes in channel form and drainage characteristics. Ph.D. Thesis, Limnology and Marine Science, University of Wisconsin, Madison. 135p.

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

A Report for University of Wisconsin System
Groundwater Research Project WR07R003

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15 June 2011

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PROJECT SUMMARY

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

Project I.D.: WR07R003

Investigator(s): PI- Emily Stanley, Professor, Center for Limnology, University of Wisconsin Madison

PA/RA- David Bylsma, Nelson Institute for Environmental Studies, University of Wisconsin Madison, and Stephen Powers, Center for Limnology, University of Wisconsin Madison

Period of Contract: July 1 2007-June 30 2010

Background/Need: Approximately 70% of the population in Wisconsin relies on groundwater as a drinking water source, and 10% of the State's private wells have nitrate (NO_3^-) concentrations that exceed the EPA's maximum contaminant level of 10 mg/L. Nitrite (NO_2^-) may be formed as a bi-product of NO_3^- enrichment, and prior research revealed its presence in surface waters of agriculturally dominated areas of the State. This observation leads to a compelling need to determine if NO_2^- is also present in Wisconsin ground waters and to identify the sources and pathways of NO_2^- generation in surface waters. By examining NO_2^- formation and distribution, we addressed multiple UWS groundwater research priorities, including: (1) transport of pollutants in groundwater; (2) impact of agricultural practices on groundwater quality; and (3) interactions of groundwater and surface water including chemical transformations in the hyporheic zone and influence of groundwater discharge on water quality.

Objectives: The goal of this project was to address the question: What conditions lead to the accumulation of nitrite (NO_2^-) in surface water environments in an agricultural watershed? This overarching question was addressed via three specific questions:

Q1. Is NO_2^- present in groundwater in N-rich areas of southern Wisconsin?
Q2. When and where is NO_2^- present along groundwater flow paths?
Q3. What processes and conditions are responsible for surface water NO_2^- accumulation?

Methods: Research activities were divided into three elements: (1) monthly surface and groundwater sampling to determine spatial and temporal patterns of NO_2^- occurrence at the East Branch Pecatonica River (Iowa Co, WI); (2) surveys of groundwater and springs in Mud Branch (Lafayette Co.) and Big Spring (Adams Co.) to determine if NO_2^- was present in groundwater in other agricultural streams in the State; and (3) laboratory and field experiments to identify possible pathways and conditions favoring NO_2^- production.

Results and Discussion: Assessment of nutrient chemistry in the East Branch Pecatonica River and its surrounding groundwater revealed a consistent pattern of highest NO_2^- concentrations occurring in surface waters but not groundwater. Streamwater concentrations varied over time, but were often highest during warm summer months. The groundwater nitrogen pool was, as expected, dominated by NO_3^-. NO_2^- was often at or below detection limits across all wells, suggesting that NO_2^- generation occurs either in the stream channel or as NO_3^--rich groundwater discharges to the surface environment. This same pattern of NO_3^- presence/NO_2^- absence in groundwater and presence of both forms of N in surface water was consistent with observations from other N-rich streams in southern Wisconsin.

More detailed sampling of stream bed sediments in the East Branch Pecatonica revealed erratic vertical concentration profiles, but notably, NO_2^- was often present in hyporheic sediments. Laboratory experiments confirmed the subsequent prediction that stream bed sediments were capable of generating NO_2^-. These experiments also revealed that the dominant pathway of NO_2^- generation was reduction of NO_3^- under low oxygen conditions rather than oxidation of NH_4^+. Rates of NO_2^- generation increased as a function of the initial NO_3^- concentration up to ca. 5 mg N/L before reaching a plateau rate of production. Rates also varied among sediment types; gravel size classes had a limited capacity to generate NO_2^- in these lab experiments, while silty, organic-rich sediments supported high production rates.

Conclusions/Implications/Recommendations: Collectively, these surveys and experiments suggest that NO_2^- presence in agricultural streams is the result of elevated NO_3^- concentrations, and that its generation is favored under warm, low-oxygen, N-rich conditions in silty stream bed sediments. Discharge of NO_3^- rich groundwater into silty hyporheic habitats appears to be a common configuration favoring NO_2^- accumulation in the surface water environment. This result has both positive and negative implications. On the positive side, presence of NO_2^- indicates active nitrogen cycling in these N-rich streams, and its presence is consistent with occurrence of denitrification (i.e., microbial removal of NO_3^- from the aquatic environment), and field experiments indicate that NO_2^- turnover is rapid. On the negative side, NO_2^- generation puts a solute into circulation that is known to have chronic effects on sensitive aquatic biota at relatively low concentrations. Highest concentrations during warm summer months may add to the stress of warmer temperatures on organisms such as cool water fish species. Further, NO_2^- generation appears to be favored within the thick layers of silty sediments that are often pervasive in many agricultural streams of southern Wisconsin. Removal of these sediments during stream restoration could have the potential to reduce occurrence of NO_2^-. A critical future research avenue will be to unequivocally determine if the reduction pathway that is associated with NO_2^- accumulation is in fact denitrification, as we suspect, or an alternative pathway (such as dissimilatory nitrate reduction to ammonium) as some researchers have hypothesized.

Key Words: Nitrate, nitrite, nitrate reduction, groundwater pollution, hyporheic zone, agricultural stream

Funding: University of Wisconsin System

INTRODUCTION

There is an abundance of information demonstrating that a widespread consequence of agricultural land use is enrichment of ground- and surface waters with nitrogen (N). Fertilizer N is applied to farm fields in a variety of forms, but generally accumulates as nitrate (NO_3^-) in aquatic environments. A survey of western and southern Wisconsin revealed that the occurrence of high NO_3^- concentrations in streams in agricultural watersheds is also accompanied by the presence of nitrite (NO_2^-) during summer baseflow conditions (Stanley and Maxted 2008). This form of N was present at low absolute concentrations and made up a small percent of the total N pool (~0.5-5%), but it nonetheless occurred at environmentally significant levels at many sites. For example, the European Union NO_2^- limit for waters supporting salmonids is 3 µg N/L (Kelso et al. 1997), a concentration that was exceeded at all sites with >40% agriculture in this survey. Thus, the presence of NO_2^- in many Wisconsin streams- particularly those capable of supporting cold- and coolwater fishes that are often sensitive to pollutants- is a worrisome observation. Further, if NO_2^- also accompanies NO_3^- in the groundwater environment, it could conceivably pose human health risks for drinking water wells tapping into N-enriched aquifers. The goal of this research project was to determine if NO_2^- is present in groundwater or if it is generated in streams following the discharge of NO_3^- rich groundwater by addressing the question: *What conditions lead to the accumulation of nitrite (NO_2^-) in surface water environments in an agricultural watershed?*

Nitrite can be considered a 'gateway molecule' in the N cycle, as many transformations involve NO_2^- production or consumption as an intermediate step. These transformations include the well-studied processes of nitrification and denitrification, as well as other pathways that are less well understood, but may nonetheless be extremely important in freshwater systems (e.g., dissimilatory nitrate reduction to ammonium, or DNRA; Burgin and Hamilton 2007). At the coarsest scale, presence of NO_2^- may result either from oxidation of ammonium (NH_4^+) or the reduction of nitrate (NO_3^-), and examples of NO_2^- generation via either pathway have been reported in aquatic environments (e.g., Kelso et al. 1997, Stief et al. 2002, Smith et al. 2006). Our goal was to determine which of these two pathways may be more common. To do so, we considered these two pathways to be alternative hypotheses explaining NO_2^- presence in N-rich streams (Fig.1).

Specific predictions can be generated about changes or conditions that would occur if NO_2^- is generated via NH_4^+ oxidation (Hypothesis 1) versus NO_3^- reduction (Hypothesis 2), including the likely location of each process and other forms of N that would be present or be generated or consumed along with NO_2^- production (Fig. 1). We tested these predictions through (1) monthly surface and groundwater sampling to determine spatial and temporal patterns of NO_2^- occurrence at the East Branch Pecatonica River (Iowa Co, WI) in 2007-2008; and (2) surveys of groundwater and springs in Mud Branch (Lafayette Co.) and Big Spring (Adams Co.) to determine the occurrence of NO_2^- in groundwater in other agricultural streams in Wisconsin; and (3) field and laboratory experiments to identify possible pathways and conditions favoring NO_2^- production.

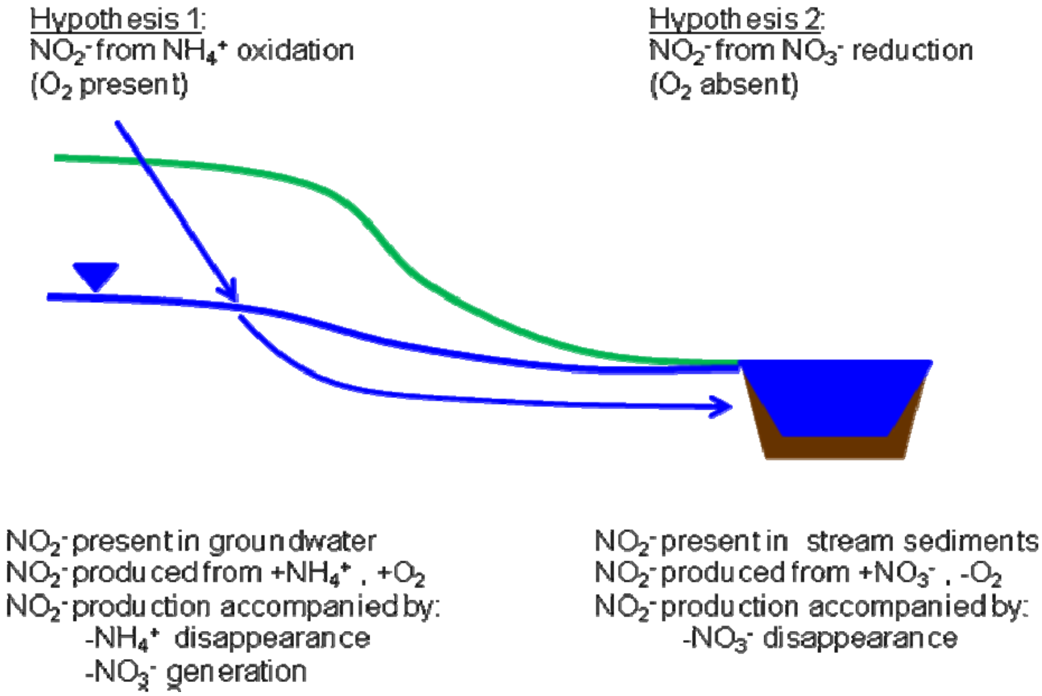

Fig. 1. Alternative pathways of NO_2^- production in the hillslope/stream environment. Arrows indicate direction of groundwater flow from the hillslope to the stream channel. Blue (dark) line denotes the position of the water table. If NO_2^- is generated by oxidation of NH_4^+, the process is expected to occur in oxygenated soil or groundwater environments. Controlled experiments would yield high NO_2^- when sediments are aerated and given ample amounts of NH_4^+; NO_3^- would be generated along with NO_2^- (i.e., the process of nitrification). If NO_2^- is generated by reduction of NO_3^-, then NO_2^- should be present in fine sediments and saturated soils which are typically anoxic, and sediments supplied with NO_3^- following O_2 removal should generate NO_2^- as the NO_3^- is reduced (disappears).

PROCEDURES AND METHODS

Study Sites- The East Branch of the Pecatonica River (EBP) is located in the Driftless region of southwest Wisconsin (Iowa County) and passes through a narrow valley constrained on both sides by steep hillsides. Typical of many streams in this part of the State, the EBP is extremely N-rich, with NO_3-N concentrations in excess of 5 mg/L throughout the year. Land use in the basin is dominated by agriculture, including extensive row cropping in the valley; however, there are also large tracts of land being managed for conservation purposes, and our primary study area was subject to restoration overseen by The Nature Conservancy in 2006. The goal of the restoration was to remove the accumulated layer of anthropogenic soil from the valley as well as the woody riparian vegetation that had become established on this soil layer (Booth et al. 2009). As a consequence of these management activities, extensive deposits of silty stream bed sediments were lost, exposing coarser sand and gravel substrates. However, several areas in the study reach retained silty sediments despite the restoration, resulting in a heterogeneous composition of stream bed sediments.

Multiple piezometers and instruments were installed by Eric Booth and Stephen Loheide for an affiliated GCC project (WR07R005), allowing us to monitor groundwater chemistry at several locations in the valley adjacent to the channel. Additional site and instrumentation information is available in Booth and Loheide (2010). We also opportunistically collected samples from tile drainages along a stream reach adjacent to a corn field.

To determine if patterns observed at EBP were representative of other N-rich agricultural streams, groundwater and surface water samples were also collected for N determination from Mud Branch (Lafayette Co.) and Big Spring (Adams Co.) for analysis of all inorganic N fractions (NH_4^+, NO_2^-, and NO_3^-). Wells at these sites were already present, and had historically been used (and in some cases continued to be used) for drinking water purposes for private land owners, and were situated within 10-50 m of the stream.

Objective 1: Spatial and temporal patterns of N at EBP- Ground- and stream water samples were collected monthly starting in 2007 from EBP, although groundwater sampling was not possible in January-March because of freezing. Four pairs of piezometers were sampled, and each pair consisted of a shallow piezometer that ended within a silty alluvial soil layer (typically 40-50 cm) and a deep piezometer (ca. 60-90 cm) that sampled water from the underlying Holocene gravel/sand stratum. All samples were collected in acid-washed bottles using a Geopump peristaltic pump equipped with an in-line filter (0.4 µm cellulose acetate membrane). Bottles were placed on ice and transported to the lab for analysis. Each sample was divided into 2 subsamples; the first sub-sample was frozen for later determination of NO_3-N and NH_4-N, and NO_2-N was determined within 24 h using the second subsample. NO_2-N was measured colorimetrically after addition of sulfanilamide and dihydrochloride (APHA 1998) using a Beckman DU-640 UV/VIS spectrophotometer (Beckman-Coulter, Fullerton, California, USA). NO_3-N and NH_4-N were determined on an Astoria Pacific Instrument nutrient autoanalyzer following protocols for the North Temperate Lakes Long-Term Ecological Research program (NTL-LTER; http://lter.limnology.wisc.edu).

Objective 2: Presence of NO_2^- in groundwater of other N-rich streams: Surface and groundwater samples were collected during repeated summertime surveys at Big Spring (BS) and Mud Branch (MB). Samples were collected, filtered, and analyzed for all inorganic N fractions using the same methods as at EBP.

Objective 3: Sediment experiments to determine NO_2^- production pathways- Three sets of experiments were performed to determine how and where NO_2^- was being generated (Experiment 1 and 3) and if the oxidative or reductive pathway was likely responsible for NO_2^- generation (Experiment 2).

Experiment 1- Because of the presence of both fine and densely-packed sediments, conventional hyporheic sampling using wells or piezometers was not possible in most sections of the EBP study reach. Instead, we collected 7 sediment cores as a means of assessing vertical distribution of inorganic N forms in the stream bed. Samples were intended to capture the range of bed sediment types, from fine organic silts to small gravel. A clear plastic tube (2.54 cm ID) was slowly pushed into the bed as far as possible, then sealed at both ends and transported to the laboratory for processing. Sediment cores varied from 10 to 20 cm, depending on sediment size and depth to refusal. In the lab, plastic sleeves were cut longitudinally to expose the sediments, which were then cut into 2-3 cm slices. Each subsample was placed in a 125 mL beaker and combined with 50 mL milli-Q H_2O, sealed, shaken vigorously for 30 sec, then allowed to settle for 15 minutes before being filtered through a Whatman GF/F filter for NO_2-N determination. Sediments were dried and weighed, and vertical profiles were described as g water-extractable N per g dry sediment.

Experiment 2- Five replicate sediment samples were collected randomly from the EBP study reach and refrigerated until sediment assays were performed, typically 24-48 h later. Each replicate was divided in half and each half was randomly assigned to one of the two major treatments. The first treatment was intended to promote NO_2^- formation via the oxidative pathway (test of Hypothesis 1). Approximately 30-40 g of wet sediment was placed into a container and amended with 100 mL water enriched with NH_4^+ and mixed. Five enrichment levels were made using a certified NH_4^+ standard solution to achieve final concentrations of 0, 0.5, 1, 2.5, or 5 mg NH_4-N/L. After removing an initial sample for later inorganic N analyses, slurries were aerated using an aquarium aerator and incubated at room temperature for 2 h before taking a final water sample. The second treatment was intended to promote NO_2^- formation via reduction (test of Hypothesis 2), and thus amendments included 0, 0.5, 2, 5, or 10 mg NO_3-N/L, followed by sparging with N_2 gas for 5 min to deoxygenate the sediment slurries. Samples were sealed during incubation to prevent oxygenation. Initial and final samples were filtered through an 0.7 µm GF/F filter and analyzed for the different inorganic N fractions as described above. Sediments were dried and weighed and rates were expressed as NO_2-N production per g sediment per h.

Experiment 3- We evaluated the effects of sediment texture by collecting 5 replicate sediment samples from areas dominated by gravel, silt, or deposits that were composed of a mixture of the two size classes ("mixed"). Approximately 40 g of wet sediments were placed into a jar and amended with 100 mL of unfiltered stream water. The control treatment used for this experiment was unfiltered stream water without any sediments. No effort was made to either oxygenate or deoxygenate samples, although jars were sealed during the incubation. Five subsamples were taken from each replicate at 0, 15, 30 60, and 120 minutes to document the time course of NO_2^- generation as well as assessing effects of sediment texture. Water samples were filtered and processed as described above.

RESULTS AND DISCUSSION

Objective 1: Spatial and temporal patterns of N at EBP and Objective 2: Presence of NO_2^- in groundwater of other N-rich streams- Routine monthly sampling of stream water and 4 pairs of wells revealed that surface and groundwater N was, as expected, dominated by NO_3^- in EBP. Streamwater NO_2^- concentrations varied over time, but were highest during warm summer months (Fig. 2). There was no relationship between stream water NO_2^- and NO_3^- concentrations, but NO_2^- and NH_4^+ were highly correlated (r = 0.75), in part due to 2 dates when NH_4^+ and NO_2^- concentrations spiked simultaneously.

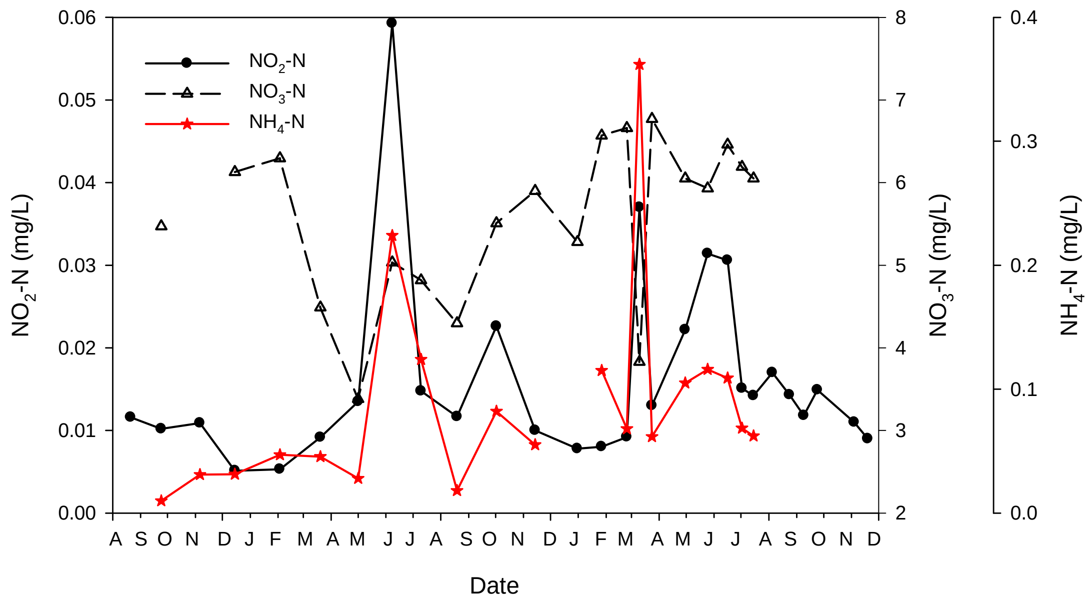

Fig. 2 Surface water concentrations of NO_2-N, NO_3-N and NH_4-N fractions in EBP. Notice that each inorganic N fraction has its own axis and scale.

Only minor temporal variation was observed in most piezometers and NO_3^- concentrations were typically an order of magnitude higher than both NH_4^+ and NO_2^-. NO_2^- concentrations were often near or below detection for most piezometer/date combinations, although one piezometer (W06-F) showed moderate NO_2^- levels (Fig. 2), reflecting occasional high relative concentrations (0.03-0.06 mg/L) interspersed among dates when levels were typically less than 0.010 mg/L. NO_2^- was also extremely low in opportunistically collected samples from a tile discharge draining an upstream cornfield at EBP. Consistent with this pattern, groundwater NO_2^- concentrations were lower than stream water at Mud Branch and below detection limits at Big Spring (Fig. 3). Results of these surveys provide strong evidence against a groundwater source and the nitrification pathway of NO_2^- generation (i.e., Hypothesis 1; see Fig.1).

Objective 3: Sediment experiments to determine conditions and pathways of NO_2^- production-Experiment 1- Because surveys of near-stream wells, seeps, and tile drains demonstrated that NO_2^- concentrations were consistently lower than in stream water and often below detection limits, we concluded that NO_2^- generation was likely occurring within the stream channel, and in particular, within stream bed sediments. This first experiment was intended to validate this conclusion by determining if NO_2^- was in fact present in the benthic/hyporheic environment by extracting inorganic N from sediments. Vertical profiles of NO_2^- were erratic, but demonstrated the presence of this intermediate ion in all samples (Fig. 4), indicating active NO_2^- production in EBP stream bed sediments.

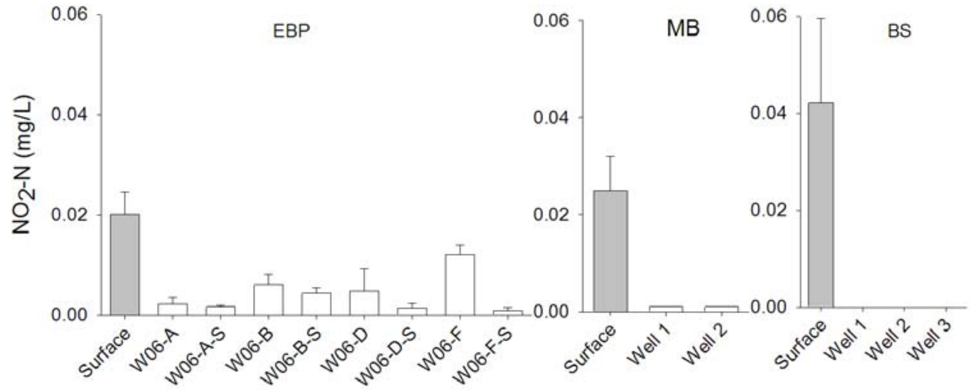

Fig. 3. Average NO_2-N concentrations (+1 SE) in stream water (grey bar) and ground water (open bars) in East Branch Pecatonica River (EBP), Mud Branch (MB) and Big Spring (BS) Wisconsin. EBP values represent means from monthly samples; values at MB and BS are from 3-5 summertime surveys of wells and stream water.

Experiment 2- Strong differences in NO_2^- generation were apparent between experimental treatments intended to promote its formation via either an oxidative or reductive pathway (Fig. 5). For the $+NH_4/+O_2$ treatment, NO_2^- concentrations at time 0 (i.e., NO_2^- initially present in the sediments) declined within 30 min then remained consistently low throughout the remainder of the incubation. We interpret this initial decline as NO_2^- oxidation to NO_3^-, and once any initial NO_2^- was converted, no further build-up was apparent. Nitrification is a 2-step process in which NH_4^+ is first converted to NO_2^- and then to NO_3^-. The second step (NO_2^- to NO_3^-) is thermodynamically more efficient, making NH_4^+ conversion to NO_2^- the rate-limiting step in this process. Thus, if nitrification was occurring in these sediments, then it would appear that NO_2^- build-up was prevented by its rapid conversion to NO_3^-. We observed a decline in added NH_4^+ over the course of the experiment, consistent with nitrification; however, we failed to detect a measurable increase in NO_3^- (results not shown), leaving some degree of uncertainty regarding the processing of the added NH_4^+. NH_4^+ may have been sorbed onto sediment surfaces (Triska et al. 1994) and not subjected to additional transformation. Alternatively, we cannot dismiss the possibility that aeration of the water overlying the sediments was not sufficient to oxygenate the entire sediment layer that settled on the bottom of assay containers. If some sediment anoxia existed during the incubation, then any NO_3^- produced could have been subject to denitrification, consistent with the observation of low NO_3^- concentrations at the end of the 2 h period.

Addition of NO_3^- and removal of O_2 from sediment slurries had a strong positive effect on NO_2^- generation (Fig. 5). Rates of NO_2^- production increased as a function of added NO_3^- concentration up to 5 mg NO_3-N/L before reaching an asymptote. At the same time, added NO_3^- was depleted from all addition levels, resulting in uniformly low final concentrations. We also observed consistent positive, but small, increases in NH_4^+ concentrations (0.1-0.2 mg NH_4-N/L). These results suggest that most added NO_3^- was subject to denitrification, with a minor fraction

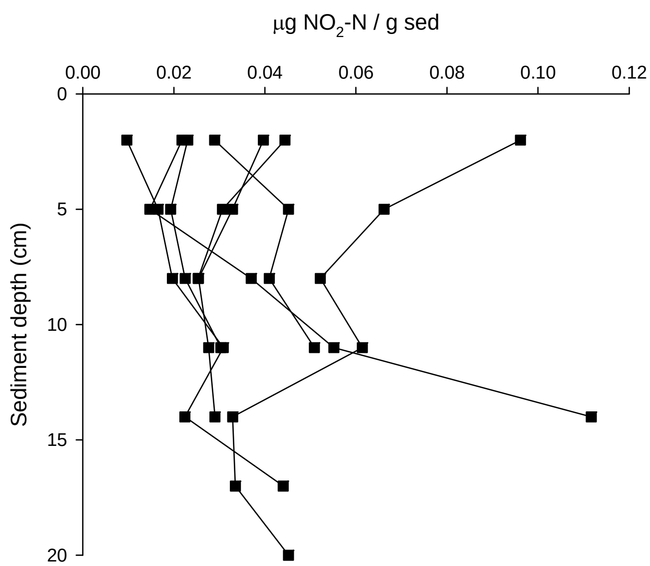

Fig. 4. Vertical profiles of NO_2-N extracted from 7 sediment cores collected from the bed of East Branch Pecatonica River.

(at most) of the added N getting converted to NH_4^+ via DNRA or related process. Thus, this experiment suggests that NO_2^- is predominantly generated as a bi-product or a measurable transition step associated with sedimentary denitrification in the EBP.

That NO_3^- reduction was apparently the overwhelming source of NO_2^- was an unexpected result given that nitrification has been identified as the dominant source in some other study systems (e.g., Smith et al. 1997, Chen et al. 2010). And even if it was not the main pathway, some contribution from nitrification was expected based on results from a detailed process-based study using paired ^{15}N and ^{18}O tracers and combinations of isotopic enrichments in an agricultural stream in Indiana (Böhlke et al. 2007). These investigators estimated that while most NO_2^- production was attributable to NO_3^- reduction, as much as 30% apparently resulted from nitrification.

Experiment 3- Production rates of NO_2^- were high and increased steadily over time in fine silty EBP sediments (Fig. 6). In contrast, we observed virtually no NO_2^- accumulation in gravel or mixed sediment classes, indicating that silty sediment deposits are hot spots of NO_2^- production in EBP. Differences among sediment categories began to emerge within 30 min, and were distinct within 60 min, suggesting rapid N processing within silt.

As expected from the results of Experiment 2, NO_3^- in the water overlying silt and mixed sediments declined over the 2 h incubation, although NO_3^- changes in gravel treatments were not significantly different from controls. However, in contrast to Experiment 2, we saw significant rates of NH_4^+ accumulation in the silt treatment (Fig. 6). This NH_4^+ could have been released from the sediments as a result of agitation during the experiment, or, alternatively, could be indicative of an different pathway of NO_3^- reduction, namely dissimilatory nitrate reduction to ammonium (DNRA). Burgin and Hamilton (2007) have argued that reduction of NO_3^- to NH_4^+ is in fact widespread in wetland sediments, and may have led to an overestimation of the capacity of these and similar ecosystems to remove excess N via denitrification. It is difficult to determine which process dominates in the EBP; absence of NH_4^+ production coupled with disappearance of added NO_3^- in Experiment 2 provides strong evidence for denitrification, while NH_4^+ production/NO_3^- disappearance in Experiment 3 points to DNRA. Similarly, simultaneous peaks in NH_4^+ and NO_{2-} in surface water (Fig. 1) suggest some coupling in the production of these two N fractions. Which process dominates under what circumstances remains to be

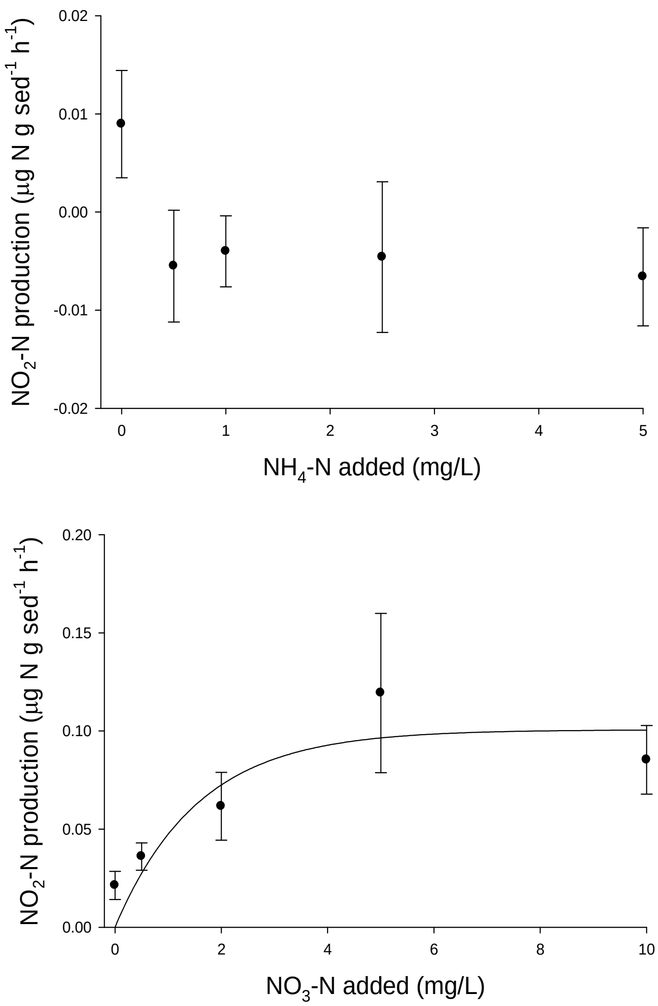

Fig. 5. Average (± 1 SE) NO_2-N production per g dry sediment as a function of treatment type and N concentration. Top panel corresponds to Hypothesis 1: NO_2-N generation via oxidation of NH_4-N under oxygenated conditions. Negative production denotes a net decrease in NO_2-N concentration relative to initial streamwater level. The bottom panel corresponds to Hypothesis 2: NO_2-N generation following addition of NO_3-N and elimination of dissolved oxygen. Line represents best fit curve ($p<0.05$).

determined definitively, and has strong implications for removal of groundwater-supplied NO_3^- discharged into EBP and other similar N-rich Wisconsin streams

CONCLUSIONS AND RECOMMENDATIONS

Referring back to the original alternative hypotheses (Fig. 1; H1: NO_2^- is generated via oxidation of NH_4^+ in soil and groundwater environments; H2: NO_2^- results from reduction of NO_3^- in near stream and stream bed environments), we found strong support for NO_2^- production resulting from reduction of NO_3^- in stream bed sediments, and conversely, no support for the alternative hypothesis. Thus, a key finding of this study is that, despite elevated NO_3^- concentrations, the groundwater environment does not appear to be the site of NO_2^- generation, which means that this ion is unlikely to pose an additional threat or stressor to drinking water derived from groundwater sources in most agricultural areas.

NO_2^- presence in agricultural streams is associated with elevated NO_3^- concentrations (Stanley and Maxted 2008), and its generation is favored under warm, low-oxygen, N-rich conditions in silty stream bed habitats. Discharge of NO_3^- rich groundwater into silty hyporheic sediments may be a common configuration favoring NO_2^- accumulation in surface water environments. Our interest in NO_2^- reflects the potential of this solute to pose human health threats if present in drinking water (and as noted above, we do not find evidence for this threat), as well as to sensitive aquatic biota such as amphibians and salmonids. NO_2^- generation that results from inputs of NO_3^- rich water to streams that also contain abundant stocks of sediments prone to anoxia introduces a solute that is known to have chronic effects on sensitive aquatic biota at low concentrations. Highest concentrations during warm summer months may add to the stress of warmer temperatures on organisms such as some cool water fish species. Restoration activities at EBP were intended, in part, to eliminate the thick layer of anoxic sediments that are pervasive in Driftless Area streams (and in fact, in many agricultural areas; Wood and Armitage 1997), and thus, may help to reduce NO_2^- production. However, while NO_2^- build-up is not ideal, our experimental results demonstrated that its presence indicates active nitrogen cycling in stream sediments. If denitrification is the primary process responsible for NO_2^- generation, then removal of a stream's silt layer may reduce ecosystem capacity to remove at least some of the NO_3^- that is, unfortunately, prevalent in these agricultural systems. Denitrification is a process that many natural resource managers are now targeting in management and restoration activities (Craig et al. 2008), so if the silt layer is an active site of denitrification, and if restoration activities favor its removal, then additional actions (e.g., establishment of effective lateral riparian wetlands) should to maintain some denitrification capacity. However, while results of one of our experiments pointed strongly to denitrification as the process responsible for both NO_2^- generation and NO_3^-loss, a later experiment was more ambiguous and suggested that excess NO_3^- may simply be converted to a different form of N (NH_4^+ via DNRA) rather than being removed from the aquatic environment, as is the case with denitrification. Thus, the logical next scientific step is to determine if denitrification or DNRA prevails, if these processes vary in space and time, and if so, what drives the shift from the N-removing to the N-transforming process in streams receiving steady high doses of groundwater NO_3^-, such as the East Branch Pecatonica.

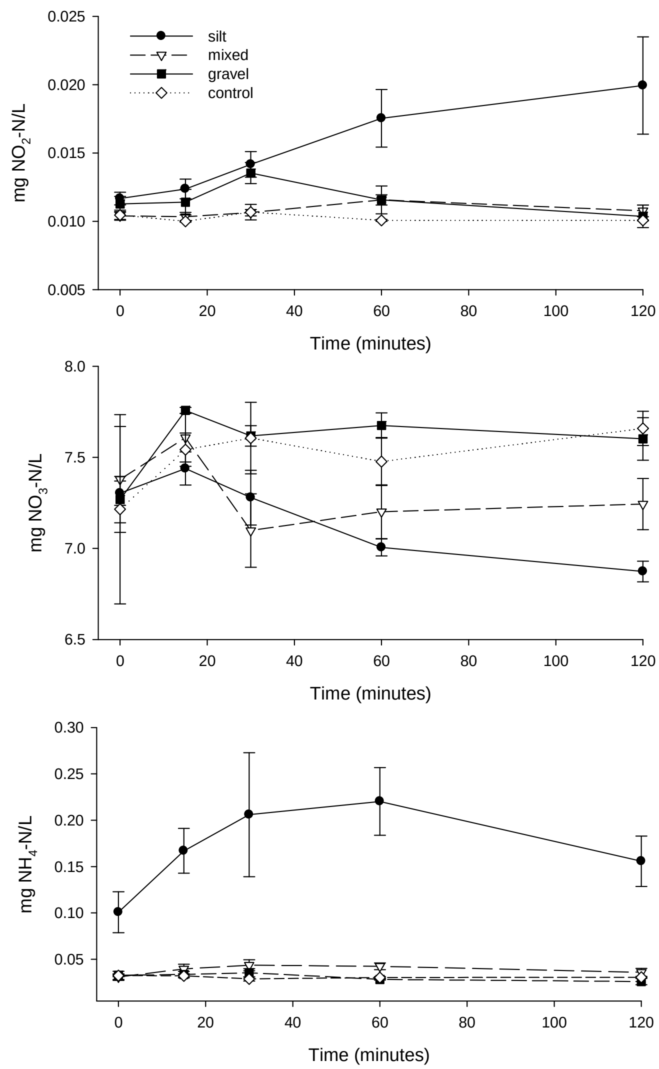

Fig. 6. Average (± 1 SE) change in NO_2-N, NO_3-N, and NH_4-N (bottom) concentrations in water mixed with silt, gravel, or mixed composition stream bed sediments. Control represents unfiltered stream water only.

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APPENDIX A

Presentations and Seminars

Stanley, E.H. 2008. Potential sources of nitrite in southern Wisconsin agricultural streams. American Society of Limnology and Oceanography annual meeting, St. John's, Newfoundland.

Stanley, E.H. 2008. On the receiving end: nitrogen in Wisconsin streams. Invited seminar, Program in Ecology, Duke University, Durham, N.C.

Powers, S.M. and E.H. Stanley. 2009. Terrestrial and aquatic controls of inter-annual variability in phosphorus yields. North American Benthological Society annual meeting, Grand Rapids, MI.

Stanley, E.H. 2009. On the receiving end: nitrogen in Wisconsin streams. Department of Zoology, University of Wisconsin, Madison, WI.

Powers S.M. and E.H. Stanley. 2010. Stream and wetland nitrate uptake across extremes in channel form. Joint meeting of American Society of Limnology and Oceanography and North American Benthological Society. Santa Fe, NM.

Stanley E.H. 2010. Nitrogen dynamics in Wisconsin streams. St. Olaf College, Northfield, MN.

Stanley, E.H. 2010. Occurrence and generation of nitrite in ground and surface waters in an agricultural watershed. Wisconsin Groundwater Coordinating Council, Madison, WI.

Publications

Powers, S.M., R.A. Johnson, and E.H. Stanley. Nutrient retention and the problem of hydrologic disconnection in streams and wetlands. In review.

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

Publications

1. Kolker, A., Olson, M., Krabbenhoft, D.P., Tate, M.T., and Engle. M.A., 2010, Patterns of mercury dispersion from local and regional emission sources, rural Central Wisconsin, USA, Atmos. Chem. Phys., 10, 1–10, 2010.
2. Engle, M.A., Tate, M.T., Krabbenhoft, D.P., Schauer, J.J., Kolker, A., Shanley, J.B., Bothner, M.H. 2010, Comparison of Atmospheric 1 Mercury Speciation and Deposition at Nine Sites across Central and Eastern North America, Geophysical Research (in press).
3. Engle, MA, MT Tate, DP Krabbenhoft, A Kolker, ML Olson, ES Edgerton, JF DeWild, and AK McPherson. 2008. Characterization and cycling of atmostpheric mercury along the centeral US Gulf of Mexico coast. Applied Geochemistry 23, 419-437
4. Geboy N, DP Krabbenhoft, MA Engle, and T Sabin. 2011. The Solubility of Mercury-Containing Aerosols in Fresh and Sea Water. In the Proceedings of the 10th International Conference on Mercury as a Global Pollutant, Halifax, Nova Scotia. 1 page.
5. Engle, M.A., Tate, M.T., Krabbenhoft, D.P., Schauer, J.J., Kolker, A., Shanley, J.B., Bothner, M.H. 2010, Comparison of Atmospheric Mercury Speciation and Deposition at Nine Sites across Central and Eastern North America, J. Geophys. Res., 115, D18306, doi:10.1029/2010JD014064

Annual Progress Report

Selected Reporting Period: 3/1/2010 - 2/28/2011

Submitted By: David Krabbenhoft
Submitted: 5/27/2011

Project Title

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

Project Investigators

James Hurley, University of Wisconsin

Progress Statement

This project looks at two mercury related questions: (1) mercury in watersheds; and, (2) mercury cycling and transport in the atmosphere. During reporting period the project completed its second year of "recovery" (i.e., no longer loading mercury to the study watershed) on the Mercury Experiment to Assesses Atmospheric Loadings in Canada and the US (METAALICUS) project. Our portion of the project is to monitor the watershed-scale response of the artificial load of mercury that was administered from 2001 through 2007 using three different stable isotopes (198Hg, 201Hg, 202Hg) to the study wetland, uplands and lake, respectively. During this phase of the project, we will quantify the response of the watershed to a mercury "load reduction" through continuous monitoring of the isotope concentrations and water flux from the terrestrial flows into the study lake. On the atmospheric studies, the project performed one assessment study of mercury deposition spanning time and space domain near a emission stack in central Wisconsin; and significantly enhanced our field monitoring system by securing the extra instrumentation needed to make "gradient" measurements (Eddy Correlation method) of mercury concentrations in the atmosphere above our study sites.

Principal Findings and Significance

Principal Findings and Significance

Description	Our results show that in coastal settings, the intersection of terrestrially based mercury emission sources interacting with chemical oxidants formed in the marine boundary layer result in exacerbated mercury deposition in the near coastal environments. These finds have direct implications for water-resource rich ecosystems along the East Coast of the US, and people who fish in those waters. Also, the application of the mercury depositon model developed by this project to these field settings provides a scientifically based explanation for why coastal areas in the southeastern US are among the highest mercury deposition zones.
Description	Results from the past year of data collection revealed that despite the cessation of loading the watershed on the METAALICUS project, concentrations in runoff continued to increase. This phenomenon reveals the inherent time lags that are part of the natural response to changes in loading watersheds. On the atmospheric studies portion of the project the assessment revealed the importance of the marine boundary layer for facilitating atmospheric mercury reactions and deposition.
Description	The expanded ability to measure mercury concentration in the atmosphere using the Eddy Correlation method will significantly improve our ability to understand the bi-directional nature of mercury fluxes between the atmosphere and the land/water surface.

Journal Articles & Other Publications

Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
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	

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Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Patterns of mercury dispersion from local and regional emission sources, rural Central Wisconsin, USA
Author(s)	Kolker, A., Olson, M., Krabbenhoft, D.P., Tate, M.T., and Engle. M.A.,
Publication/Publisher	Atmos. Chem. Phys.,
Year Published	2010
Volume & Number	10, 1–10
Number of Pages	10
Description	Abstract. Simultaneous real-time changes in mercury (Hg) speciation- reactive gaseous Hg (RGM), elemental Hg (Hg°), and fine particulate Hg (Hg-PM2.5), were determined from June to November, 2007, in ambient air at three locations in rural Central Wisconsin. Known Hg emission sources within the airshed of the monitoring sites include: 1) a 1114 megawatt (MW) coal-fired electric utility generating station; 2) a Hg-bed chlor-alkali plant; and 3) a smaller (465 MW) coal-burning electric utility. Monitoring sites, showing sporadic elevation of Hg°, Hg-PM2.5, and RGM were positioned at distances of 25, 50 and 100 km northward of the larger electric utility. Median concentrations of Hg°, Hg-PM2.5, and RGM were 1.3–1.4 ng m−3, 2.6–5.0 pg m−3, and 0.6–0.8 pg m−3, respectively. A series of RGM events were recorded at each site. The largest, on 23 September, occurred under prevailing southerly winds, with a maximum RGM value (56.8 pg m-3) measured at the 100 km site, and corresponding elevated SO2 (10.4 ppbv; measured at 50 km site). The finding that RGM, Hg°, and Hg-PM2.5 are not always highest at the 25 km site, closest to the large generating station, contradicts the idea that RGM decreases with distance from a large point source. This may be explained if: 1) the 100 km site was influenced by emissions from the chlor-alkali facility or by RGM from regional urban sources; 2) the emission stack height of the larger power plant promoted plume transport at an elevation where the Hg is carried over the closest site; or 3) RGM was being generated in the plume through oxidation of Hg°. Operational changes at each emitter since 2007 should reduce their Hg output, potentially allowing quantification of the environmental benefit in future studies.
Any Additional Citation Information	

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

Publication Type	Proceedings/Symposium (Not Peer-Reviewed)
Title	The Solubility of Mercury-Containing Aerosols in Fresh and Sea Water
Author(s)	Geboy, N., Krabbenhoft, D., Engle, M., and Sabin, T.
Publication/Publisher	Proceeding of the 10th International Conference on Mercury as a Global Pollutant
Year Published	2010
Volume & Number	1
Number of Pages	1
Description	Abstract presented at this international meeting
Any Additional Citation Information	

Students & Post-Docs Supported

Student Name	Nicholas Ostrowski
Campus	University of Wisconsin-Madison

Advisor Name	Kenneth Bradbury
Advisor Campus	University of Wisconsin-Madison

Degree	Masters
Graduation Month	August
Graduation Year	2012
Department	IES
Program	Letters and Science
Thesis Title	
Thesis Abstract	

Use of the 2009 Behavioral Risk Factor Surveillance Survey to Assess the Safety of Private Drinking Water Supplies

Basic Information

Title:	Use of the 2009 Behavioral Risk Factor Surveillance Survey to Assess the Safety of Private Drinking Water Supplies
Project Number:	2008WI306O
Start Date:	7/1/2008
End Date:	3/1/2011
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Social Sciences
Focus Category:	Groundwater, Water Quality, Education
Descriptors:	
Principal Investigators:	Lynda Knobeloch, Marty S. Kanarek

Publications

There are no publications.

Use of the Behavioral Risk Factor Surveillance Survey to

Assess the Safety of Private Drinking Water Supplies

FINAL REPORT
WR08R001

Prepared by Lynda Knobeloch, PhD, Senior Toxicologist
Wisconsin Department of Health Services
1 W Wilson Street, Room 150
Madison, WI
August 2010

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PROJECT SUMMARY

Title: Use of the 2008-2009 Behavioral Risk Factor Surveillance Survey to Assess the Safety of Private Drinking Water Supplies

Project ID: WR08R001

Investigators: Lynda Knobeloch, Senior Toxicologist, Wisconsin Dept of Health Services
Marty Kanarek, Professor, Department of Population Health Sciences, UW-Madison

Period of Contract: July 2008 through June 2009

Background and Need

Over 850,000 households in Wisconsin use a privately-owned well as a drinking water source. Unlike households supplied by municipal water, private wells are not regulated and therefore do not require regular testing. Testing of private water supplies may be limited by several factors such as household income and knowledge of testing procedures and water quality parameters. Despite the private well tracking efforts by the DNR's Groundwater Retrieval Network (GRN), the Center for Watershed Science and Education, and DATCPs' groundwater database, there are many data gaps. We know little about the households that are testing their well water and even less about those that are not. We are particularly interested in learning more about wells used by infants, children, pregnant women and the elderly and hope to learn more about how they use their water and test it for safety, as well as about their perceptions of the quality of their well water.

Objectives

The intent of this research is to improve our understanding of the number and location of families that need assistance or information regarding drinking water safety and make it easier for public health care providers and water supply consultants to provide targeted outreach to this population. We hope findings will be useful to state and local agencies for the purpose of addressing data gaps and assessing the need for educational, professional and financial resources to increase testing of private wells and minimize ongoing exposure to common groundwater contaminants.

Methods

A module of questions about well-water testing was added to the 2008 and 2009 Behavioral Risk Factor and Surveillance System (BRFSS) surveys and administered to households that obtained their water from a privately-owned well. These questions were designed to provide us with a better understanding of water quality testing done on private well water supplies which are used by approximately one-third of Wisconsin families. Our analysis included demographic information collected as part of the BRFSS survey.

Results and Discussion

Findings from this survey indicate that about one Wisconsin family in nine (11%) obtain their drinking water from a well they have never tested for bacteriological or nitrate contamination. This population includes an estimated 140,600 children. We can also estimate that one family in six, including approximately 213,000 children, obtains their drinking water from a well they have never tested for contamination with solvents, gasoline, fuel oil, toxic metals, or pesticides.

The principle reason well owners provided when asked why they didn't test their water was that the water seemed to be safe based on its taste, odor and appearance. Nearly half of the homeowners who had never tested their water stated that they didn't know what to test for or weren't sure where to send their water for testing. In addition, some of the responses to our survey suggest that well owners may be confused about the parameters included in their well test. For example, more than a quarter of the well owners in our survey reported testing for volatile organic chemicals and nearly a third of the families reported tests for pesticides. While these rates may be accurate, they are higher than anticipated based on existing databases maintained by the State Laboratory of Hygiene and Department of Natural Resources. Further evidence of confusion is provided in responses concerning the safety of test results. Of 4% of those who reported testing their water said the test result was unsafe. About half of the unsafe results were due to bacteria and half were due to a high nitrate level. Thus, while a 2007 random survey of private wells conducted by the Wisconsin Department of Agriculture, Trade and Consumer Protection estimated that 9% of wells statewide exceeded the nitrate enforcement standards, only 2% of the nitrate test results reported by BRFSS participants were recalled by well owners in our survey as unsafe. Similarly, while a statewide study conducted in 1995 found that more than 20% of private wells contained coliform bacteria, less than 2% of the participants in our survey who tested for bacteria reported the result as "unsafe." Reasons for these apparent discrepancies are unclear but suggest that some well owners may not understand their laboratory report.

Conclusions and Recommendations

Several actions are suggested which would help well owners ensure the safety of their water supply:

1. State agencies, the State Laboratory of Hygiene, and the University of Wisconsin-Extension should work together to develop a uniform, web-based outreach program aimed at educating well owners about water quality testing and water treatment. Ideally this website could include active links to licensed laboratories. Since many Wisconsin families depend on in-home water filtration devices, it may also be helpful to include a listing of water treatment devices that have been approved by the Department of Commerce.

2. Public and private water testing laboratories should consider the use of advertising campaigns, promotional sales, discounted test packages that include testing for a broad range of chemicals that have been detected in regional groundwater, coupons, and seasonal campaigns to encourage and facilitate water quality testing in the counties they serve.

3. Existing wells should be inspected and the water should be tested for a panel of priority contaminants prior to property sales.

4. Newly constructed wells should be tested for priority contaminants before they are put into service.

5. All local health departments that serve rural populations should be encouraged to take advantage of fee-exempt testing offered by the Wisconsin Dept of Health Services.

Related Publications

None to date

Key Words: Private well, Testing, Nitrate, Bacteria, Arsenic, Drinking water, Safety

Funding: Water Resources Institute, University of Wisconsin-Madison

Use of the 2008-2009 Behavioral Risk Factor Surveillance Survey to Assess the Safety of Private Drinking Water Supplies

Introduction

Over 850,000 households in Wisconsin use a privately-owned well as a drinking water source. Unlike households supplied by municipal water, private wells are not regulated and therefore do not require regular testing. Testing of private water supplies may be limited by several factors such as household income and knowledge of testing procedures and water quality parameters. Despite the private well tracking efforts by the DNR's Groundwater Retrieval Network (GRN), the Center for Watershed Science and Education, and DATCPs' groundwater database, there are many data gaps. We know little about the households that are testing their well water and even less about those that are not. We are particularly interested in learning more about wells used by infants, children, pregnant women and the elderly and hope to learn more about how they use their water and test it for safety, as well as about their perceptions of the quality of their well water.

This research is intended to improve our understanding of the number and location of families that need assistance or information regarding drinking water safety and make it easier for public health care providers and water supply consultants to provide targeted outreach to this population. We hope findings will be useful to state and local agencies for the purpose of addressing data gaps and assessing the need for educational, professional and financial resources to increase testing of private wells and minimize ongoing exposure to common groundwater contaminants.

Methods

The Behavioral Risk Factor Surveillance System (BRFSS) is a collaborative project of the Centers for Disease Control and Prevention (CDC) and U.S. states and territories. The BRFSS, administered and supported by CDC's Behavioral Surveillance Branch, is an ongoing data collection program designed to measure behavioral risk factors for the adult population (18 years of age or older) living in households. The BRFSS objective is to collect uniform, state-specific data on preventive health practices and risk behaviors that are linked to chronic diseases, injuries, and preventable infectious diseases that affect the adult population. Factors assessed by the BRFSS include tobacco use, health care coverage, HIV/AIDS knowledge and prevention, physical activity, and fruit and vegetable consumption. Data are collected from a random sample of adults (one per household) through a telephone survey.

The Wisconsin BRFSS is managed by the Wisconsin Department of Health Services (DHS) following guidelines provided by the CDC. DHS participates in developing the survey instrument. The survey is then administered by the University of Wisconsin Survey Center under a contract with DHS. The data are transmitted to the CDC's National Center for Chronic Disease Prevention and Health Promotion's Behavioral Surveillance Branch for editing, processing, weighting, and analysis. An edited and weighted data file is provided to DHS for analysis in March or April of the following year. DHS and other agencies use BRFSS data for a variety of purposes, including identifying demographic variations in health-related behaviors, targeting services, addressing emergent and critical health issues, proposing legislation for health initiatives, and measuring progress toward state and national health objectives. Weighted data from this survey are expected to be representative of the state's population.

The questionnaire has three parts: 1) the core component; 2) optional modules; and 3) state-added questions. The *core* is a standard set of questions asked by all states. Optional CDC modules are sets of questions on specific topics (e.g., cardiovascular disease, arthritis, women's health) that states elect to use on their questionnaires. In 2009, 29 optional modules were supported by CDC. Each year, the states and

CDC agree on the content of the core component and optional modules. In addition, states are allowed to add questions which are not edited or evaluated by CDC.

In 2008 and 2009, Wisconsin used computer-assisted telephone interviewing (CATI). Following guidelines provided by CDC, the University of Wisconsin Survey Center conducts interviews. The core portion of the questionnaire lasts an average of 15 minutes. Interview time for modules and state-added questions is dependent upon the number of questions used, but generally extend the interview period by an additional 5 to 10 minutes.

All data in the BRFSS are weighted to correct for selection biases caused by regional and demographic variations in survey coverage and participation. An additional reason for weighting is to make the total number of cases equal to Wisconsin's adult population. All analyses shown in this report are based on weighted survey data unless otherwise specified.

A module of questions about well-water testing was added to the 2008 and 2009 Behavioral Risk Factor and Surveillance System (BRFSS) surveys and administered to households that obtained their water from a privately-owned well. These questions were designed to provide us with a better understanding of water quality testing done on private well water supplies which are used by approximately one-third of Wisconsin families. Our analysis included demographic information collected as part of the BRFSS survey.

Results and Discussion

Of 11,628 participants in the 2008 and 2009 Behavioral Risk Factor Surveillance Survey, 7,329 people who participated between July 1, 2008 and December 31, 2009 were asked whether their household water was supplied by a privately-owned well. Based on weighted analysis of their responses, 36% of Wisconsin households use a private well as their primary drinking water source. Households with private wells were significantly less likely to have an annual income below $20,000 than households served by public water supplies (6% vs 10%). According to weighted responses from members of these households, 41% drink unfiltered tap water, 44% drink tap water that is filtered either at the point of entry or point of use, 7% drink bottled water and 5% drink water from another source.

Of families that use a private well, two-thirds had submitted a well water sample to a laboratory for analysis since moving into their homes. Among people who had never tested their water supplies, 82% indicated that they hadn't done so, at least in part, because their water tasted and looked fine; 48% didn't test because they had a filtration system; 45% were not sure which tests to order and 42% didn't know where to send their water to be tested. While only 13% listed cost as a factor, testing rates were strongly associated with household income with only 33% of very low income (<$20,000/year) households reporting a previous test compared to a 71% test rate among households with annual incomes of $75,000 or more. Education was a less important predictor with well tests reported by 58% of participants with less than a high school education versus 67% of others. The prevalence of well testing also varied by county and region of residence (see Table 1) suggesting an effect of outreach programs and well testing offered by many local health departments. The presence of children in the home had no effect on test rates and the number of pregnancies was too small to assess an effect on water testing.

Of those who tested their water, 63% had done so within the last 5 years. The primary reason for testing is unclear since most BRFSS participants listed the reason as 'other.' While our survey didn't ask about real estate transactions, many of the well tests may be been done at the point of sale since banks, realtors and buyers often require assurance that the well serving the home is safe. Thirty percent of those who tested their wells said they wanted to know more about the quality of their water, 11% tested their water after hearing a news story or were advised to test, and 8% tested their water because of a pregnancy or newborn in the home.

Bacteria and nitrate tests were reported by 52% and 46%, respectively, of respondents who used water from a privately owned well. Tests for pesticides, volatile organic compounds, arsenic and fluoride were less common, being reported by 31%, 26%, 27% and 23% of well owners, respectively. Nearly all (96%) of the well owners who had tested their water thought their test results were within safe limits and 81% of those who obtained their drinking water from a privately-owned well reported the quality of their water as 'excellent' or 'good.'

Approximately one-third of Wisconsin's families depend on a privately-owned well as the sole source of the water they drink and use to prepare foods, bathe, do laundry and conduct household chores. While each of these families is responsible for ensuring the safety of their drinking water, very few of them are likely to be aware of the wide range of contaminants that have been detected in Wisconsin's groundwater. While most well owners understand the importance of testing their water for coliform bacteria and nitrate contamination, awareness of the need to test drinking water for naturally-occurring minerals like manganese, arsenic and radium; industrial solvents; petroleum compounds and agricultural pesticides is not as prevalent. While public water supplies are routinely monitored for many of these parameters, the 2008-9 BRFSS survey confirms that most private well owners in Wisconsin have never tested their water for these substances.

Findings from this survey indicate that about one Wisconsin family in nine (11%) obtain their drinking water from a well they have never tested for bacteriological or nitrate contamination. This population includes an estimated 140,600 children. We can also estimate that one family in six, including approximately 213,000 children, obtains their drinking water from a well they have never tested for contamination with solvents, gasoline, fuel oil, toxic metals, or pesticides.

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Recommendations and Conclusions

Based on findings from this survey, several actions are suggested which would help well owners ensure the safety of their water supply:

1. State agencies, the State Laboratory of Hygiene, and the University of Wisconsin-Extension should work together to develop a uniform, web-based outreach program aimed at educating well owners about water quality testing and water treatment. Ideally this website could include active links to licensed laboratories. Since many Wisconsin families depend on in-home water filtration devices, it may also be helpful to include a listing of water treatment devices that have been approved by the Department of Commerce.

2. Public and private water testing laboratories should consider the use of advertising campaigns, promotional sales, discounted test packages that include testing for a broad range of chemicals that have been detected in regional groundwater, coupons, and seasonal campaigns to encourage and facilitate water quality testing in the counties they serve.

3. Existing wells should be inspected and the water should be tested for a panel of priority contaminants prior to property sales.

4. Newly constructed wells should be tested for priority contaminants before they are put into service.

5. All local health departments that serve rural populations should be encouraged to take advantage of fee-exempt testing offered by the Wisconsin Dept of Health Services.

2008-9 Behavioral Risk Factor Surveillance System
Well Water Questionnaire with Weighted Response Frequencies

The questions included in the BRFSS module and the weighted frequency of responses are shown below:

1. What is the source of the water that comes into your home?

a.	A private well serving just your household	36%
b.	A community well or shared well	<1%
c.	A municipal water supply	64%
d.	Don't know	<1%
e.	Refused	<1%

If A, go to question 2. If B, C, D or E, STOP HERE.

The remaining questions were only asked if the household was served by a privately owned well.

2. Which of the following best describes your primary household drinking water?

a.	Unfiltered tap water	40%
b.	Filtered tap water	31%
c.	Bottled water	7%
d.	Filtered water from the refrigerator	13%
e.	Unfiltered water from the refrigerator	1%
f.	Water from another source	5%
g.	Don't know	<1%
h.	Refused	<1%

3. Have you ever sent a sample of your water to a laboratory for analysis?

a.	YES	66%
b.	NO	32%
c.	Not sure	2%

If NO, go to question 4. If YES, go to question 5.

4. If no, why have you NOT tested your water? (list ALL that apply)

a.	Too expensive	13%
b.	Not sure what to test for	45%
c.	Not sure where to send samples	42%
d.	Tastes and looks fine	82%
e.	Have a water filter	48%
f.	Other	27%

5. If yes, how long ago was it tested?

a.	Within the last year	24%
b.	One to 5 years	39%
c.	Over 5 years ago	35%
d.	Don't know	1%

6. What was the primary reason you tested your water?

a.	Tasted or smelled bad	3%

b.	Discolored or cloudy	1%
c.	Someone recommended testing or heard a news story	11%
d.	Small child in the house or pregnancy	8%
e.	Illness in family	<1%
f.	Wanted to know more about the quality of the water	30%
g.	Other reason	44%
h.	Don't know	<1%

7. What was your water tested for?

a.	Bacteria	77%
b.	Nitrate	69%
c.	Fluoride	34%
d.	Volatile chemicals like gasoline and solvents	39%
e.	Pesticides	46%
f.	Arsenic	40%

8. Did the test results indicate your water was safe to drink?

a.	YES	96%
b.	NO	4%
c.	Not sure	<1%

If answered NO, proceed to question 9. If answered yes, skip to question 11.

9. Which parameters were unsafe?

a.	Bacteria	42%
b.	Nitrate	53%
c.	Fluoride	0%
d.	Volatile chemicals like gasoline and solvents	3%
e.	Pesticides	15%
f.	Arsenic	7%
g.	Other	10%

10. If any of the testing results indicated your water was unsafe to drink, did you…(check all that apply)

a.	Stop drinking your well water	55%
b.	Buy a water filter	47%
c.	Drink water from another source	66%
d.	Install a new well	15%
e.	Boil the water	10%
f.	Contact your health department or DNR office	31%
g.	Look for more information on the web	15%
h.	Did something else	38%
i.	Did nothing	3%

11. How would you describe the quality of your water?

a.	Excellent	41%
b.	Very Good	40%
c.	Acceptable	16%
d.	Poor	3%
e.	Not sure	<1%
f.	Refused	<1%

12. Do you think you would be more likely to test your water if you had additional assistance or information about water quality?

a.	YES	42%
b.	NO	56%
c.	Not Sure	2%

13. Are any residents in your household currently pregnant?

a.	YES	1%
b.	NO	99%

14. Do any children under the age of 2 years live in your home?

a.	YES	2%
b.	NO	98%

Table 1. Well Testing Rates by County and DHS Region

County	N	Weighted Testing rate %	Unweighted Testing rate %	County	N	Weighted Testing rate %	Unweighted Testing rate %
Adams	60	70	72	Menominee	75	73	73
Ashland	27	66	67	Milwaukee	35	51	37
Barron	42	86	83	Monroe	34	69	76
Bayfield	78	60	63	Oconto	41	81	76
Brown	28	79	75	Oneida	70	65	69
Buffalo	53	58	72	Outagamie	27	84	74
Burnette	84	70	68	Ozaukee	31	69	68
Calumet	21	71	81	Pepin	68	60	85
Chippewa	20	89	80	Pierce	47	78	81
Clark	46	71	76	Polk	64	54	66
Columbia	39	59	74	Portage	30	73	80
Crawford	54	72	72	Price	66	73	74
Dane	32	90	88	Racine	47	63	64
Dodge	22	53	55	Richland	50	85	84
Door	57	86	84	Rock	27	71	74
Douglas	42	65	67	Rusk	35	81	83
Dunn	48	75	79	Saint Croix	32	32	66
Eau Claire	20	83	75	Sauk	19	26	58
Florence	68	83	81	Sawyer	83	51	61
Fond du Lac	27	77	78	Shawano	38	66	71
Forest	69	71	72	Sheboygan	41	64	76
Grant	38	81	87	Taylor	70	66	67
Green	38	66	71	Trempealeau	17	47	59
Green Lake	42	58	71	Vernon	37	75	70
Iowa	37	54	73	Vilas	77	61	66
Iron	57	49	67	Walworth	42	55	67
Jackson	41	76	76	Washburn	55	48	56
Jefferson	22	56	68	Washington	56	59	57
Juneau	53	76	74	Waukesha	47	65	66
Kenosha	33	47	55	Waupaca	26	89	85
Kewaunee	31	76	81	Waushara	41	69	71
LaCrosse	27	79	81	Winnebago	32	87	84
Lafayette	33	71	79	Wood	39	53	64
Langlade	61	80	79	Region			
Lincoln	49	88	88	Southern	509	67	74
Manitowoc	21	82	81	Southeast	320	57	59
Marathon	52	84	81	Northeast	686	75	75
Marinette	44	63	64	Western	844	67	73
Marquette	81	71	74	Northern	907	68	71

*County not available for 26 responses

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CDC. Overview of the Behavioral Risk factor Surveillance Survey. http://www.cdc.gov/brfss/technical_infodata/surveydata/2009.

Wisconsin Groundwater Coordinating Council. Report to the Legislature, August 2009.

Assessing levels of potential health effects of endrocrine disrupting chemicals in groundwater associated with Karst areas in Northeast Wisconsin

Basic Information

Title:	Assessing levels of potential health effects of endrocrine disrupting chemicals in groundwater associated with Karst areas in Northeast Wisconsin
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Principal Investigators:	Angela BauerDantion, Michael Edward Zorn

Publication

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Assessing Levels of Endocrine Disrupting Chemicals in Groundwater Associated with Karst Areas in Northeast Wisconsin

WRI Project Number WR08R004

Project Investigators:
Angela Bauer-Dantoin, Professor and Chair, Human Biology, UW-Green Bay
Kevin Fermanich, Associate Professor, Natural and Applied Sciences, UW-Green Bay
Michael Zorn, Associate Professor, Natural and Applied Sciences, UW-Green Bay
Sarah Wingert, Graduate Student, Environmental Science & Policy, UW-Green Bay

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Project Summary

Title: Assessing Levels of Endocrine Disrupting Chemicals in Groundwater Associated with Karst Areas in Northeast Wisconsin

Project I.D.: WRI Project Number WR08R004

Investigators: Angela Bauer-Dantoin, Professor and Chair, Human Biology, UW-Green Bay
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Michael Zorn, Associate Professor, Natural and Applied Sciences, UW-Green Bay
Sarah Wingert, Graduate Student, Environmental Science & Policy, UW-Green Bay

Period of Contract: July, 2008 – January, 2010 (no cost extension granted in August, 2009)

Background/Need:
In recent years, concern has risen over the presence of various nonpoint source pollutants in drinking water, including a class of organic chemicals called endocrine disrupting chemicals (EDCs). The growing prevalence of EDCs in environmental systems has been linked to the disruption of aquatic endocrine systems and increased incidence of certain human cancers. Groundwater in the Silurian aquifer of northeastern Wisconsin may be particularly susceptible to nonpoint source contamination due to the existence of shallow soils, dolomite bedrock, and karst features, which combine to facilitate the transport of surface runoff to groundwater. Land application of manure containing synthetic and endogenous hormones may be a significant source of nonpoint source pollutants, including EDCs, to groundwater in the heavily farmed regions of northeast Wisconsin.

Objectives:
The specific objectives of the study were:
1. To test for indicators of livestock and/or human fecal contamination (E. coli, fecal coliform, nitrates) in groundwater near farmland in the northeast Wisconsin counties of Brown, Calumet, Fond du Lac and Kewaunee.
2. To assess levels of EDC activity in groundwater near farmland in the northeast Wisconsin counties of Brown, Calumet, Fond du Lac and Kewaunee.
3. To determine whether EDC activity and fecal waste indicators in groundwater near farmland change after major recharge periods (e.g., rainfall; spring thaw).
4. To discern whether levels of groundwater contamination by EDCs correlate with other water quality indicators (nitrates, fecal coliform, E. coli levels).
5. To measure estradiol levels in water samples through use of an enzyme-linked immunosorbent assay (ELISA).

Methods:
The MCF-7 breast cancer cell proliferation assay (E-screen) was used to determine if groundwater samples collected from four northeast Wisconsin counties, including Brown, Calumet, Fond du Lac, and Kewaunee, exhibited estrogenic behavior. Groundwater samples were collected four times between the summer of 2008 and the spring of 2009 (in August, November, Frebruary and March), and the samples were analyzed for estrogenicity, 17β-estradiol concentrations, nitrate, conductivity, total coliform, enterococci, and *E. coli.* The wells chosen for this study were located in agricultural areas of northeast Wisconsin, were cased into the Silurian aquifer, and were chosen in light of past contamination with bacteria and/or nitrate.

Results and Discussion:

Estrogenic activity was detected in a portion of the groundwater samples during all four sampling periods, despite apparent toxicity and/or anti-estrogenic effects in the E-screen assay. The estrogenic equivalency found in the samples used in the study are below the range known to cause endocrine disruption in wildlife and are within the range of levels found in other studies that utilized the E-screen to analyze water samples. Levels of estrogenicity were highest during the months of August and November. Specific 17β-estradiol concentrations in samples were not measurable with the ELISA, presumably due to cross-reactivity and/or matrix effects. Unsafe levels of bacteria and nitrate occurred during all four sampling periods. Average bacterial contamination increased following snowmelt events in February and March 2009. Coliform, enterococci, and *E. coli* were positively correlated throughout the study, with the strongest correlations occurring in the March 2009 sampling period. Correlations were not found between nitrate and bacteria, or nitrate and estrogenicity. One weak, positive correlation was found between *E. coli* and estrogenicity in the March 2009 sampling period.

Conclusions/Implications/Recommendations:

Results from the study indicate that groundwater contamination with EDCs, bacteria and nitrates is a common problem in karst areas of northeast Wisconsin. EDC contamination was greatest during the months of August and November, times at which land application of manure is frequent. Potential sources of EDC contamination within our study area (e.g., pharmaceuticals from leaky septic systems, land-applied manure, estrogenic pesticides) remain speculative based on the information provided in this study, and their identification provides an intriguing avenue for future research. It will also be worthwhile to identify fracture zones, bedrock openings, and other potential hazardous areas that allow for quick transport of surface runoff to the groundwater. The impact of individual well characteristics (well depth, depth to bedrock, age, and soil type) on water quality parameters, likewise, is worthy of study. Finally, the specific contaminants exerting estrogenic activity within the water samples should be analyzed with a more reliable method of detection than the ELISA, such as liquid chromatography-mass spectrometry.

Related Publications:

Wingert, S.E.; Bauer-Dantoin, A. Fermanich, K.J.; Zorn, M.E. Assessing Levels and Potential Health Effects of Endocrine Disrupting Chemicals in Groundwater Associated with Karst Areas in Northeast Wisconsin. The 33rd Annual Meeting of the American Water Resources Association (AWRA) Wisconsin Section. March 5-6, 2009. Stevens Point, Wisconsin.

Wingert, S.E. Assessing Levels of Endocrine Disrupting Chemicals in Groundwater Associated with Karst Areas in Northeast Wisconsin. Master's Thesis in Environmental Science and Policy, University of Wisconsin – Green Bay, December, 2010.

Key Words: endocrine disruptors, groundwater, estrogenicity, E-screen, E.coli, nitrates, fecal coliform

Funding: State of Wisconsin Groundwater Research and Monitoring program through the University of Wisconsin Water Resources Institute (WRI)

Introduction

There is widespread concern over the presence of organic compounds within groundwater that have the ability to mimic or interfere with the activities of endogenous hormones within the body. These endocrine disrupting chemicals (EDCs) come from a variety of sources (National Research Council, 1999), including industrial effluent (polychlorinated biphenyls, plasticizers), human waste (synthetic hormones from contraceptives), and animal waste (endogenous as well as synthetic hormones injected into livestock to induce growth). Many EDCs have been shown to mimic or block the actions of endogenous sex hormones (estrogens and androgens) within the body. Given that sex hormones are the principal regulators of the development and function of a wide variety of tissues, there exists great potential for EDCs to cause physiological abnormalities in exposed organisms (reviewed in Colburn et al., 1996).

Of particular concern for humans is the possible association between EDC exposure and endocrine-related cancers, such as breast cancer. Cumulative exposure to estrogen is a major risk factor for the development of breast cancer (Toniolo et al., 1995; Dorgan et al., 1996), and thus there is concern that exposure to estrogenic EDCs may increase one's risk for developing breast cancer. Indeed, not only have laboratory studies linked EDC exposure with the development of breast cancer in mice (Murray et al., 2006), but human studies likewise have found a correlation between elevated levels of EDCs such as DDT and the development of breast cancer in young women (Cohn et al., 2007). Additional concerns have been raised about EDC exposure and a male's risk for developing androgen-sensitive cancers, including testicular cancer (Skakkebaek et al., 2001; Weir et al., 2000) and prostate cancer (Fleming et al., 1999; Ho et al., 2006).

In addition to posing cancer risks, EDCs are thought to interfere with reproductive function in both males and females (reviewed in Colburn, 1996). Animal studies that have documented a negative impact of EDCs on germ cell production in both sexes (Sakaue et al., 2001; Susiarjo et al., 2007); as a result, it has been proposed that EDC exposure is responsible for the decline in sperm counts observed in males in industrialized countries (Toppari et al., 1996; Toppari et al., 2002). EDCs also impair fertility in laboratory animals by interfering with the signaling of endogenous sex hormones during development of the reproductive system (Gray et al., 1999; Fisher et al., 1999). Thus, EDC exposure is thought to be responsible for the marked increase in disorders of human sexual development such as hypospadias and testicular dysgenesis that has been observed in industrialized countries (Toppari et al., 1996; Toppari et al., 2002).

A critical step toward minimizing exposure to EDCs and thus decreasing the associated health risks is identifying routes of contamination within the environment. Recently, attention has turned to livestock waste as a source of EDCs. Manure is a rich source of EDCs, since it contains not only endogenous estrogens from cattle (estradiol, estriol and estrone; Hanselman et al., 2006; Peterson et al., 2000) but also synthetic steroids administered to livestock as growth-enhancing agents (Herschler et al., 1995). Manure-borne EDCs are introduced into the environment as a result of the standard practice of applying animal wastes to pastures and croplands as fertilizers. Several studies have suggested that land application of animal wastes results in EDC contamination of agricultural drainage water and groundwater (Hanselman et al., 2006; Peterson et al., 2000) with concentrations of EDCs that are known to exert biological effects (Irwin et al., 2000; Panter et al., 1998).

Groundwater contamination by manure runoff is of particular concern to the residents of northeast Wisconsin, given the unique geology of the region. Northeast Wisconsin is characterized by carbonate bedrock areas, shallow soil depths, and karst features (sink holes and bedrock openings) that allow ready access of surface contaminants to well water. A recent report of the Northeast Wisconsin Karst Task Force (2007) indicates that a significant proportion of water supply wells in northeast Wisconsin have been contaminated by bacteria or high levels of nitrate. Numerous incidences of contamination have been linked to manure runoff within recent years, particularly during the spring thaw. Indeed, when the Calumet County Land and Water Conservation Department conducted voluntary well water testing in spring of 2007, they found that 32% of the samples tested positive for some level of coliform bacteria (an indicator of contamination by livestock and/or human waste) and high nitrate levels (Calumet County, 2007). These results are consistent with previous data collected in Calumet County during 2002-2006. Similar findings were obtained by the Brown County Land Conservation Department in an analysis of well water samples collected from the town of Morrison (Brown County Land Conservation Department, 2007).

The majority of coliform-positive well water samples identified in the aforementioned studies came from areas in northeast Wisconsin that are heavily utilized as farmland and have relatively shallow soils over fractured dolomite. Thus, it is likely that groundwater contamination in these counties is due to the application of livestock manure as fertilizer to pastures and croplands. Given that livestock manure contains appreciable amounts of steroid hormones (Hanselman et al., 2006; Peterson et al., 2000), concerns arise that manure-born EDCs are also contaminating well water. Thus, in the present study, we conducted experiments to assess whether coliform- and E. coli-positive groundwater samples obtained from the northeast Wisconsin counties of Brown, Calumet, Fond du Lac and Kewaunee contain measurable levels of manure-born EDCs (e.g., 17β estradiol, estriol and testosterone), through use of the MCF-7 breast cancer cell proliferation assay (also known as the E-screen assay). Levels of EDCs were measured at four time points to determine seasonality and possible changes associated with recharge periods (heavy rainfall or spring thaw). Finally, estradiol concentrations in water samples were assessed through use of the enzyme-linked immunosorbent assay.

Procedures and Methods

Well Selection and Sample Collection

The study area consisted of rural land in northeast Wisconsin with known instances of past contamination of the uppermost Silurian aquifer. Private groundwater wells within five counties, including Brown, Calumet, Dodge, Fond du Lac, and Kewaunee Counties, were selected to investigate the potential for groundwater contamination with estrogenic chemicals. Besides the fact that each of these counties has areas that are susceptible to contamination, these counties were chosen because we were able to identify representatives from local environmental agencies that were willing to help us contact well owners and sample the wells. Ten wells per county were chosen for sampling in Brown, Calumet, and Kewaunee counties. Eight wells were selected from Fond du Lac County and two wells were chosen from Dodge County immediately south of the Fond du Lac wells. For sample collecting and analysis purposes, the Dodge County wells were included with the Fond du Lac wells due to their close proximity.

The wells chosen for the study were not selected in a statistically rigorous manner, and were not chosen with the intent to represent county-level water quality trends. Rather, the wells were selected based on five characteristics: they were cased into the Silurian aquifer; they were shallow in depth; historical sampling data for bacteria and nitrate existed; the well owners agreed to participate in the study; and the wells were located in areas with suspected or known sources of agricultural contamination. Eight wells from each county were designated "susceptible" to contamination based on past high levels of contamination, while two wells from each county were deemed "control" wells based on low levels of past contamination (no or low bacteria counts and less than 2 mg/L NO3--N). Samples were collected from each well in mid-August 2008, mid-November 2008, mid to late February 2009, and mid-March 2009 by a county representative or UW-Green Bay researcher.

Bacterial and Nitrate Analyses

Bacteria samples were analyzed within 24 hours of collection at the UW-Oshkosh Halsey Science Center's Environmental Microbiology Laboratory. *Escherichia coli* (*E. coli*) and total coliform were measured using the Colilert procedure, and enterococci were measured using the Enterolert procedure (IDEXX 2010). Nitrate samples were analyzed for nitrate-nitrite levels within 48 hours of collection in our laboratory using a Lachat QuickChem 8500 Flow Injection Analysis System and the Lachat Instruments QuikChem Method 10-107-04-1-A (Wendt 2000). Results were reported as mg/L N, with a lower limit of detection of 0.1 mg/L N.

Sample Extraction for Biological Assays

The organic compounds from the samples collected for the estrogenicity tests were extracted at the UW-Green Bay lab within 48 hours of collection. One sample from each well was extracted following the Wisconsin State Laboratory of Hygiene's Aquatic Life Toxicity Testing Laboratory protocol for the extraction of organic compounds from water (ESS Bio Method 108.0) utilizing C-18 disks (3M Empore high performance extraction disk #2215). Samples were stored in 15 mL vials in a 4-degree Celsius refrigerator until the nitrogen dry-down procedure could be performed. During the nitrogen dry-down procedure, a sample extract was dried almost completely with ultra high purity nitrogen, and the 15 mL vial was rinsed with methanol three times. The remaining sample extract and methanol rinses were transferred to a 1.5 mL amber vial, and evaporated with nitrogen to 1 mL. The extracts in methanol were stored in a freezer.

Field blanks, duplicates, spikes, and a high-purity water blank were run through the extraction procedure for quality assurance purposes. For each sampling period, four duplicates (one per county) and two spiked samples were chosen randomly from the refrigerator and extracted for use in the biological assays. In the spiked samples, 1 mM 17β-estradiol was used to achieve a concentration of 2 x 10^{-11} M (20 pM) estradiol in the one liter sample. The spiked samples were extracted using the procedure described above and then concentrated to 2 x 10^{-8} M (20,000 pM) in the sample extracts using the nitrogen evaporation procedure.

Before use in the biological assays, 500 µL of each sample extract was transferred to a new, clean 1.5 mL amber vial, evaporated with nitrogen, and re-suspended in 500 µL of diluted extraction buffer. The extraction buffer was obtained from Oxford Biomedical Reseach, Inc.'s Estradiol Enyzme Immunoassay Kit (EA 70) and diluted five times with high-purity water prior to use. Sample extracts in the diluted extraction buffer were stored in a freezer until use in the E-screen and ELISA assays.

E-screen Assay

The E-screen assay was used to measure the general estrogenic activity of groundwater samples. The human breast cancer cells used in the assay, the MCF-7 BOS cells, were obtained from the laboratory of Dr. Ana Soto and Dr. Carlos Sonnenschein at the Tufts University School of Medicine in Boston, Massachusetts. The cells were grown in the UW-Green Bay lab and cared for following a procedure obtained from the Soto laboratory.

To harvest the cells for the E-screen assay, tissue culture flasks were rinsed with phosphate buffered saline and trypsinized with 1.5 mL of trypsin-EDTA solution. Cells were counted with a hemocytometer and diluted to a concentration of 7,000 cells per mL with DMEM and seeded in 24-well tissue culture plates (1 mL/tissue culture well). After 24 hours of incubation, the DMEM was removed and an estradiol standard dose response curve and the groundwater samples were added to the plates in experimental media. DMEM without the pH indicator phenol red was used as the experimental media due to phenol red's estrogenic properties (Shappell 2006). The experimental media was supplemented with 1% antibiotic/antimycotic solution and 5% charcoal-dextran stripped FBS (CD-FBS).

The standard curve for each assay contained 16 concentrations of 17β-estradiol, ranging from 5 x 10^{-14} M (0.05 pM) to 1x10^{-8} M (10,000 pM) 17β-estradiol. A dilution series was created for each groundwater sample included in an assay. A total of five different dilutions were used for each individual groundwater sample: 1:100, 1:200, 1:400, 1:800, and 1:1600. Standards and experimental samples were plated at a volume of 500 µL/tissue culture well. Additional wells were included in the assay that included – along with each dilution of experimental sample – the estrogen receptor antagonist, ICI 182,780, in order to determine if any proliferative effects generated by samples could be attributed to actions exerted specifically via the estrogen receptor. After an incubation period of five days, the assay was assessed for cell proliferation using the sulforhodamine B (SRB) protein assay. The absorbance of each sample, after staining with SRB dye, was read at a wavelength of 515 nm with a Molecular Devices microplate reader. The standard curve was fit with a four-parameter logistic equation using the Softmax PRO v. 2.6 analytical software package, and estradiol equivalency (EEq) was determined by inserting the absorbance readings into the equation generated by the standard curve (Soto et al. 1995). Results were reported as pM EEq.

The limit of quantification varied for each assay, ranging from 0.4 to 1 pM. The least sensitive assay had a lower limit of quantification (LOQ) of 1 pM (1.0 x 10-12 M) EEq in the sample extracts. For consistency, 1 pM EEq was chosen as the lower LOQ for use across all assays. Only groundwater samples exhibiting an estrogenic response above the lower LOQ of 1 pM were analyzed statistically.

ELISA

Attempts were made to measure concentrations of 17β-estradiol in the groundwater sample extracts using enyzme-linked immunosorbent assay (ELISA) kits obtained from Oxford Biomedical Research, Inc. (Product Number EA 70). Specific 17β-estradiol concentrations in samples were not measurable with the ELISA, due to cross-reactivity and/or matrix effects.

Statistical Analyses

Statistical analyses were employed using SAS statistical software to determine if any trends existed between estrogenicity and other parameters, including nitrate, total coliform, *E. coli*, enterococci, and conductivity. Spearman's rank correlation test was used to examine potential correlations between the results of all seven tests (PROC CORR; Cody and Smith 2006; Peterson et al. 2000). Seasonality was also assessed by comparing the results of the four sampling periods. For nitrate results, a repeated measures analysis for a repeated measure on one factor was conducted to examine seasonality, with the well identification number as the random effect and the sampling period as the fixed effect (PROC MIXED; Cody and Smith 2006; Shappell 2006). For the remaining five parameters, seasonality was analyzed using the Signed Rank Test, a non-parametric test for non-normal, paired data sets (PROC UNIVARIATE; Cody and Smith 2006). A nonparametric statistical test (comparison of mean Wilcoxon scores, using the t approximation test) was used to determine if the results of the control wells differed significantly from the susceptible wells (PROC NPAR1WAY; Cody and Smith 2006). The results were also analyzed for county-level differences using a one-way analysis of variance test for the nitrate and conductivity results (PROC GLM; Cody and Smith 2006), and the Kruskal-Wallis test for the remaining five parameters (PROC NPARIWAY; Cody and Smith 2006). County-level differences were not expected since the groundwater wells were chosen based on similar characteristics, but differences could occur due to sampling technique (each county was sampled separately by different people) or differences in the geologic make-up of an area. All statistical results were analyzed for significance at the 0.05 level.

Results and Discussion

Weather Conditions

Groundwater samples were collected on the following dates: August 11 and 12, 2008 (first sampling period), November 17 and 18, 2008 (second sampling period), February 13, 17, 24, and March 2, 2009 (third sampling period), and March 18 and 19, 2009 (fourth sampling period). Precipitation data from the National Oceanic and Atmospheric Administration's (NOAA) National Weather Service (NWS) station in Green Bay was obtained prior to each sampling period (NOAA 2009). The largest rain event prior to the first sampling period occurred 26 days before sampling, with a precipitation total of 1.32 inches. No other major rain events occurred prior to the first sampling period, and no significant rain events occurred within 16 days of the second sampling period. Precipitation data were not available from the Green Bay station from October 22 to October 31, 2009, so only the two weeks prior to sampling are included for the second sampling period. Due to the lack of significant rain events prior to both the first and second sampling periods, it was assumed that groundwater levels in the study area were at low-flow or base-flow conditions during the first and second sampling periods.

The third and fourth sampling periods were executed with the intent of capturing potential groundwater recharge events following instances of snowmelt. In February 2009, record temperature highs occurred in the Green Bay area on the 7th, 8th, and 10th day of the month, while daily maximum temperatures hung above freezing from the 6th to the 12th, and topped out at 50 degrees Fahrenheit on the 10th. No major precipitation events occurred between February 1st and 10th , but the Green Bay area had a foot of snow accumulated from past precipitation events. The record temperatures caused half of the snow to melt by February 10th, and only one inch of snow remained on February 12th.

Objective 1: To test for indicators of livestock and/or human fecal contamination (E. coli, fecal coliform, nitrates) in groundwater near farmland in the northeast Wisconsin counties of Brown, Calumet, Fond du Lac and Kewaunee

During each sampling period, a number of groundwater wells were found to be contaminated with each of the three types of bacteria: coliform, enterococci, and *E. coli* (see Table 1). A bacterial detection of 1 MPN (most probable number) units or greater is unsafe by public water drinking standards. Total coliform levels ranged from below detection (<0.1 MPN) to above detection (>2,419.6 MPN), enterococci levels ranged from below detection to 579.4 MPN, and *E. coli* levels ranged from below detection to 816.4 MPN (See Tables 1-4 of Appendix B for individual well data during the four sampling periods). The highest average coliform and enterococci levels and the highest number of *E. coli* detections occurred during the fourth sampling period (during the spring thaw). Coliform was detected most frequently, followed by enterococci. In the first, third, and fourth sampling periods, coliform was detected in more than 50% of our wells, and enterococci was detected in more than 25% of the wells. *E. coli* was detected the least frequently, with two contaminated wells in the first sampling period, one in the second sampling period, three in the third sampling period, and ten in the fourth sampling period.

Table 1: Percentage of groundwater wells contaminated with coliform, enterococci, and *E. coli* during each sampling period.

Sampling Period	Coliform			E. coli			Enterococci		
	Unsafe	Safe	N	Unsafe	Safe	N	Unsafe	Safe	N
1	62.5%	37.5%	40	12.5%	87.5%	40	27.5%	72.5%	40
2	40.5%	59.5%	37	2.7%	97.3%	37	10.8%	89.2%	37
3	59.0%	41.0%	39	7.7%	92.3%	39	29.7%	70.3%	37
4	64.9%	35.1%	37	27.0%	73.0%	37	46.0%	54.1%	37

E. coli and enterococci are both indicators of animal or human waste and hence could be from the same source. Fecal coliform bacteria (*E. coli*) have been shown to be less resistant in the environment than fecal enterococci and are also found at a lower ratio in animal feces than fecal enterococci (Celico et al. 2004). This might explain why *E. coli* was found less frequently than enterococci. In 59 spring water samples from a fractured limestone aquifer in Italy, Celico et al. (2004) found that approximately 52% of their samples were contaminated with enterococci, while only 22% were contaminated with *E. coli*. This aquifer is known to be impacted by manure from grazing cattle. These percentages are similar to the results we found in the fourth sampling period.

With the exception of the first sampling period, the control groundwater wells exhibited less bacterial contamination than the susceptible wells. Four control wells (C03, B07, K04, and K13) had detectable levels of total coliform twice during this study. Three of these wells (B07, K04, and K13) also had at least one enterococci detection. No *E. coli* hits were recorded for the control wells in any of the sampling periods, and no coliform or enterococci detections occurred in the control wells during the fourth sampling period.

The nitrate results were relatively consistent among the four sampling periods (see Table 2), with the average concentration of the control groundwater wells slightly above 1 mg/L N for each sampling period and the average concentration of the susceptible wells ranging between 11 mg/L to 14 mg/L N (see Tables 1-4 of Appendix B for individual well nitrate data during the four sampling periods). Results ranged from below detection (<0.1 mg/L N) to 31.1 mg/L. For each sampling period, there was a significant difference between the average concentration of the control groundwater wells and the average concentration of the susceptible wells: the control wells had much lower concentrations than the susceptible wells. No significant differences were found between the average nitrate concentrations of each county for any of the four sampling periods, though Brown County consistently had the highest average concentrations and Fond du Lac County consistently had the lowest.

Table 2: Percentage of wells falling in different nitrate pollution categories during each sampling period.

Sampling Period	0-2 mg/L N	2-5 mg/L N	5-10 mg/L N	>10 mg/L N	# Wells Sampled
1	17.5%	7.5%	20.0%	55.0%	40
2	21.6%	8.1%	21.6%	48.7%	37
3	18.0%	12.8%	18.0%	51.3%	39
4	11.1%	33.3%	33.3%	22.2%	39

Objective 2: To assess levels of EDC activity in groundwater near farmland in the northeast Wisconsin counties of Brown, Calumet, Fond du Lac, and Kewaunee

We detected estrogenic activity in groundwater during all four sampling periods. Based on the number of wells run through the E-screen in each sampling period, 58%, 31%, 14%, and 5% of our groundwater samples exhibited estrogenicity in the first, second, third, and fourth sampling periods, respectively (Table 3). Cell proliferation was determined to be estrogen-dependent through use of the estrogen receptor antagonist, ICI 182,780, which inhibited cell growth in the presence of our samples. Estradiol equivalency ranged from 0.0114 pM to 12.87 pM (0.003 ng/L to 3.51 ng/L or 1.14 x 10-14 M to 1.29 x 10-11 M) (see Tables 1-4 of Appendix B for individual EEq well data during the four sampling periods).

Table 3: Percentage of sampled groundwater wells with detectable estradiol equivalents in the E-screen during each sampling period (lower LOQ of 1 pM EEq in sample extracts). Unknowns = samples in which estrogenicity was below the level of detectability in the E-screen assay.

Sampling Period	Below Detection	Detections	Unknown	N
1	35.0%	50.0%	15.0%	40
2	59.5%	27.0%	13.5%	37
3	80.6%	13.9%	5.6%	36
4	94.6%	5.4%	0.0%	37

The EEqs found in our study are within the range of levels found in other studies that utilized the E-screen. For instance, Shappell et al. (2007) found EEqs between 0.1 pM and 858 pM in lagoons, manure pits, and wetlands receiving swine wastewater. Water samples collected from 20 ponds and wetlands located in agricultural areas near Fargo, North Dakota produced EEqs within approximately one order of magnitude: 1 x 10^{-13} M (0.1 pM) to 1.0 x 10^{-12} M (1 pM) (Shappell 2006). In comparison, approximately 62% of the EEqs in our groundwater study fell within this order of magnitude; the remaining 27% and 10% fell between 1 x 10^{-14} M (0.01 pM) and 1.0 x 10^{-13} M (0.1 pM), and 1 x 10^{-12} M (1 pM) and 1.0 x 10^{-11} M (10 pM), respectively. The fact that most of our samples were either lower than the range found by Shappell et al.

(2007) or near the bottom of the range can be attributed to the fact that Shappell was looking at surface water bodies directly impacted by pollution, and we were looking at groundwater that may or may not be impacted by pollution. One would expect the concentrations of estrogenic chemicals originating at the surface to be somewhat reduced as they enter the water table, whether it be by filtration through the unsaturated zone, degradation by microbes, or dilution through mixing with other water sources. During transport through the aquifer, concentrations may become even more diluted before reaching a groundwater well, depending on the distance from the source of the estrogenic chemicals.

No public drinking water health standard exists for estradiol equivalency. However, studies have shown that low concentrations of estradiol in surface waters (10-100 ng/L or 36.7 - 367 pM) can disrupt the endocrine systems of aquatic species, including fish, turtles, and frogs (Hanselman et al. 2003). In a study analyzing the reproductive capacity of a fish population, with the goal being population sustainability, the Environment Agency of England and Wales estimated 36.7 pM (10 ng/L) estradiol as the "lowest observable effect concentration", and 3.67 pM (1 ng/L) as the threshold concentration yielding no effect on the fish (Shappell et al. 2007). Others have predicted that the "no-observed-effect-concentration" for 17β-estradiol is between 5-25 ng/L (Harper and Sinha 2006). While the vast majority of our samples tested well below the 1 ng/L "no effect" threshold identified by the Environment Agency of England and Wales, our E-screen results show that some wells may have fallen within this range. Wells C02, C03, and C04, and wells F05, C03, F07, C04, and B12 exhibited EEqs above 0.1 ng/L (0.367 pM) during the first and second sampling periods, respectively, while samples C04-2 and B12-2 recorded values above the 1 ng/L threshold. No groundwater samples had an EEq greater than 0.1 ng/L in the third or fourth sampling period.

Objective 3: To determine whether EDC activity and fecal waste indicators in groundwater near farmland change after major recharge periods (e.g., rainfall; spring thaw).

Several significant, seasonal differences in bacterial levels were observed in susceptible wells across the four time points examined. Average coliform contamination was significantly greater in the fourth sampling period as compared to the first, second, and third sampling period as indicated by the Signed Rank Test ($p=0.0017$, $p=<0.0001$, $p=0.0014$, respectively). Average coliform levels in the third sampling period were also significantly greater than those of the second sampling period ($p=0.0019$). In other words, the second sampling period had less average contamination than the fourth and third sampling period, but was not significantly different from the first ($p=0.0554$).

Similar to coliform, the susceptible wells had significantly less average enterococci contamination in the second sampling period than the first, third, and fourth sampling periods ($p=0.0469$, $p=0.0059$, $p=<0.0001$, respectively). Enterococci contamination of the susceptible wells in the fourth sampling period was also significantly greater than the third sampling period ($p=0.0249$). The fourth sampling period had greater average enterococci values as compared to the first sampling period, but the difference was not significant ($p=0.6993$). Differences between the average *E. coli* results of the susceptible wells were similar to the coliform and enterococci parameters: the *E. coli* contamination in the fourth sampling period was significantly greater than the contamination of the first and second sampling periods ($p=0.0164$, $p=0.002$, respectively).

In combination, the seasonality results of the bacteria parameters indicate that bacteria levels were greatest during the spring thaw compared to summer and fall. The fourth sampling period had the most bacterial contamination, the third sampling period had the second-greatest amount of bacterial contamination, and the second sampling period had the least amount of bacterial contamination. As stated earlier, the presence of enterococci and/or *E. coli* in a groundwater well indicates that the well was contaminated with some type of human or animal waste. Due to the nature of *E. coli* and enterococci, both of which are found in the intestines of warm-blooded animals, our results suggest as many as 46% of our wells were contaminated with animal or human waste in the fourth sampling period.

When the dataset was analyzed as a whole, a significant difference was found among the four sampling periods for nitrate ($p=0.0151$). The Tukey adjustment indicated that this was due to a significant difference between the first and fourth sampling periods ($p=0.0086$). When the control and susceptible wells were analyzed separately, it was found that the control wells did not differ significantly among the four sampling periods (p=0.6543). Thus, the difference between sampling periods was due to a difference in contamination of the susceptible wells, which had significantly greater nitrate contamination in the first sampling period as compared to the fourth (p=0.0081).

Unlike bacteria and nitrate results, EEqs were significantly lower in the fourth sampling period vs. sampling periods one (p=0.0006) and two (p=0.002). No significant differences were found between the first and second sampling periods, which had the greatest average EEqs and the most estrogenicity detections (p=0.6995). Sampling period three also had significantly less contamination than sampling period one (p=0.001). No differences were found between sampling periods three and four, which had the fewest E-screen detections (p=0.2188), or sampling period two and three (p=0.25).

Overall, fewer estrogenicity detections were found in the groundwater wells as compared to bacteria and nitrate detections in all the sampling periods. This could be due to several reasons. Firstly, estrogen contamination may simply occur less frequently in our subject wells than bacteria and nitrate contamination events. Perhaps there are fewer sources of estrogen contamination in our study area than bacteria or nitrate sources. Secondly, some samples may have had estrogenic activity that measured below the LOQ of our assay, preventing it from being detected. Thirdly, the E-screen is a biological assay that depends on the consistent response of a living cell line. If the groundwater extracts contained chemicals that were toxic to cell growth, the ability of the E-screen to properly measure estrogenicity would be compromised. In samples containing both estrogenic and toxic chemicals, toxicity could inhibit an estrogenic response (cell proliferation). This would affect the estrogenicity results by either reducing EEqs or pushing values below the LOQ and preventing detection all together. Toxicity occurred very frequently in our assays, especially during the third and fourth sampling period. As such, it is possible that the estrogenicity of the groundwater samples may be greater than our results indicate, particularly during the third and fourth sampling period, since cell death due to the presence of toxic chemicals in the sample prevents or lowers EEq detection by the E-screen. Thus, it is possible that wells with apparent toxicity that registered below detection in the E-screen may have contained estrogenic chemicals, but the dose-dependent response of the cells was masked by the toxic components of the sample. These limitations of bioassay such as the E-screen highlight the need for a method that allows the identification and detection of specific estrogenic chemicals in complex water samples containing unknown compounds, such as gas chromatography-mass spectrometry (GC-MS; Drewes et al. 2005; Chen et al. 2006; Soliman et al. 2007).

Objective 4: To discern whether levels of groundwater contamination by EDCs correlate with other water quality indicators (nitrates, fecal coliform, E. coli levels)

Our study did not find strong correlations between estrogenicity and the other water quality parameters. We did not find any strong correlations between our E-screen data and the other water quality parameters, though one significant, weak correlation was found: a positive correlation between the *E. coli* results and the E-screen results in the fourth sampling period. The weakness of this correlation (r=0.364) makes it difficult to draw a conclusion. As discussed above, the weak relationship between *E. coli* and estrogenicity in the fourth sampling period was driven by two samples, F05-4 and F07-4. Both of these samples tested positive for estrogenicity, *E. coli*, coliform, and enterococci.

Several possible explanations exist for the lack of correlation between our water quality parameters. For example, toxicity of groundwater samples during the fourth sampling period – which may have led to low or undetectable EEqs - may have prevented the detection of a correlation of bacteria and estrogenicity data. Also, sources of contamination are plentiful, and estrogenic activity may be coming from a source other than that which causes bacterial contamination (e.g., estrogenic pesticides; pharmaceuticals from leaky underground septic tank).

Objective 5: To measure estradiol levels in water samples through use of an enzyme-linked immunosorbent assay (ELISA)

Attempts were made to measure concentrations of 17β-estradiol in the groundwater sample extracts using enyzme-linked immunosorbent assay (ELISA) kits obtained from Oxford Biomedical Research, Inc.

(Product Number EA 70). Specific 17β-estradiol concentrations in samples were not measurable with the ELISA, due to cross-reactivity and/or matrix effects.

Conclusions and Recommendations

Results from the study indicate that groundwater contamination with EDCs, bacteria and nitrate is a common problem in karst areas of northeast Wisconsin. EDC contamination was greatest during the months of August and November, times at which land application of manure is frequent. Potential sources of EDC contamination within our study area (e.g., pharmaceuticals from leaky septic systems, land-applied manure, estrogenic pesticides) remain speculative based on the information provided in this study, and their identification provides an intriguing avenue for future research. It will also be worthwhile to identify fracture zones, bedrock openings, and other potential hazardous areas that allow for quick transport of surface runoff to the groundwater. The impact of individual well characteristics (well depth, depth to bedrock, age, and soil type) on water quality parameters, likewise, is worthy of study. Finally, the specific contaminants exerting estrogenic activity within the water samples should be analyzed with a more reliable method of detection than the ELISA, such as liquid chromatography-mass spectrometry.

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Appendix A: Publications and Presentations

Wingert, S.E.; Bauer-Dantoin, A. Fermanich, K.J.; Zorn, M.E. Assessing Levels and Potential Health Effects of Endocrine Disrupting Chemicals in Groundwater Associated with Karst Areas in Northeast Wisconsin. The 33rd Annual Meeting of the American Water Resources Association (AWRA) Wisconsin Section. March 5-6, 2009. Stevens Point, Wisconsin.

Wingert, S.E. Assessing Levels of Endocrine Disrupting Chemicals in Groundwater Associated with Karst Areas in Northeast Wisconsin. Master's Thesis in Environmental Science and Policy, University of Wisconsin – Green Bay, December, 2010.

Appendix B: Water quality indicators for individual wells during each sampling period

Table 1: Results from the first sampling period (August 11-12, 2008).

County	Well ID	Group	Sample Date	Nitrate + Nitrate (mg/L N)	Conductivity (mS/cm)	Coliform (MPN/100 mL)	Enterococci (MPN/100mL)	*E. coli* (MPN/100 mL)	Escreen (EEq in pM)*, Above LOD	All Escreen Detects (Eeq in pM)
Brown	B02	Susceptible	8/12/2008	15.60	1.107	5.2	0.0	0.0	unknown	unknown
Brown	B04	Susceptible	8/12/2008	11.60	0.848	19.9	0.0	0.0	unknown	unknown
Brown	B05	Susceptible	8/12/2008	23.60	1.228	1.0	0.0	0.0	BD	0.086
Brown	B06	Susceptible	8/12/2008	19.80	1.141	0.0	0.0	0.0	BD	0.068
Brown	B07	Control	8/12/2008	<0.1	0.953	90.4	20.1	0.0	0.040	0.040
Brown	B08	Susceptible	8/12/2008	22.00	1.036	4.1	0.0	0.0	0.184	0.184
Brown	B10	Control	8/12/2008	<0.1	1.600	0.0	0.0	0.0	0.279	0.279
Brown	B11	Susceptible	8/12/2008	21.90	1.390	0.0	0.0	0.0	0.120	0.120
Brown	B12	Susceptible	8/12/2008	9.27	0.899	6.3	0.0	0.0	BD	0.049
Brown	B14	Susceptible	8/11/2008	18.90	0.932	1.0	0.0	0.0	0.163	0.163
Calumet	C01	Susceptible	8/11/2008	13.20	0.867	0.0	0.0	0.0	0.250	0.250
Calumet	C02	Susceptible	8/11/2008	14.50	0.979	6.3	0.0	0.0	0.374	0.374
Calumet	C03	Control	8/11/2008	<0.1	0.274	18.7	0.0	0.0	0.461	0.461
Calumet	C04	Susceptible	8/11/2008	18.90	0.790	108.1	8.5	0.0	0.383	0.383
Calumet	C05	Control	8/11/2008	1.24	1.011	0.0	0.0	0.0	unknown	0.236
Calumet	C06	Susceptible	8/11/2008	14.40	0.825	1732.9	156.5	1.0	unknown	unknown
Calumet	C10	Susceptible	8/11/2008	7.12	0.930	195.6	13.5	6.3	0.040	0.040
Calumet	C11	Susceptible	8/11/2008	6.15	0.850	2.0	0.0	0.0	0.028	0.028
Calumet	C12	Susceptible	8/11/2008	6.74	0.787	>2419.6	275.5	0.0	0.011	0.011
Calumet	C15	Susceptible	8/11/2008	24.00	1.021	0.0	0.0	0.0	0.042	0.042
Fond du Lac	F01	Susceptible	8/11/2008	3.39	1.023	1046.2	13.5	25.6	unknown	unknown
Fond du Lac	F02	Susceptible	8/11/2008	6.70	0.895	0.0	0.0	0.0	BD	0.031
Fond du Lac	F03	Control	8/11/2008	4.11	0.860	0.0	0.0	0.0	0.172	0.172
Fond du Lac	F04	Susceptible	8/11/2008	15.70	1.106	2.0	0.0	0.0	BD	0.072
Fond du Lac	F05	Susceptible	8/11/2008	1.78	0.932	78.5	0.0	0.0	BD	BD
Fond du Lac	F06	Control	8/11/2008	0.26	0.602	0.0	0.0	0.0	0.299	0.299
Fond du Lac	F07	Susceptible	8/11/2008	15.00	0.769	59.4	5.2	1.0	BD	BD
Fond du Lac	F08	Susceptible	8/11/2008	12.30	0.884	0.0	0.0	0.0	0.094	0.094
Dodge	F09	Susceptible	8/11/2008	6.31	1.065	0.0	0.0	0.0	BD	0.017
Dodge	F10	Susceptible	8/12/2008	17.50	0.921	88.2	1.0	1.0	unknown	unknown
Kewaunee	K01	Susceptible	8/12/2008	24.30	0.862	0.0	0.0	0.0	BD	0.036
Kewaunee	K02	Susceptible	8/12/2008	20.20	0.777	0.0	0.0	0.0	0.146	0.146
Kewaunee	K03	Susceptible	8/12/2008	11.00	0.878	2.0	0.0	0.0	0.040	0.040
Kewaunee	K04	Control	8/12/2008	4.10	0.906	187.2	6.3	0.0	BD	BD
Kewaunee	K05	Susceptible	8/12/2008	5.13	0.773	6.3	0.0	0.0	BD	BD
Kewaunee	K06	Susceptible	8/12/2008	19.90	0.821	0.0	0.0	0.0	0.102	0.102
Kewaunee	K07	Susceptible	8/12/2008	13.00	0.886	10.9	4.1	0.0	BD	BD
Kewaunee	K08	Susceptible	8/12/2008	15.10	0.952	4.1	0.0	0.0	0.067	0.067
Kewaunee	K09	Susceptible	8/12/2008	8.51	0.680	0.0	0.0	0.0	BD	BD
Kewaunee	K13	Control	8/12/2008	0.82	1.047	1119.9	129.6	0.0	BD	0.069

**Unknown* refers to results that were unquantifiable due to cell death (as a result of groundwater sample toxicity). *BD* refers to results that were below the detection limits of the assay.

Table 2: Results from the second sampling period (November 17-18, 2008).

County	Well ID	Group	Sample Date	Nitrate + Nitrate (mg/L N)*	Conductivity (mS/cm)	Coliform (MPN/100mL)	Enterococci (MPN/100mL)	*E. coli* (MPN/100 mL)	Escreen (EEq in pM)**, Above LOD	All Escreen Detects (Eeq in pM)
Brown	B02	Susceptible	11/17/2008	14.8	1.055	<1	<1	<1	BD	0.048
Brown	B04	Susceptible	11/17/2008	12.5	0.84	2	<1	<1	0.111	0.111
Brown	B05	Susceptible	11/17/2008	19.4	1.095	<1	<1	<1	BD	BD
Brown	B06	Susceptible	11/17/2008	17.4	1.03	<1	<1	<1	0.219	0.219
Brown	B07	Control	11/17/2008	0.0343	0.967	3	<1	<1	BD	0.006
Brown	B08	Susceptible	11/17/2008	15.2	0.973	<1	<1	<1	BD	0.029
Brown	B10	Control	11/17/2008	0.1	1.475	43.5	<1	<1	BD	BD
Brown	B11	Susceptible	11/17/2008	31.1	1.71	<1	<1	<1	0.255	0.255
Brown	B12	Susceptible	11/17/2008	10.8	0.955	<1	<1	<1	12.875	12.875
Brown	B14	Susceptible	11/17/2008	15.5	0.83	5.1	<1	<1	BD	BD
Calumet	C01	Susceptible	11/18/2008	NS	NS	NS	NS	NS	NS	NS
Calumet	C02	Susceptible	11/18/2008	11.5	0.966	<1	<1	<1	BD	BD
Calumet	C03	Control	11/18/2008	0.0144	0.262	9.7	<1	<1	1.066	1.066
Calumet	C04	Susceptible	11/18/2008	15.3	0.751	1	<1	<1	7.190	7.190
Calumet	C05	Control	11/18/2008	1.47	1.009	<1	<1	<1	unknown	BD
Calumet	C06	Susceptible	11/18/2008	NS	NS	NS	NS	NS	NS	NS
Calumet	C10	Susceptible	11/18/2008	7.37	0.818	980.4	<1	13.4	BD	BD
Calumet	C11	Susceptible	11/18/2008	6.71	0.925	1	<1	<1	BD	BD
Calumet	C12	Susceptible	11/18/2008	NS	NS	NS	NS	NS	NS	NS
Calumet	C15	Susceptible	11/18/2008	28	0.994	<1	<1	<1	BD	BD
Fond du Lac	F01	Susceptible	11/18/2008	3.72	1.075	6.3	1	<1	BD	0.009
Fond du Lac	F02	Susceptible	11/18/2008	6.62	0.907	<1	<1	<1	BD	BD
Fond du Lac	F03	Control	11/18/2008	4.51	0.851	<1	<1	<1	0.096	0.096
Fond du Lac	F04	Susceptible	11/18/2008	15.3	1.069	<1	<1	<1	BD	0.016
Fond du Lac	F05	Susceptible	11/18/2008	1.58	0.933	<1	<1	<1	0.600	0.600
Fond du Lac	F06	Control	11/18/2008	0.256	0.582	<1	<1	<1	BD	0.010
Fond du Lac	F07	Susceptible	11/18/2008	6.99	0.819	17.3	1	<1	1.663	1.663
Fond du Lac	F08	Susceptible	11/18/2008	12.8	0.85	<1	<1	<1	unknown	unknown
Dodge	F09	Susceptible	11/18/2008	5.7	1.074	<1	<1	<1	BD	0.044
Dodge	F10	Susceptible	11/18/2008	17.3	0.966	11	<1	<1	BD	0.076
Kewaunee	K01	Susceptible	11/17/2008	16.6	0.979	<1	<1	<1	BD	BD
Kewaunee	K02	Susceptible	11/17/2008	20.1	0.795	<1	<1	<1	unknown	unknown
Kewaunee	K03	Susceptible	11/17/2008	7.5	0.787	<1	<1	<1	BD	BD
Kewaunee	K04	Control	11/17/2008	1.79	0.784	<1	<1	<1	unknown	0.169
Kewaunee	K05	Susceptible	11/17/2008	4.03	0.779	21.6	<1	<1	BD	0.005
Kewaunee	K06	Susceptible	11/17/2008	6.49	1.021	<1	<1	<1	BD	0.010
Kewaunee	K07	Susceptible	11/17/2008	12.5	0.87	61.3	2	<1	unknown	unknown
Kewaunee	K08	Susceptible	11/17/2008	15.1	0.937	52.9	1	<1	BD	BD
Kewaunee	K09	Susceptible	11/17/2008	6.49	0.634	<1	<1	<1	BD	BD
Kewaunee	K13	Control	11/17/2008	0.702	1.012	2	<1	<1	0.117	0.117

**NS* means a well was not sampled during this sampling period.

***Unknown* refers to results that were unquantifiable due to cell death (as a result of groundwater sample toxicity). *BD* refers to results that were below the detection limits of the assay.

Table 3: Results from the third sampling period (February-March 2009).

County	Well ID	Group	Sample Date	Nitrate + Nitrate (mg/L N)*	Conductivity (mS/cm)	Coliform (MPN/100mL)	Enterococci (MPN/100mL)	*E. coli* (MPN/100mL)	Escreen (EEq in pM)**, Above LOD	All Escreen Detects (Eeq in pM)
Brown	B02	Susceptible	2/24/2009	13.6	0.989	387.3	7.3	0	BD	BD
Brown	B04	Susceptible	2/24/2009	9.00	0.723	209.8	1	0	BD	BD
Brown	B05	Susceptible	2/24/2009	19.7	1.095	114.5	<1	0	BD	0.042
Brown	B06	Susceptible	2/24/2009	15.0	1.013	4.1	1	0	unknown	BD
Brown	B07	Control	2/24/2009	0.01	1.031	<1	<1	0	BD	BD
Brown	B08	Susceptible	2/24/2009	23.7	1.161	14.8	10.7	0	BD	0.063
Brown	B10	Control	2/24/2009	0.01	1.530	<1	<1	0	BD	0.071
Brown	B11	Susceptible	2/24/2009	29.5	1.890	<1	<1	0	BD	0.026
Brown	B12	Susceptible	2/24/2009	9.01	0.926	98.7	<1	0	BD	BD
Brown	B14	Susceptible	2/24/2009	13.6	0.836	6.3	<1	0	BD	BD
Calumet	C01	Susceptible	2/24/2009	14.5	0.872	<1	<1	0	BD	0.028
Calumet	C02	Susceptible	2/24/2009	15.1	0.761	<1	<1	0	BD	BD
Calumet	C03	Control	2/24/2009	0.01	0.325	<1	<1	0	unknown	unknown
Calumet	C04	Susceptible	2/24/2009	NS	NS	NS	NS	NS	NS	NS
Calumet	C05	Control	2/24/2009	1.36	1.023	<1	<1	0	BD	0.087
Calumet	C06	Susceptible	2/24/2009	14.7	0.771	<1	<1	0	not run	not run
Calumet	C10	Susceptible	2/24/2009	9.27	1.045	290.9	<1	0	0.125	0.125
Calumet	C11	Susceptible	2/24/2009	8.43	0.833	38.4	<1	0	BD	0.041
Calumet	C12	Susceptible	2/24/2009	10.0	0.776	178.9	<1	0	not run	not run
Calumet	C15	Susceptible	2/24/2009	25.0	1.208	<1	<1	0	BD	BD
Fond du Lac	F01	Susceptible	2/13/2009	3.38	0.958	3	<1	0	BD	BD
Fond du Lac	F02	Susceptible	2/13/2009	5.71	0.857	<1	<1	0	BD	BD
Fond du Lac	F03	Control	2/13/2009	4.46	0.827	<1	<1	0	BD	BD
Fond du Lac	F04	Susceptible	3/2/2009	16.5	NS	4.1		0	BD	BD
Fond du Lac	F05	Susceptible	2/13/2009	1.90	0.956	<1	<1	0	BD	BD
Fond du Lac	F06	Control	2/13/2009	0.231	0.930	<1	<1	0	BD	BD
Fond du Lac	F07	Susceptible	2/13/2009	7.58	0.687	770.1	5.2	344.1	not run	not run
Fond du Lac	F08	Susceptible	2/13/2009	14.3	0.852	1	<1	0	0.104	0.104
Dodge	F09	Susceptible	3/2/2009	5.41	NS	1	NS	0	BD	BD
Dodge	F10	Susceptible	2/13/2009	13.2	0.574	>2419.6	285.1	816.4	0.150	0.150
Kewaunee	K01	Susceptible	2/17/2009	12.1	0.752	2	<1	0	BD	BD
Kewaunee	K02	Susceptible	2/17/2009	18.1	0.797	2	<1	0	0.112	0.112
Kewaunee	K03	Susceptible	2/17/2009	18.9	0.860	101.2	10.4	0	BD	0.025
Kewaunee	K04	Control	2/17/2009	2.73	0.832	2	<1	0	BD	0.019
Kewaunee	K05	Susceptible	2/17/2009	4.93	0.654	81.6	8.2	2	BD	0.020
Kewaunee	K06	Susceptible	2/17/2009	12.2	0.890	10.4	2	0	BD	BD
Kewaunee	K07	Susceptible	2/17/2009	11.5	0.417	274.8	10.4	0	BD	BD
Kewaunee	K08	Susceptible	2/17/2009	13.2	1.007	<1	<1	0	BD	0.035
Kewaunee	K09	Susceptible	2/17/2009	4.92	0.614	<1	<1	0	0.040	0.040
Kewaunee	K13	Control	2/17/2009	0.563	0.973	<1	2	0	BD	0.079

**NS* means a well was not sampled during this sampling period.

** *Unknown* refers to results that were unquantifiable due to cell death (as a result of groundwater sample toxicity). *BD* refers to results that were below the detection limits of the assay. *Not run* means the sample was not run through the E-screen assay.

Table 4: Results from the fourth sampling period (March 18-19, 2009).

County	Well ID	Group	Sample Date	Nitrate + Nitrate (mg/L N)*	Conductivity (mS/cm)	Coliform (MPN/100 mL)	Enterococci (MPN/100mL)	*E. coli* (MPN/100mL)	Escreen (EEq in pM)**, Above LOD	All Escreen Detects (Eeq in pM)
Brown	B02	Susceptible	3/19/2009	NS	NS	NS	NS	NS	NS	NS
Brown	B04	Susceptible	3/19/2009	12.6	0.672	727	24.6	3.1	BD	BD
Brown	B05	Susceptible	3/19/2009	17.3	1.006	261.3	7.5	3.1	BD	BD
Brown	B06	Susceptible	3/19/2009	14.9	0.999	17.1	<1	<1	BD	BD
Brown	B07	Control	3/19/2009	0.1	1.031	<1	<1	<1	BD	0.012
Brown	B08	Susceptible	3/19/2009	21.5	1.017	2	<1	<1	BD	0.031
Brown	B10	Control	3/19/2009	0.1	1.550	<1	<1	<1	not run	not run
Brown	B11	Susceptible	3/19/2009	22.5	1.530	<1	<1	<1	BD	BD
Brown	B12	Susceptible	3/19/2009	9.03	0.754	>2419.6	10.8	6.3	BD	BD
Brown	B14	Susceptible	3/19/2009	16.3	0.937	36.9	1	39.7	BD	BD
Calumet	C01	Susceptible	3/19/2009	14.4	0.865	<1	<1	<1	BD	BD
Calumet	C02	Susceptible	3/19/2009	13.2	0.604	25.9	<1	<1	BD	BD
Calumet	C03	Control	3/19/2009	0.1	0.387	<1	<1	<1	BD	0.069
Calumet	C04	Susceptible	3/19/2009	11.8	0.580	195.6	2	<1	BD	0.016
Calumet	C05	Control	3/19/2009	1.40	1.014	<1	<1	<1	BD	BD
Calumet	C06	Susceptible	3/19/2009	14.7	0.775	<1	<1	<1	BD	BD
Calumet	C10	Susceptible	3/19/2009	7.50	0.698	>2419.6	8.5	85.7	BD	BD
Calumet	C11	Susceptible	3/19/2009	7.12	0.753	816.4	<1	<1	BD	BD
Calumet	C12	Susceptible	3/19/2009	8.59	0.632	>2419.6	5.2	<1	BD	BD
Calumet	C15	Susceptible	3/19/2009	NS	NS	NS	NS	NS	NS	NS
Fond du Lac	F01	Susceptible	3/18/2009	2.71	0.884	461.1	4.1	<1	BD	BD
Fond du Lac	F02	Susceptible	3/18/2009	5.50	0.826	<1	<1	<1	BD	BD
Fond du Lac	F03	Control	3/18/2009	4.12	0.881	<1	<1	<1	BD	BD
Fond du Lac	F04	Susceptible	3/18/2009	NS	NS	NS	NS	NS	BD	BD
Fond du Lac	F05	Susceptible	3/18/2009	4.15	0.996	110.6	11.9	27.5	0.118	0.118
Fond du Lac	F06	Control	3/18/2009	0.272	0.589	<1	<1	<1	BD	BD
Fond du Lac	F07	Susceptible	3/18/2009	6.74	0.635	206.4	8.5	3.1	0.113	0.113
Fond du Lac	F08	Susceptible	3/18/2009	14.4	0.855	32.7	3	<1	BD	BD
Dodge	F09	Susceptible	3/18/2009	5.83	1.120	8.5	<1	<1	BD	BD
Dodge	F10	Susceptible	3/18/2009	11.5	0.832	46.4	2	<1	BD	BD
Kewaunee	K01	Susceptible	3/18/2009	9.09	0.735	23.1	<1	<1	BD	BD
Kewaunee	K02	Susceptible	3/18/2009	18.0	0.782	81.6	1	<1	BD	BD
Kewaunee	K03	Susceptible	3/18/2009	13.3	0.937	1046.2	123.6	36.2	BD	BD
Kewaunee	K04	Control	3/18/2009	3.83	0.909	<1	<1	<1	BD	BD
Kewaunee	K05	Susceptible	3/18/2009	2.75	0.392	>2419.6	579.4	27.5	BD	BD
Kewaunee	K06	Susceptible	3/18/2009	11.1	0.711	14.6	1	<1	BD	BD
Kewaunee	K07	Susceptible	3/18/2009	7.92	0.413	1732.9	248.1	1	BD	0.016
Kewaunee	K08	Susceptible	3/18/2009	12.8	1.017	80.9	<1	<1	BD	0.043
Kewaunee	K09	Susceptible	3/18/2009	5.67	0.629	<1	<1	<1	BD	0.017
Kewaunee	K13	Control	3/18/2009	0.730	1.087	<1	<1	<1	BD	BD

**NS* means a well was not sampled during this sampling period.
***BD* refers to results that were below the detection limits of the assay. *Not run* means the sample was not run through the E-screen assay.

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

Basic Information

Title:	Combination of Co-Precipitation with Zeolite Filtration to Remove Arsenic from Contaminated Water
Project Number:	2009WI216B
Start Date:	3/1/2009
End Date:	3/1/2011
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Congressional District:	WI 1st
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Focus Category:	Toxic Substances, Treatment, Groundwater
Descriptors:	
Principal Investigators:	Zhaohui Li

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3. Zhaohui Li, Andria J. Koski, Justin S. Merrill, Jeffrey J, Randolph, Stephan R. Kurdas, Jonathan H. Friend, Sarah J. Antinucci, Allison E. Reiley, Caren J. Ackley, Nancy A Fenske, Laura A . Schulz, Jiin-Shuh Jean, C.-C. Liu, A .H.M.S. Reza. 2010. Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred. Taylor Francis Group. Arsenic in the Environment.
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7. Li, Z., W.-T. Jiang, J.-S. Jean, H. Hong, L. Liao, G. Lv, (2011) Combination of hydrous iron oxide precipitation with zeolite filtration to remove arsenic from contaminated water, Desalination, 280, 203-207. DOI:10.1016/j.desal.2011.07.009

8. Liu C-C, J P Maity, J-J Jean, O Sracek, S Kar, Z Li, J Bundschuh, C-Y Chen, H-Y Li (2011) Biogeochemical interactions among arsenic, iron, humic substances, and microbes in mud volcanoes in southern Taiwan, J. Environ. Sci. Health Part A, 46, 1218-1230. http://dx.doi.org/10.1080/10934529.2011.598793
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Combination of Co-Precipitation with Zeolite Filtration to Remove Arsenic from Contaminated Water

Project Completion Report

By

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September 27, 2011

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Project Summary

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

Project ID: WR08R002

Investigators: Dr. Zhaohui Li, Professor of Geosciences, Department of Geosciences, University of Wisconsin – Parkside

Period of Contract: 07/01/2008 – 06/30/2010

Background/Need: Groundwater containing arsenic contamination imposes a great threat to people worldwide as well as to the residents of the state of Wisconsin. Developing new and cost-effective methods to remove arsenic from groundwater and drinking water becomes imminent. With several patents granted, using iron/aluminum hydroxide to remove arsenic from water is a proven technology. However, the key issue is the filtration media. Currently, the filtration media used were limited to sand, granular activated carbon, granular activated alumina, but not zeolite.

Objectives: In this research, zeolite was proposed to use as the filtration media to remove arsenic-containing iron hydroxide co-precipitates. The hypothesis was that zeolite had a larger surface area and higher cation exchange and sorption capacity, and the use of zeolite in lieu of sand media to filtrate the arsenic-containing iron hydroxide co-precipitates should be cost competitive to that of sand media while the performance would be much better than sand. Furthermore, due to an increase in capacity, less system faulting and less solid waste would be produced. In addition to removal of iron hydroxide co-precipitates, zeolite could also remove other undesired metal cations simultaneously.

Methods: Tests were conducted in batch, column as well as large 1-dimensional flow through system. Batch tests were focused Fe(II) and Fe(III) adsorption on zeolite, Fe(II) and Fe(III) removal by co-precipitation, initial Fe input on As removal, initial As input and As species on As removal by co-precipitation on iron hydroxide, the influence of solution pH on iron hydroxide co-precipitation formation. The column studies to were performed to investigate the efficiency of added Fe(III) to the removal of As in a continues flow system. Finally, a 1-dimensional large flow through system was used to test the As removal from syntehtic water, groundwater, as well as water from acid mine drainage to verify the batch and column test results. Aqueous concentrations of As, Fe^{TOT}, and solution pH were monitored with time for water quality.

Results and Discussion: Batch results showed that addition of $FeCl_3\cdot 6H_2O$ followed by addition of NaOH to elevate the solution pH to induce $Fe(OH)_3$ co-precipitation is an effective way to remove dissolved arsenic from water. Meanwhile, zeolite is a good sorbent for dissolved Fe(II) and Fe(III) with the calculated sorption capacity of 60 and 140 mmol/kg, respectively. Sorption of arsenic on Fe-modified zeolite was also strong with a sorption capacity of 100 and 50 mg/kg for As(III) and As(V) sorption on Fe-zeolite, respectively. Solution pH had a significant effect on arsenic sorption on Fe-zeolite. A drastic decrease in As sorption was found at pH 10 and above. On the contrary, the influence of solution pH on removal of As from water by co-precipitation of $Fe(OH)_3$ was different. When solution pH was lower than 6, removal of As was minimal due to minimal formation of $Fe(OH)_3$ precipitation. More over, when solution was above 10, arsenic becomes more mobile and will be less sorbed on $Fe(OH)_3$ precipitates. Thus, the optimal solution pH for As removal by co-precipitation was between 6 and 10. Efficiencies of As removal from water by $Fe(OH)_3$ co-precipitation was highly related to the amount of Fe added, thus, the amount of $Fe(OH)_3$ formed. On the contrary, the efficacy of the filtration system was reversely related to the amount of Fe added, i.e., system clogged more quickly as the amount of Fe added increased.

Large column tests using synthetic water and real water showed some interesting but also contradicting results. The co-precipitation followed by zeolite filtration method worked well for synthetic water with an initial As concentration of 1000 µg/L and Fe concentration of 1 mM with a 95% As removal up to 30 pore volumes (PVs). It also worked well for an acid mine drainage (AMD) water with an input As concentration of 147 µg/L and input Fe concentration of 101 mg/L with a non detectable effluent As concentration up to 20 PVs. On the other hand, the As removal was less effective for groundwater collected from Chia-Nan Plain that has an initial As concentration of 511 µg/L with minimal dissolved Fe. After addition of 0.2 mM Fe(III), the As removal was less than 40%, showing extremely inefficiency, possible due to the extremely reduced groundwater condition and the lower amount of Fe(III) added. Similar results were found for large column studies to remove As from water using Fe-zeolite as a sorbent.

Conclusions/ Implications/ Recommendations:

The research shows that addition of Fe(III) followed by raising solution pH to neutral and slightly alkaline conditions can effectively induce iron hydroxide precipitation. The precipitates could be removed by either sand filtration or zeolite filtration. The latter may cause some cloudiness for the water, i.e. an increased turbidity, in the beginning, due to large particle size, thus, large pore size, as well as the presence of fine particles. However, the system could maintain its long lasting filtration flow while the sand filtration system clogged quickly than the zeolite system, particularly for the removal of As from acid mine drainage after addition of NaOH to induce iron hydroxide precipitation. Although no clogging was found when zeolite was used, the cloudy water may impose a limitation to the method, particularly at the beginning of use. In addition, adding the correct amounts of Fe to produce minimal Fe precipitation with maximum As removal is also a challenge as it is affected by many factors such as solution pH and Eh, dissolved Fe and As concentration.

Related Publications:

Li,Z., Jean, J.-S., Koski*, A. J., Schulz*, L., Liu, C.-C., Reza, S., Merrill*, J. S., Randolph*, J. J., Kurdas*, S. R., Friend*, J. H., Antinucci*, S. J., Reiley*, A. E., Fenske*, N., Ackley*, C. (2011) Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred, *Environ. Earth Sci.*, under review after minor revision.

Key Words: Arsenic, Iron, co-precipitation, Sand, Filtration, Zeolite.

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Introduction

Arsenic (As) is a naturally occurring element present in soil and water. Three sulfide minerals, realgar, orpiment, and arsenopyrite, are the major contribution of As to soil and water. Known for centuries to be an effective poison, As is used in Chinese traditional medicines to cure several types of diseases. However, chronic uptake of As resulted in numerous As poisoning. Arsenic ingestion may result in internal malignancies, including cancers of the kidney, bladder, liver, lung, and other organs. Vascular system effects have also been observed, including peripheral vascular disease, which in its most severe form results in gangrene or Blackfoot Disease.

Arsenic poisoning is most common in developing countries such as Bangladesh and India, and some parts of China such as Inner Mongolia and Xinjiang. In just Bangladesh alone, it is estimated that drinking As-contaminated water could have harmed as many as 77 million people.

A significant number of investigations have been conducted to develop cost effect remediation technologies to remove arsenic from contaminated water. A recent study indicated that co-precipitation/adsorption consists of 80% of full-scale, aboveground treatment technologies for arsenic removal (USEPA, 2002). Co-precipitation/adsorption technique involves in reaction of $FeCl_3$ with water or hydroxide to form $Fe(OH)_3$ precipitates, which than absorb arsenate due to surface complexation.

$$\equiv FeOH^0 + AsO_4^{3-} + 3\,H^+ \rightarrow \equiv FeH_2AsO_4 + H_2O \quad (1)$$

$$\equiv FeOH^0 + AsO_4^{3-} + 2\,H^+ \rightarrow \equiv FeHAsO_4^- + H_2O \quad (2)$$

The precipitates of iron hydroxide containing sorbed arsenate can be separated from water using sand filtrations (Meng et al. 2001). In addition, in using the co-precipitation/adsorption technology, it is necessary to convert As(III) in to As(V), as trivalent arsenic occurs in non-ionized form and is not subject to significant removal. Several approaches, including UV radiation, oxidation by hydrogen peroxide, and by permanganate, have been tested. In addition to co-precipitation/adsorption methods, iron coated sand has been proposed as sorbents to remove arsenate from water (Joshi and Chaudhury, 1996).

Zero valent iron (ZVI) is effective in removal of arsenic from water (Su et al., 2001; 2003; Farrell et al., 2001). In bench-scale experiments conducted at the University of Colorado-Denver, two different arsenic concentrations (200 and 2000 μg/L) were tested with 3 different loadings of ZVI: 2.5 g, 1.25 g and 0.625 g ZVI per liter of water. At the lowest loading of 0.625 g of zero valent iron, > 90% arsenic removal was achieved with a contact time of 3 hours. A similar technology, Arsenic Remediation Technology (AsRT) was developed at the University of Connecticut to achieve 90% of As removal for over 1000 pore volumes of water.

More practically, a technology called 3-Kalshi was developed to treat arsenic contaminated water in Bangladesh (Khan et al. 2000). A "kalshi" is the clay water pitcher used for collecting water throughout Bangladesh. The top kalshi is made of 3 kg (about 1/6 kalshi volume) iron filings and 2 kg coarse sand. The combined media fills about 1/3 kalshi volume. The rest of the space contains source water for treatment. The middle kalshi is made of 2 kg of fine sand and 1 kg of wood charcoal of a consistent size. The combined media fills about 1/6 kalshi volume. The bottom kalshi is for collecting treated water. A Three-Gagri filter was similar to that 3-Kalsi Filter use to treat arsenic contaminated water in Nepal (Pokhrel et al. 2009). It consists of three clay pots staggered vertically with a 1 cm in diameter hole in the bottom of the middle and top filters. The top and middle filters work as a reactor, and the bottom filter stores the treated water. The top filter contains the following, from bottom to top: a layer of polyester cloth, 3 kg of iron nails (3 cm depth), 2 kg of coarse sand (4 cm depth) and raw water. The middle filter contains the following from bottom to top: a layer of polyester cloth, about 50 kg of brickbats, 2 kg of fine sand (3.5 cm depth), 1 kg of charcoal (6 cm depth), 2 kg of brickbats (3 cm depth), and filtered water from the top filter. The Three-Gagri filters were initially introduced in a limited scale in Nepal for arsenic removal. Studies showed that these filters could remove 95–99% of arsenic (Pokhrel et al. 2009).

In most of these techniques, sand packs were used as filtration to separate precipitates from water. Compared to sand, zeolites have larger surface area, large interparticle and intraparticle pores, which will be ideal as filtration media to remove iron/aluminum hydroxide precipitates. In addition, zeolite can remove other undesired cations by cation exchange while sand cannot. However, using zeolite as the filtration media to remove arsenic containing iron/aluminum hydroxide was not reported.

Natural zeolitic rocks have been evaluated to remove arsenic from waters at a concentration of about 100 µg/L. The removal efficiency was 60–80% for chabazite-phillipsite raw materials and 40–60% for clinoptilolite-bearing ones (Ruggieri et al. 2008). A large zeolitic content in the chabazite-phillipsite raw materials increase the As removal. Instead, the inverse situation is observed in the clinoptilolite-bearing rocks (Ruggieri et al. 2008).

Procedures and Methods

Chemicals

The arsenate and arsenite used were $Na_2HAsO_4 \cdot 7H_2O$ and $NaAsO_2$, both from Fisher Scientific Pittsburg, PA). The $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ used were from Katayama Chemical (Osaka, Japan).

Batch Fe(II) and Fe(III) adsorption on zeolite and batch As (III) and As(V) sorption on Fe-zeolite

To each 50 mL centrifuge tube, 1.0 g of zeolite and 20.0 mL of Fe(II) or Fe(III) solution at concentrations from 0.1 to 10 mmol/L were combined. The mixture was shaken at 150 rpm for 24 hours at room temperature (25ºC). Then the mixture was centrifuged at 5000 rpm for 10 min and the supernatant was passed through a 0.45 µm syringe filter before being analyzed for equilibrium Fe concentrations. The amount of Fe adsorbed was calculated from the difference between the initial and equilibrium concentrations.

For As sorption, 1.0 g of Fe-zeolite was mixed with 50 mL of arsenic solutions in 50 mL centrifuge tubes. The initial As concentrations were 0.1 to 20 mg/L. The mixture was shaken at 150 rpm for 24 hours. The mixture was allowed to settle and the supernatant analyzed for equilibrium As solution concentration. For kinetic study on As sorption, 1.0 g of Fe-zeolite was mixed with 20 mL of 0.5 mg/L As solution in 50 mL centrifuge tubes for varying amounts of time. The samples were centrifuged for 5 min and the supernatant passed through a 0.45 µm syringe filter before being analyzed.

Batch study on influence of pH, initial Fe and As input on As removal and equilibrium Fe concentration

To study the influence of solution pH, 178 mL of DI water and 2 mL of 100 ppm As (V) solution were added to a 250 mL Erlenmeyer flask. After 20 mL of 10 mM $FeCl_3 \cdot 6H_2O$ were added, the pH dropped to 3.10. Then the pH of the solution was slowly raised by adding 1 M NaOH.

To determine the influence of added Fe to the removal of As from water, 196 mL of DI water and 2 mL of 100 mg/L As (V) solution were added to a 250 mL Erlenmeyer flask. Then 10 mM Fe solution was added in 2 mL increment. Each time after addition of Fe, the pH was adjusted to a value between 7 and 9 and samples were taken for As analysis.

To determine the influence of input Fe to the final concentration of Fe in water, 100 mL of DI water and 0.1 mL of 100 mg/L As (V) solution were added to a 250 mL Erlenmeyer flask. Then 10 mM Fe solution was added at 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mL. After addition of Fe, the pH was adjusted to a value between 7 and 9 and samples were taken for Fe analysis.

Column study on removal of As by filtrating iron hydroxide precipitates

Each 60 mL syringe sleeve was filled with 50 mL with zeolites (about 50 g as the bulk density of zeolite is about 1 g/cm^3). To each 1 L of 0.1 mg/L As solution, 1, 3, or 10 mL of 10 mM Fe stock was added to reach a final Fe concentration of 10, 30 and 100 μM. The solution pH was raised to between 7 and 9 by adding 1 M NaOH drop-wise before being passed through the column. Similarly, quantitative Fe was added to a final concentration of 10 mM in 1 L of 1.0 mg/L As solution. The solution pH was raised to between 7 and 9 by adding 1 M NaOH before being passed through the column.

Modification of zeolite by Fe(III)

To each 500 mL centrifuge bottle, 120 g of zeolite and 360 mL of 20 mM Fe(III) solution was combined. The mixture was shaken at 150 rpm for 20 hours at room temperature before pH was measured and 2 M NaOH solution was added to raise the pH. This procedure was repeated every 2 hours for a total of three times to bring the final solution pH to 9. The mixture was allowed to settle and the supernatant removed, followed by washing the zeolite with 360 mL DI water. The chloride concentration of supernatant was checked with $AgNO_3$ until no white precipitation was made, which was confirmed after the zeolite was washed with 6 portions of DI water. The modified zeolite was allowed to dry naturally. Test of Fe in the supernatant was 0.15 mg/L less than 0.3 mg/L for the secondary water standard.

Large column tests

The large columns had a diameter of 4.5 cm or 5.0 cm and 70 cm in length. To each column, 400 g of 8-14 mesh zeolite or Fe(III)-modified zeolite was packed. In one test, 10 L of 100 μg/L As (V) solution was made. Then 270 mg of $FeCl_3 \cdot 6H_2O$ was added to make a final Fe concentration of 5.6 mg/L followed by addition of 3.1 mL of 1 M NaOH to raise the pH to 9.1. The mixture was stirred vigorously to induce precipitation and then passed through the column at a flow rate about 300 mL/min. Samples were taken every liter. For real water collected from groundwater from Chia-Nan Plain aquifer, the added Fe(III) was equivalent to 0.2 mM, or 11.2 mg/L. While for a water collected from an acid mine drainage, Fe(III) was not added, as it contains 101 mg/L of dissolved Fe already. Only pH was raised by adding appropriate amounts of NaOH. The flow rate was between 125 and 150 mL/min.

Chemical analysis

The total dissolved iron (Fe^{TOT}) was determined using Loviband MutiDirect Photometric System (The Tintometer Ltd., Dortmund, Germany) with an analytical range of 0.02 to 1.0 mg/L. Proper dilution was made for higher solution Fe^{TOT} concentrations. The As analysis was made on either PE Optima 7000 DV ICP-OES with a detection limit of 1 μg/L or PSA Millennium System Excalibur (PS Analytical Ltd., UK) with a detection limit of 0.1 μg/L.

SEM observation and Fe determination on zeolite

Observation under scanning electron microscope (SEM) was performed on JEOL JSM-840A, Japan at a voltage of 15 kV and a current of 0.4 nA. The elements analysis was made with energy dispersion spectrum Bruker XFlash detector 5010. Samples were coated with Au for SEM image observation and C for EDS element analysis.

Results and Discussion

Sorption of Fe (II) and Fe(III) on zeolite is plotted in Fig. 1. The zeolite has a higher affinity for Fe(III) than Fe(II). The results were modeled with both Langmuir and Freundlich sorption isotherms. For the Fe(III) adsorption both models fit the experimental data equally well with a coefficient of determination r^2 = 0.99 and 0.98, respectively. The calculated Fe(III) sorption capacity was 144 mmol/kg. On the contrary, the Langmuir sorption isotherms fit the experimental data better than the Freundlich sorption isotherm for De(II) sorption on zeolite with r^2 = 0.99 and 0.95, respectively. The calculated Fe(II) sorption capacity was only 58 mmol/kg (Fig. 1).

Sorption of As (III) and As(V) on Fe-zeoliete can be seen in Fig. 2. As(III) had a higher sorption on Fe-zeolite than As(V). The experimental data were modeled with both Langmuir and Freundlich sorption isotherms. For both As(III) and As(V) sorption the Freundlich sorption isotherm fit the experimental data better than the Langmuir sorption isotherm with r^2 = 0.99 and 0.85, respectively. The calculated As (III) and As(V) sorption capacity on Fe-zeolite was 100 and 50 mg/kg, respectively (Fig. 2).

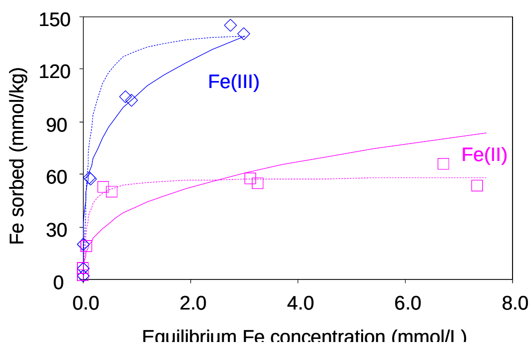

Fig. 1. Sorption of Fe(II) and Fe(III) on zeolite. The dashed lines are the Langmuir fits while the solid lines are the Freundlich fits to the experiment data.

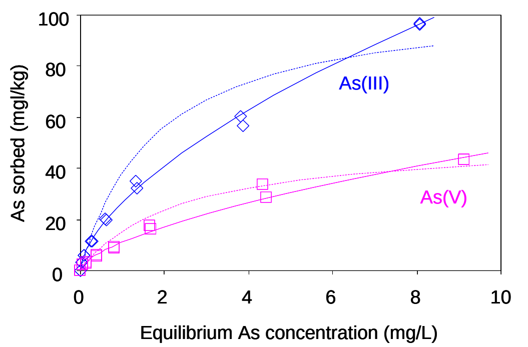

Fig. 2. Sorption of As(III) and As(V) on Fe-zeolite. The dashed lines are the Langmuir fits while the solid lines are the Freundlich fits to the experiment data.

The results of As sorption kinetic study were plotted in Fig. 3. The observed data were fitted to pseudo-first order and pseudo-second order reaction and the latter fit the experimental data better. The rate constants were 0.01 and 0.06 g/mg-h for As(V) and As(III) sorption on Fe-zeolite. The initial rates were 1.4 and 3.6 mg/g-h for As(V) and As(III) sorption on Fe-zeolite, respectively. Influence of equilibrium solution pH on As sorption on Fe-zeolite is plotted in Fig. 4. As(V) sorption was more or less constant at 11 mg/kg when solution pH was between 3 and 6. Further increase in solution pH caused significant reduction in As sorption. At pH 10, the amount of As(V) sorbed was only 2 mg/kg (Fig. 4). Sorption of As(III) on Fe-zeolite was somehow slightly different. Higher As(III) sorption was found at pH 6 to 9, above which significant decrease in As(III) sorption was also found. However, the As(III) sorption was lower at solution pH 3 to 5 compared to 6–9 (Fig. 4).

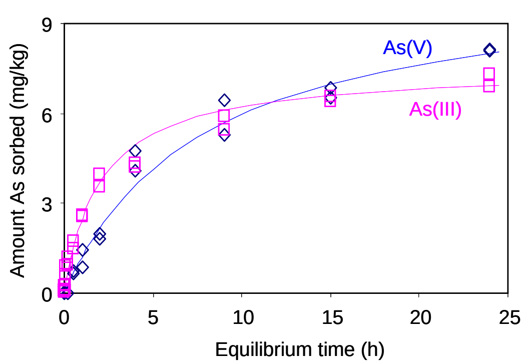

Fig. 3. Kinetics of As sorption on Fe-zeolite. The lines are pseudo-second order fits to the observed data.

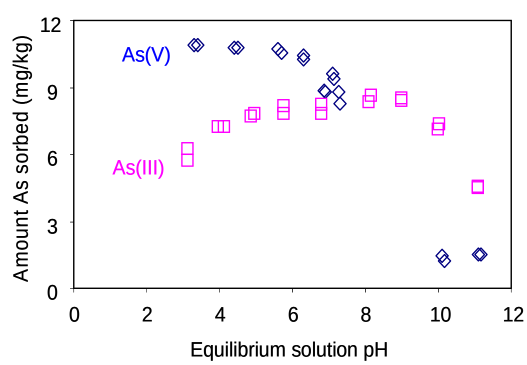

Fig. 4. Influence of equilibrium solution pH on As sorption on Fe-zeolite.

For As removal by $Fe(OH)_3$ co-precipitation, solution pH had strong influence on dissolved As concentration and Fe^{TOT}. When solution pH was 6.5–9.5, extensive precipitation of iron hydroxide occurred, which resulted in an Fe^{TOT} concentration much less than 0.3 mg/L (Fig. 5). Sorption of As(V) and As(III) on co-precipitated iron hydroxide is plotted in Fig. 6. The As sorption capacity is much higher than that on Fe-zeolite, with an initial Fe(III) concentration of 56 mg/L and the initial As concentration from 0.5 to 6 mg/L.

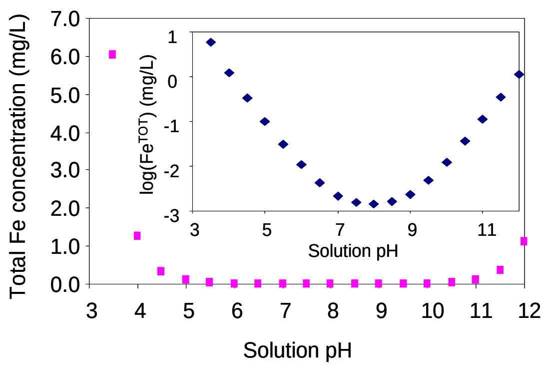

Fig. 5. Total Fe solution concentration as a function of solution pH. Fe removal was due to precipitation of iron hydroxide.

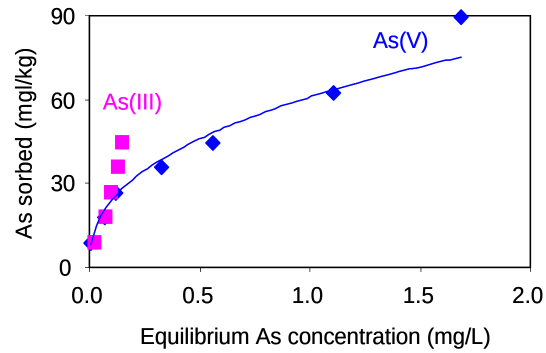

Fig. 6. As (III) and As(V) sorption on co-precipitated iron hydroxide.

The first test was to determine the amount of Fe needed at different initial As concentration. To 100 mL of 0.1 mg/L As solution, the amount of added Fe had an obvious effect on the equilibrium As concentration. However, the does of Fe used was not large enough to remove the As (Fig. 7a). Thus, a second trial with an initial As concentration of 1 mg/L and larger does of input Fe was made. It was anticipated that a minimum of 50 mg/L of Fe is needed to reduce an input As concentration from1 mg/L to 10 µg/L or below (Fig. 7b).

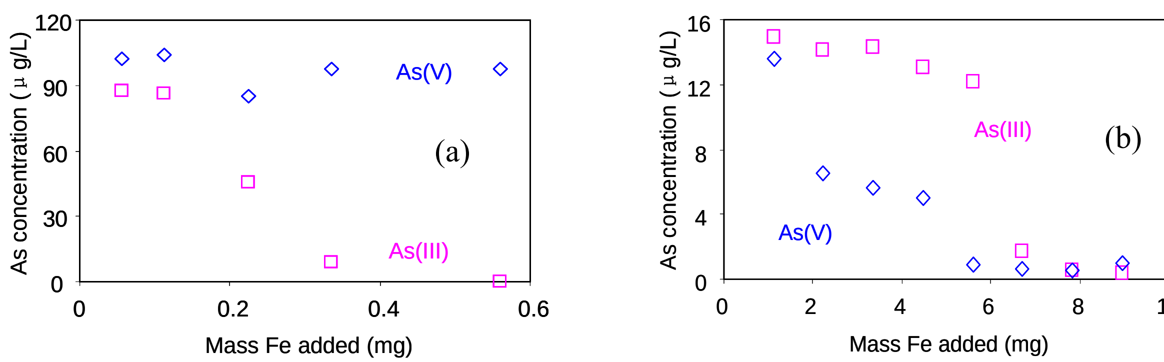

Fig. 7. Total Fe mass added per 100 mL of 0.1 mg/L (a) and 100 mL of 1.0 mg/L (b) As solution.

The solution As(V) and As(III) concentrations in batch co-precipitation tests were in the range of lower µg/L when the input As concentration was 1000 µg/L, a few hundreds, or even up to 1000 folds reduction in As concentration (Fig. 8). Again confirming that the maximum removal of As by co-precipitated iron hydroxide was in the pH 6.5 to 9 range.

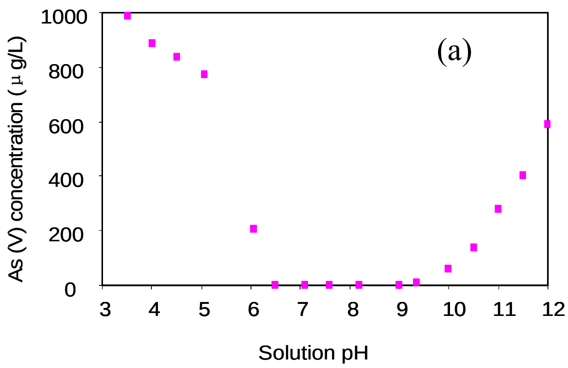

Fig. 8. As(V) (a) and As(III) (b) solution concentration as a function of solution pH. Arsenic removal was due to sorption onto iron hydroxide precipitation.

Small column tests were made to investigate the input Fe on As removal at an initial As concentration of 100 μg/L. The results showed that a minimum of 100 μM is needed to reduce the input concentration to 10 μg/L (Fig. 9). Better removal of As(V) was achieved compared to As(III).

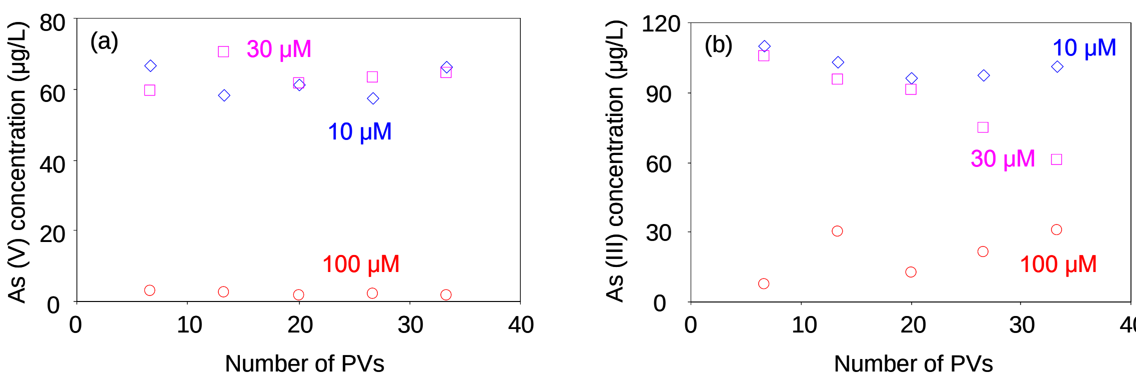

Fig. 9. Influence of added Fe^{TOT} on effluent As(V) (a) and As(III) (b) concentrations after iron co-precipitation followed by zeolite filtration. The initial As concentration was 100 μg/L.

Small column tests on As removal showed that at an initial concentration of 1000 μg/L, significant reduction in effluent As concentration could be achieved after addition of Fe(III) equivalent to 1 mM followed by inducing precipitation and then zeolite filtration (Fig. 10). The increase in As concentrations at 7 and 12 PVs in Fig. 9 was due to dry out of the columns. The effluent iron concentration was around 0.03 mg/L for all samples. Separately, at an initial As concentration of 100 μg/L, and an initial Fe concentration of 0.1 mM, after inducing iron hydroxide co-precipitation followed by infiltration through the zeolite column, the effluent As was below 10 μg/L up to 35 PVs (Fig. 10). The rise in effluent As concentration at 42 PV was due to column dry out. The effluent Fe concentration was below 0.3 mg/L up to 42 PVs (Fig. 11).

In comparison to Fig. 9, a column packed with course Ottawa sand was tested for As(V) removal at an initial concentration of 100 μg/L and different Fe(III) doses. A minimum of 30 μM of Fe(III) is needed to reduce the As(V) concentration to below 10 μg/L (Fig. 12). Separately, a sand column flushed with 1000 μg/L mixed with 1 mM of Fe(III) followed by inducing iron hydroxide precipitation is plotted in Fig. 13. A lower effluent As concentration could be achieve. However, due to the smaller pore size the system clogged quickly.

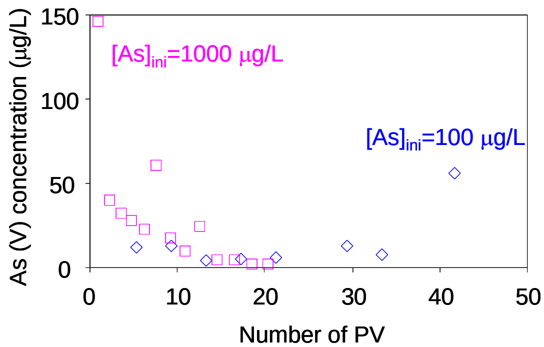

Fig. 10. Effluent As concentration from a zeolite column with input As and Fe concentrations of 1000 µg/L and 1 mM and 100 µg/L and 0.1 mM.

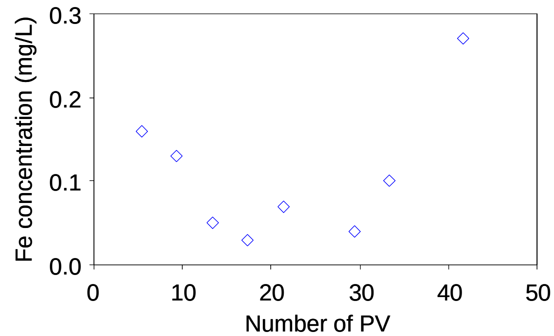

Fig. 11. Effluent Fe^{TOT} concentration from a zeolite column with input As and Fe concentrations of 100 µg/L and 0.1 mM.

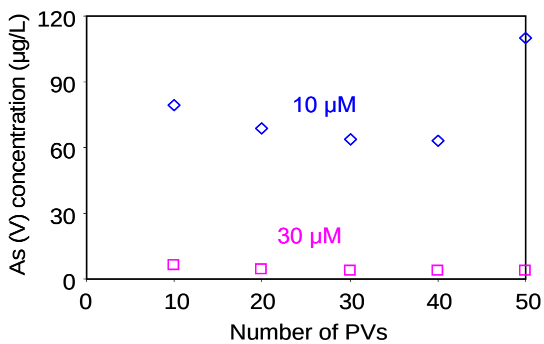

Fig. 12. Influence of added Fe(III) on effluent As(V) concentrations after iron co-precipitation followed by sand filtration. The initial As concentration was 100 µg/L.

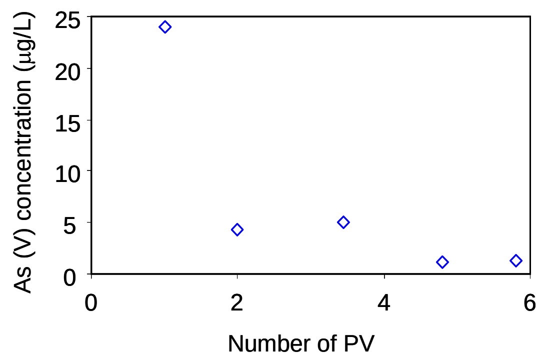

Fig. 13. Effluent As concentration from a sand column with input As and Fe concentrations of 1000 µg/L and 1 mM and 100 µg/L and 0.1 mM.

Based on the small column tests, large column tests were made for synthetic water, water from an acid mine drainage (AMD), and groundwater from Chia-Nan Plain. The As concentration in the AMD water was 147 µg/L while that of well water was 511 µg/L. Fig. 14 is the plot of effluent As and Fe from a synthetic water with an initial As(V) concentration of 1000 µg/L mixed with 0.1 mM Fe(III). Fig. 15 is the plot of effluent As concentrations after Fe co-precipitation followed by zeolite filtration for AMD and Well water. The effluent As concentration was all non detectable for AMD water. This could be attributed to the water containing significant amount of dissolved iron. The Fe(II) and Fe^{TOT} concentrations were 91 and 101 mg/L, respectively. Therefore, after addition of 55 to 70 mL of 1 M NaOH, significant amount of precipitation with black color was seen. This large amount of Fe precipitation may completely sorb the As from the water as its concentration was only 147 µg/L. On the other hand, removal of As from well water was not successful for the following reasons. The As concentration was as high as 511 µg/L. The water was under extremely reduced environment and the As species might be As(III). The amount of Fe(III) added may not be enough to remove significant amount of As from water or not enough to induce significant amount of $Fe(OH)_3$ precipitation.

Compared to co-precipitation followed by infiltration, the effluent As concentration leaching from the large Fe-zeolite column using AMD water and well water is plotted Fig. 16. The flow rate was between 125 and 150 mL/min. A similar observation was found, i.e. effluent of AMD water showed zero As concentration while that of well water showed substantial As concentration.

For the control of a large sand column, 800 g of coarse Ottawa sand was used. With a porosity of 0.3, the PV is about 250 mL, too. Thus, only 6 PVs were flushed before significant reduction in flow rate occurred. The effluent As concentration from the control column was zero.

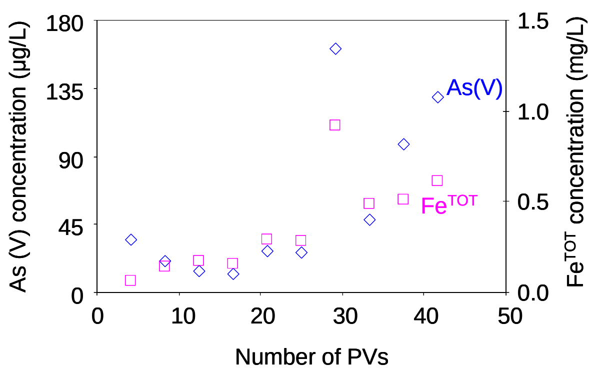

Fig. 14. Effluent As and Fe concentrations from a large zeolite column with input As and Fe concentrations of 1000 μg/L and 1 mM.

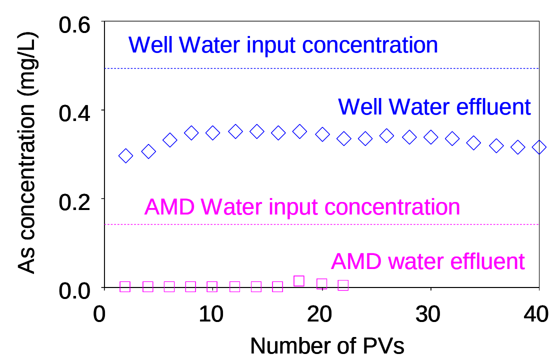

Fig. 15. Effluent As concentrations from a large zeolite column with input AMD and well water. Fe(III) added was equivalent to 0.2 mM for the well water.

SEM observation showed that the zeolite had euhedral crystals with particle size in the range of 10 μm (Fig. 17). The crystal morphology did not change after Fe modification (Fig. 17) or after As sorption (Fig. 18). However, fibrous minerals were formed after co-precipitation followed by zeolite filtration for the AMD water (Fig. 19). The $Fe(OH)_3$ precipitates were essential amorphous fine very fine particle size (Fig. 20). Its EDS spectrum showed the presence of As peak, confirming the adsorption of As on $Fe(OH)_3$ precipitates (Fig. 21)

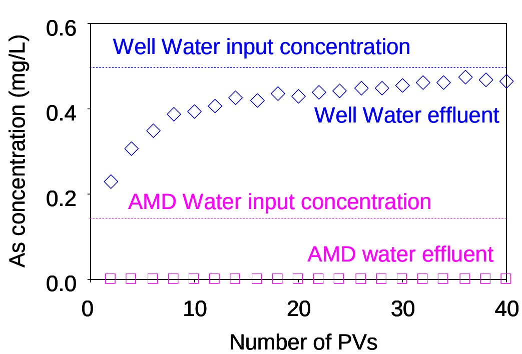

Fig. 16. Effluent As concentrations from a large Fe-zeolite column with input AMD and well water.

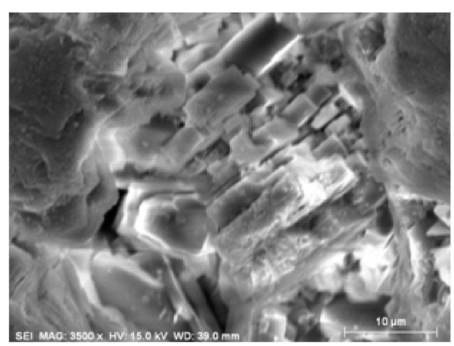

Fig. 17. SEM photo showing the euhedral clinoptilolite crystals.

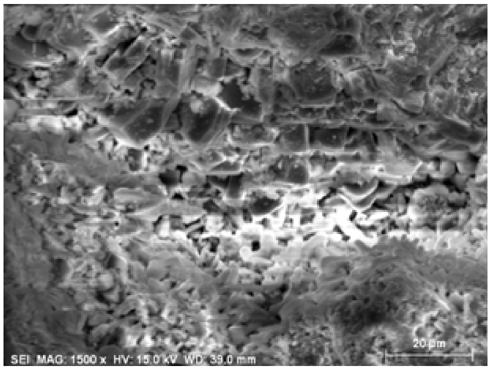

Fig. 18. SEM photo showing the euhedral clinoptilolite crystals in spent Fe-zeolite after As sorption.

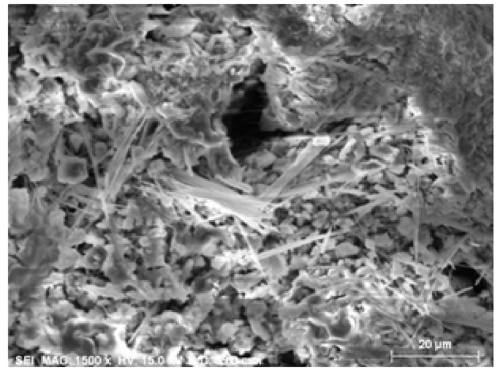

Fig. 19. SEM photo showing the euhedral clinoptilolite crystals and fibrous minerals in spent zeolite after As and Fe co-precipitation and filtration.

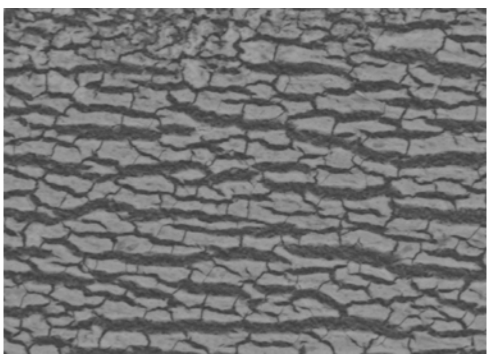

Fig. 20. SEM photo showing the fine particle size and dehydrated texture of $Fe(OH)_3$ precipitates.

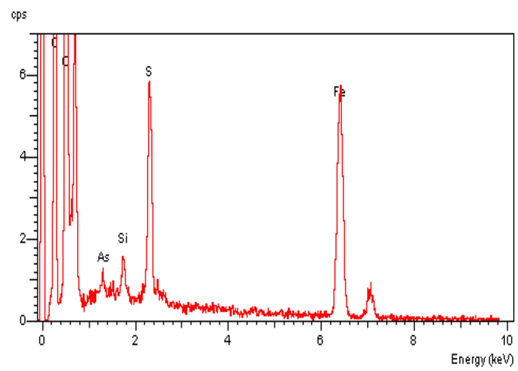

Fig. 21. EDS spectrum of Fe(OH)3 precipitates showing the presence of adsorbed As..

Conclusions and Recommendations

Removal of Arsenic from water can be achieved fairly effectively using Fe co-precipitation followed by zeolite filtration. This method works well if the water contains significant amount of dissolved iron and the water is not under extremely reduced condition. The precipitation of $Fe(OH)_3$ not only decreased the concentration of As in water, but also that of Fe, provided a good filtration system was maintained. However excess dissolved Fe would generation more precipitates once the pH of the water was adjusted between 6 and 9. More precipitation means that the system will get clogged quickly. Thus, optimizing the amount of Fe added to maximize As removal with minimal $Fe(OH)_3$ precipitation is more specific to each individual water. It requires preliminary measurement of a few field parameters such as pH, Eh, dissolved Fe (concentration), and maybe other chemical species that serve as Eh buffer to affect $Fe(OH)_3$ precipitation. A second issue is the cloudiness of the water after filtration with 4-14 mesh zeolite aggregates due to the fine particle size of each individual crystal of zeolite. More pilot tests are needed in order to assess the technology at a even larger scale. Nevertheless, this study provided preliminary data from batch and column tests to support the initial idea. And the simple and yet somehow effective technique may find its way to remove arsenic from water in a low cost manner in developing countries.

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Appendix A:

Journal Publications:

Li, Z., Hong, H., Jean, J.-S., Koski*, A. J., Liu, C.-C., Reza, S., Randolph*, J. J., Kurdas*, S. R., Friend*, J. H., Antinucci*, S. J. (2011) Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred, *Environ. Earth Sci.*, **64**, 823-831. http://dx.doi.org/10.1007/s12665-011-0938-7

Liu, C.-C. Maity, J. P., Jean, J.-J., Sracek, O., Kar, S., Li, Z., Bundschuh, J., Chen, C.-Y., Li, H.-Y. (2011) Biogeochemical interactions among arsenic, iron, humic substances, and microbes in mud volcanoes in southern Taiwan, *J. Environ. Sci. Health Part A*, **46**, 1218-1230. http://dx.doi.org/10.1080/10934529.2011.598793

Kar, S., Maity, J. P., Jean, J.-S., Liu, C.-C., Nath, B., Lee, Y.-C., Bundschuh, J., Chen, C.-Y., Li, Z. (2011) Role of organic matter and humic substances in the binding and mobility of arsenic in a Gangetic aquifer, *J. Environ. Sci. Health Part A*, **46**, 1231-1238. http://dx.doi.org/10.1080/10934529.2011.598796

Liu, C.-C., Maity, J. P., Jean, J.-S., Li, Z., Nath, N., Lee, M.-K., Reza, A.H.M. S., Lin, K.-H., Bhattacharya, P. (2011) Geochemical characteristics of the mud volcano Fluids in southwestern Taiwan and their possible linkage to elevated arsenic concentration in Chianan plain groundwater, *Environ. Earth Sci.*, re-revision in review.

Lv, G., Li, Z., Jiang, W.-T., Jean, J.-S., Hong, H., Liao, L., Lv, G. (2011) Combination of hydrous iron oxide precipitation with zeolite filtration to remove arsenic from contaminated water, *Desalination.*, **280**, 203-207. http://dx.doi.org/10.1016/j.desal.2011.07.009

Li, Z., Jean, J.-S., Jiang, W.-T., Chang, P.-H., Chen, C.-J., Liao, L. (2011) Removal of arsenic from water using Fe-exchanged zeolite, *J. Hazard. Mater.*, **187**, 318-323. http://dx.doi.org/10.1016/j.jhazmat.2011.01.030

Li, Z., Koski*, A. J., Merrill*, J. S., Randolph*, J. J., Kurdas*, S. R., Friend*, J. H., Antinucci*, S. J., Reiley*, A. E., Ackley*, C. J., Fenske*, N. A., Schulz*, L. A., Jean, J.-S., Liu, C.-C., Reza, A. H. M. S. (2010) Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred, *In* Jean, Bundschuh, Bhattacharya (eds.) *Arsenic in Geosphere and Human Diseases*, Taylor & Francis Group, London, p 553-555.

Hong, H., Yin, K., Lai, X., Du, Y., Li, Z., Jean, J.-S. (2010) Occurrence of Arsenic in Mudstone of the Endemic Blackfoot Disease Region, Taiwan, *In* Jean, Bundschuh, Bhattacharya (eds.) *Arsenic in Geosphere and Human Diseases*, Taylor & Francis Group, London, p 556-557.

Conference Presentation: (Both presentations are invited)

Li, Z., Koski*, A. J., Merrill*, J. S., Randolph*, J. J., Kurdas*, S. R., Friend*, J. H., Antinucci*, S. J., Reiley*, A. E., Ackley*, C. J., Fenske*, N. A., Schulz*, L. A., Jean, J.-S., Liu, C.-C., Reza, A. H. M. S. (2010) Characterization on arsenic sorption and mobility of the sediments of Chia-Nan plain, where black foot disease occurred, *Arsenic in Geosphere and Human Diseases*, The Third International Congress on Arsenic in the Environment, May 12 – 17, 2010, Tainan, Taiwan.

Li, Z. (2008) Sorption of arsenic by surfactant-modified zeolite and kaolinite, 2008 International Workshop on Arsenic and Humic Substances in Groundwater and Their Health Effects, May, 2008, Tainan, Taiwan.

Other Funding:

A grant award at the amount of 700,000 New Taiwan Dollar (equivalent to $22,000) was awarded to the collaboration among myself, Prof. Min-Kuo Lee from Auburn University and Prof. Jiin-Shuh Jean from National Cheng Kung University between Oct. 1, 2008 and Sept. 30, 2009. See attachment for email notice from the PI and the award letter (in Chinese) from the funding agency.

* Denotes undergraduate students from University of Wisconsin – Parkside.

Fw: 國立成功大學邁向頂尖大學計畫推動總中心函：國際合作計畫補助(案號：P97001)(不另送紙本)

簡錦樹 [jiinshuh@mail.ncku.edu.tw]

Sent: Sunday, December 28, 2008 10:51 PM

To: Ming-kuo Lee [leeming@auburn.edu]; Li, Zhaohui

Attachments: OriginalMsg.htm (19 KB) ; 國立成功大學邁向頂尖大學計畫推動總中心函113-P9~1.pdf (84 KB)

Dear Ming-Kuo and Zhaohui,

I am pleased to tell you that our application for the financial support for our international collaboration research program has been approved by NCKU as attached. However, only NT$700,000 of grant is allocated to this program, in which NT$140,000 should be used in personnel, NT$420,000 in inviting visiting professors to NCKU, and NT$140,000 used for me in travel expense to attend any conference abroad. These expenses must be fulfilled no later than September 15, 2009. The collaborative report should also be submitted to NCKU at that time.

Both of you can use NT$420,000 for a research at NCKU before September 15, 2009. I kindly invite both of you to attend the International Workshop on Arsenic and Humic Substances on May 11-12, 2009 at NCKU as we had in May 2008. At that time, I will also drill a well (~200m deep) along with 10 different depths of piezometers at Yichu where the groundwater in this area contains high arsenic concentration but without the incidence of any Blackfoot disease (BFD) cases before. This can lead us to compare the difference in groundwater quality between the Budai drilling sites with BFD cases before) and the Yichu drilling site without any BFD cases before. Each of you will share this much money, NT$210,000 each, whcih includes the round-trip flight ticket (economic-class) and living allowances (NT$8175/day for full professor and NT$6540/day for associate professor). Unfortunately, NCKU only pays the round-trip ticket to a graduate student, exclusive of living allowances. I would like to know how long you will stay at NCKU.

I look forward to hearing from you.

Happy New Year!

with best wishes,
Jiin-Shuh

----- Original Message -----
From: 陸美蓉
To: 龔慧貞 ; 饒瑞鈞 ; 羅尚德 ; 簡錦樹 ; 蔡金郎 ; 劉正千 ; 楊懷仁 ; 黃奇瑜 ; 游鎮烽 ; 陳燕華 ; 袁彼得 ; 翁偉嘵 ; 孫鎮球 ; 林慶偉 ; 李紅春 ; 吳銘志 ; 江威德 ; jennifer kung ; 楊耿明
Cc: 賴美婷
Sent: Thursday, December 25, 2008 5:27 PM
Subject: Fw: 國立成功大學邁向頂尖大學計畫推動總中心函：國際合作計畫補助(案號：P97001)(不另送紙本)

> Subject: 國立成功大學邁向頂尖大學計畫推動總中心函：國際合作計畫補助(案號：P97001)(不另
送紙本)
>

國立成功大學邁向頂尖大學計畫推動總中心 函

承辦單位：邁向頂尖大學推動總中心國際化組
聯絡方式：蘇郁雅 (06)2757575 轉 50995
電子信箱：yuya@mail.ncku.edu.tw

受文者：如正副本單位

發文日期：中華民國 97 年 12 月 17 日
發文字號：(97) 頂 國 字第 113 號
速別：
附件：

主旨：有關教授申請簽訂國際合作計畫補助乙案，審查結果詳如說明，請　查照。

說明：

一、 本案已依「發展國際一流大學及頂尖研究中心計畫簽訂國際合作計畫補助要點」，於 97 年 12 月 15 日完成審查。

二、 本案簽約之國際合作計畫三方皆含有經費，合作總經費總計 NTD$10,500,008 元，年平均經費 NTD$5,250,004 元

三、 依本校「發展國際一流大學及頂尖研究中心計畫簽訂國際合作計畫補助要點」，本案擬予以<u>補助新台幣 70 萬元</u>，本項經費限使用於一般業務費用(如邀請國外學者來訪及舉辦國際研討會)，不可用於執行計畫。另，人事費用僅可支應工讀金及獎助金，且人事費之額度不得超過補助金額之 20%、業務費不得超過補助金額之 60%、差旅費不得超過補助金額之 20%。

四、 本案之補助經費將儘速核撥至　貴單位之分配經費項下(D97-3200)，並同時函知　貴單位及相關行政單位，以便經費之使用及核銷。

五、 本組將保留補助經費之 25%，待 98 年 9 月 15 日前繳交中英文成果報告書(含電子檔)及經費使用明細，於確認無誤後，剩餘經費再行撥款。

六、 依教育部規定，一案不得由同一部會的不同經費來源共同補助。故凡已獲教育部部分補助之申請案，原則上不得再由本計畫予以補助。如獲本計畫之補助，且同時獲得其他政府部會補助者(如國科會、經濟部、農委會等)，於經費核銷時，亦須明列各不同經費來源之詳細經費分攤。

正本：地球科學系簡錦樹教授

副本：理學院、地科系、邁向頂尖大學計畫推動總中心國際化組

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

Basic Information

Title:	Grant No. G09AP00068 Influence of Coupling Erosion and Hydrology on the Long-Term Performance of Engineered Surface Barriers
Project Number:	2009WI245S
Start Date:	5/15/2009
End Date:	8/31/2012
Funding Source:	Supplemental
Congressional District:	WI-2
Research Category:	Engineering
Focus Category:	Management and Planning, Models, Hydrology
Descriptors:	
Principal Investigators:	Anders W. Andren, Craig H Benson

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 3/1/2011 - 2/29/2012

Submitted By: Craig Benson
Submitted: 5/25/2012

Project Title

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

Project Investigators

Craig Benson, University of Wisconsin-Madison

Progress Statement

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

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

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

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

We conducted a literature review on models for simulating erosion processes and evaluated a collection of models used to simulate variably saturated flow for cover systems. We selected the SIBERIA model for simulating erosion and the SVFLUX model for simulating variably saturated flow.

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

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

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

FINDINGS TO DATE

• In semi-arid and humid climates, comparable erosion control can be achieved with riprap surfaces and gravel-amended surfaces, although maximum erosion is slightly lower with a riprap surface (see next slide).

• In semi-arid and humid climates, erosion on gravel-amended surfaces is less sensitive to the geometry of the slope (angle, length, grade change) than for a riprap surface.

• In semi-arid and humid climates, terracing reduces erosion relative to that on concave slopes. The shorter length of the steeper sections combined with step grade changes in a terrace reduces head cutting and erosion.

• In semi-arid climates, deep concave side slopes have reduced maximum erosion and less average elevation change than uniform side slopes. Sediment trapping at the base of the concave slope diminishes erosion.

• Maximum erosion is not systematically related to type of climate. The magnitude of episodic events and antecedent conditions prior to episodic events have a greater influence than "wetness" of climate.

• Average erosion is consistently greater in the semi-arid climate than in the humid climate. Erosion occurred in a more widespread and distributed manner in a semi-arid climate and more as gullies in a humid climate.

• Covers with gravel-amended surface layers consistently transmitted less percolation than covers with a riprap surface (see next slide).

• A riprap surface funnels water into the underlying soils, and then traps the water in the underlying soils via a capillary break. More water is stored in the cover, and more percolation occurs (water "harvesting").

• A gravel-amended surface limits infiltration due to its lower saturated hydraulic conductivity, and permits a capillary conduit for water removal via evapotranspiration. Less water enters and is stored in the cover, and less percolation occurs.

• A cover with a gravel-amended surface layer undergoes comparable erosion, but transmits less percolation, than a riprap cover.

PROJECT STATUS

• Calibration with field information from literature is complete.

• Modeling is 90% complete. Some re-runs are being conducted to address uncertainty about mechanisms as sections of report are being prepared.

• Final report has been drafted and is 70% complete. Expect submission in late summer 2012

Principal Findings and Significance

Principal Findings and Significance

Description This project will result in design methodologies for more sustainable and effective cover systems. New cover system profiles will be developed as an outcome of this study. These profiles will be more resistant to erosion and more effective in limiting percolation into underlying waste. As a result, they will require less maintenance and be more effective in protecting groundwater.

Awards, Honors & Recognition

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

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

.....

Title	Award of Merit
Event Year	2011
Recipient	Craig H. Benson
Presented By	ASTM
Description	

.....

Title	National Academy of Engineering
Event Year	2012
Recipient	Craig H. Benson
Presented By	National Academies
Description	PI was elected to NAE in January 2012, with a citation to his work related to long-term containment of low-level radioactive wastes.

Partners

Name/Organization	
Affiliation	US Department of Energy/CRESP
Affiliation Type	Federal
Email	
Description	

.....

Name/Organization	
Affiliation	US Department of Energy/Legacy Management
Affiliation Type	Federal
Email	
Description	

Students & Post-Docs Supported

Student Name	Chris Bareither
Campus	University of Wisconsin-Madison
Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison
Degree	Post Doc
Graduation Month	
Graduation Year	
Department	Geological Engineering
Program	
Thesis Title	
Thesis Abstract	

.....

Student Name	Crystal Smith
Campus	University of Wisconsin-Madison

Advisor Name	Craig Benson
Advisor Campus	University of Wisconsin-Madison

Degree	Masters
Graduation Month	August
Graduation Year	2012
Department	Geological Engineering
Program	Geological Engineering
Thesis Title	NA
Thesis Abstract	NA

Fecal Source Tracking Using Human and Bovine Adenovirus and Polyomaviruses

Basic Information

Title:	Fecal Source Tracking Using Human and Bovine Adenovirus and Polyomaviruses
Project Number:	2009WI308O
Start Date:	7/1/2009
End Date:	3/1/2011
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Agriculture, Hydrology, Toxic Substances
Descriptors:	
Principal Investigators:	Joel Alexander Pedersen, Sharon C Long, Trina McMahon

Publication

1. Sibley SD, and JA Pedersen (2011) Detection of Known and Novel Adenoviruses in Cattle Wastes via Broad-spectrum Primers. Appl. Environ. Microbiol., 77:5001-5008.

Fecal Source Tracking Using Human and Bovine Adenovirus and Polyomaviruses

WRI Project Number WR09R002

Investigators:

Prof. Joel A. Pedersen (PI), UW-Madison, Soil Science, Environmental Chemistry & Technology

Prof. Katherine D. McMahon (Co-PI), UW-Madison, Civil and Environmental Engineering

Prof. Sharon Long (Co-PI), Wisconsin State Laboratory of Hygiene

Dr. Samuel D. Sibley, Post-Doctoral Research Associate, UW-Madison, Soil Science.

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PROJECT SUMMARY

Title: Fecal Source Tracking Using Human and Bovine Adenovirus and Polyomaviruses

Project I.D.: WRI Project Number WR09R002

Investigators:

Dr. Joel A. Pedersen (PI), UW-Madison, Soil Science, Environmental Chemistry & Technology
Dr. Katherine D. McMahon (Co-PI), UW-Madison, Civil and Environmental Engineering
Dr. Sharon Long (Co-PI), Wisconsin State Laboratory of Hygiene
Dr. Samuel D. Sibley, Post-Doctoral Research Associate, UW-Madison, Soil Science.

Period of Contract: July 1, 2009 – June 30, 2011

Background and Need: Many Wisconsin residents have as their immediate source of water a private well that has a contemporary record of suspected fecal contamination (based on repeated detection of *Escherichia coli* in well water samples). The simple *detection* of commonly targeted fecal indicator bacteria, like fecal coliform bacteria and *E. coli*, provides little information about contamination source(s) (e.g., human vs. livestock), and dedicated resources are typically lacking for more thorough investigations that may elucidate the sources of groundwater contamination. Accordingly, need exists for (i) the investigation of microbial indicators, such as host-specific adenoviruses (AdV) and polyomaviruses (PyV), whose detection in groundwater provides information on contamination sources, and (ii) the exploration of methods for collecting and detecting source-diagnostic microorganisms in groundwater samples from such "problem wells."

Objectives: The objectives of this study were: (1) to ascertain the utility of bovine AdV (BAdV) and bovine PyV (BPyV) as fecal contamination indicators by determining their prevalence in cattle wastes; (2) to quantify the efficiency of hollow fiber ultrafiltration (HFUF) for concentrating viruses from natural groundwater; and (3) to evaluate the likelihood that AdV and PyV will be detected and prove useful for fecal source attribution in private groundwater samples deemed vulnerable to fecal contamination.

Methods: Human and animal waste samples collected in southern Wisconsin were investigated for human and bovine AdV and PyV using both previously published and novel polymerase chain reaction (PCR) assays. Subsequently, selected PCR methods were applied to groundwater samples for fecal source attribution. Between March 2010 and February 2011, groundwater samples (~115 L, each) were collected by HFUF from eleven households with contemporary records of suspected fecal contamination; five of these homes were sampled on three to four separate occasions. The bacteriophage, PDR1, an enteric virus surrogate, was injected into the HFUF system during sample collection. The recovery of this virus was quantified by TaqMan® PCR to indicate the overall method efficiency of virus concentration and analysis. Groundwater samples concentrated by HFUF were analyzed for coliform bacteria, *E. coli,* livestock and human AdV and PyV, and *Rhodococcus coprophilus*, an indicator of grazing herbivore fecal contamination. Twenty-eight additional groundwater samples (≤ 600 mL) were concentrated and assayed by PCR for bovine BAdV-10 and BPyV-1 to evaluate the utility of analyzing low-volume samples for viral indicators. These samples were submitted to the Wisconsin State Laboratory of Hygiene by the Wisconsin Department of Natural Resources for microbial source-tracking (MST) analysis in response to home-owner water-quality complaints.

Results and Discussion: Using original, "broad-spectrum" PCR primer sets designed to detect an array of known and previously unidentified AdV and PyV, BAdV were detected in 13% of cattle fecal samples, 90% of cattle urine samples, and 100% of cattle manure samples; 44% of BAdV-positive samples contained DNA from two genetically distinct AdV genera, *Atadenoviridae* and *Mastadenoviridae*. BPyV were detected less frequently than BAdV in these samples, at rates of 17% in cattle feces, 14% in cattle urine and 73% in cattle manure. Four previously unknown bovine viruses were detected, three BAdV and one BPyV. Shedding rates by cattle for two specific bovine viruses, BAdV-10 and BPyV-1, supported targeting these viruses for fecal source attribution.

For private groundwater samples, the recovery of exogenous bacteriophage PRD1 by HFUF varied considerably within and between sites (0-113%). Samples with visible iron solids in HFUF concentrates demonstrated, on average, lower PRD1 recoveries (3 ± 5%, n = 8) compared with samples with no apparent iron in HFUF concentrates (23 ± 33%, n = 13), though the difference was not statistically significant (p = 0.116). The effective groundwater volumes analyzed by PCR (per 5 µL DNA extract) were 1500 mL, 256 mL or 48 mL for samples with PRD1 recoveries of 100%, 16% or 3%, respectively. Of the 24 private groundwater samples collected by HFUF, 17 were positive for coliform bacteria, eight were positive for *E. coli*, six were positive for *R. coprophilus* and three were positive for at least one viral indicator (AdV or PyV) of fecal contamination. A single viral indicator was detected at two of the five sites targeted for repeated sample collection. Of the six homes where groundwater was collected only once, one was positive for two viral markers. The detection of corroborating host-specific microbial markers is required for confident source attribution. Therefore, only for the latter site (Site R, for Rock County) could an actionable contamination source, human, be reliably attributed. Subsequent site investigation by the WI Department of Natural Resources revealed a compromised pipe in the home owner's septic system. An additional site (Site 3) showed "animal/non-human" contamination, supported by the detection in the same HFUF concentrate of an animal AdV of unknown host and *R. coprophilus*. More confident source attribution was possible for several of the low-volume groundwater samples submitted to the WSLH: 8/28 samples were positive for BPyV-1; four of these eight were also positive for BAdV-10. The effective groundwater volume analyzed by PCR for these low-volume groundwater samples was 1 to 10 mL for virus recoveries ranging from 10 to 100%, respectively.

Conclusions and Recommendations: Human AdV and PyV, BAdV-10 and BPyV-1 were detected in groundwater samples collected from private wells, demonstrating their utility as fecal source indicators. Groundwater samples collected using HFUF showed large concentration factors (~10^4) and were often contaminated by coliform bacteria. However, in most cases, even the concentration of large sample volumes did not reveal sources or overcome the intermittent nature of groundwater contamination by fecal materials. On the other hand, despite low volumes, samples analyzed in response to immediate home-owner complaints frequently yielded positive results for bovine viral indicators, resulting in definitive source attribution. Therefore, the concentration and analysis of these types of groundwater samples for AdV and PyV is recommended. Where potentially contaminated groundwater presents an immediate and unacceptable risk to human health (e.g., for vulnerable wells serving daycare facilities, nursing homes, or communities), the application of the simple HFUF method described here is also recommended. For example, at Site R, human viruses were detected in HFUF concentrate with low measured PRD1 recovery, but were absent in a 400-mL sample collected and processed in parallel. Additional optimization of HFUF methods for processing groundwater samples is advised. In particular, assessing the utility of beef extract or peptone solutions for concentrate recovery would streamline sample processing and may improve recoveries.

Related Publications:

Sibley, S.D., T.L. Goldberg and J.A. Pedersen. 2011. Detection of Known and Novel Adenoviruses in Cattle Wastes via Broad-spectrum Primers. *Appl. Environ. Microbiol.*, **77**:5001-5008.

"*Testing Well Water for Microorganisms*." Fall/Winter 2010, Aquatic Sciences Chronicle, University of Wisconsin Sea Grant and Water Resources Institute.

Key Words: Adenovirus, polyomavirus, microbial source tracking, groundwater, feces, manure.

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INTRODUCTION

Many rural homeowners have as their immediate source of water a private well that has a contemporary record of suspected fecal contamination (based on repeated detection of *Escherichia coli* in well water samples). Unfortunately, the simple *detection* of commonly targeted fecal indicators, like fecal coliforms and *E. coli*, provides little information about contamination source(s) (e.g., human vs. livestock), and dedicated resources are typically lacking for more thorough investigations that may elucidate the sources of groundwater contamination. To address these concerns, need exists to (i) investigate microbial indicators, such as host-specific viruses, whose detection in groundwater provides reliable information on contamination sources, and (ii) explore methods to concentrate and detect source-diagnostic microorganisms in groundwater samples from such "problem wells."

Adenoviruses (AdV) and polyomaviruses (PyV) have been advocated as potentially valuable, microbial indicators of fecal contamination (Hundesa et al., 2006). For both groups of viruses, species (or genotypes) infecting specific human or livestock hosts exist; many of these species have been detected in excreta of asymptomatic individuals and/or in aggregated waste samples (Maluquer de Motes et al., 2004; McQiaig et al., 2006, 2009). Because DNA viruses, such as AdV and PyV, are thought to co-evolve with their hosts (Pérez-Losada et al., 2006), PCR assays can be designed to target specific virus gene segments (e.g., capsid protein genes) that differ significantly, depending on host species. When properly designed, these PCRs can be invaluable for attributing source(s) of fecal contamination. However, the majority of research targeting viruses for fecal source attribution has focused on human viruses, in part because more complete information is available on the diversity and ecology of human (vs. livestock or wildlife) viruses that cause mild or asymptomatic infections (i.e., those viruses that are most promising for source tracking). Prior to this study, eleven distinct bovine adenoviruses (BAdV) and one bovine polyomavirus (BPyV) had been identified (Schuurman et al., 1990; Lemkuhl and Hobbs, 2008). The detection of several of these viruses in bovine excreta (Maluquer de Motes et al., 2004, Wong and Rose, 2009) encouraged their consideration as specific indicators of livestock fecal contamination.

Even with a reliable viral fecal source tracking (FST) PCR assay in hand, a significant challenge remains: fecal contamination of groundwater is expected to be intermittent, and the concentrations of fecal microbes (viruses, in particular) in aquifers may be small and variable. Therefore, it is commonly accepted that large sample volumes (e.g., 50- to 500-L) must be concentrated to capture a sufficient number of viruses to be detectable by molecular methods (Lambertini et al. 2008; Smith and Hill, 2009; Knappett et al., 2011). Thus, the optimization of methods for collecting viruses from a large water sample while eliminating (or reducing the influence of) compounds (e.g., inorganic colloids, dissolved organic matter) that interfere with molecular virus detection is a fundamental hurdle in nearly all current FST investigations of surface water and groundwater. Several methods have been advocated for concentrating groundwater samples. However, most of these have been primarily (or exclusively) validated in laboratory settings and usually without explicit consideration for how the methods might be implemented efficiently in a field setting by anyone other than the a highly trained practitioner. One of the most promising, yet challenging, methods in this category is hollow fiber ultrafiltration (HFUF).

Hollow fiber ultrafiltration is a size-exclusion method for concentrating microorganisms. Water under pressure is forced into ("dead-end" format; Smith and Hill, 2009) or cycled through ("tangential flow" format; Hill et al., 2005) a sterile, prepackaged hemodialysis filter containing thousands of hollow, porous plastic fibers. Water exits the filter through pores (30 kDa molecular weight cutoff, ~5 nm) in the fiber sidewalls, while particles, including microorganisms and other natural colloids, are retained. Laboratory investigations of HFUF in dead-end and tangential flow formats have been completed by the Centers for Disease Control and others for the detection of microbial pathogens in water (Hill et al., 2005). Recently, HFUF was employed *in situ* for the concentration of microorganisms in surface water (Leskinen and Lim, 2008) and groundwater (Gibson and Schwab, 2011; Knappett et al., 2011). Yet, few environmental investigations have employed the simpler "dead-end" filtration format, which requires little operator training, is conducive to rapid response implementation for field sampling (Smith and Hill, 2009).

The objectives of this study were: (1) to ascertain the utility of bovine AdV (BAdV) and bovine PyV (BPyV) as fecal contamination indicators by determining their prevalence in cattle wastes; (2) to quantify the efficiency of hollow fiber ultrafiltration (HFUF) for concentrating viruses from large natural groundwater samples; and (3) to evaluate the likelihood that AdV and PyV will be detected and prove useful for fecal source attribution in private groundwater samples deemed vulnerable to fecal contamination. Human and animal waste samples collected in southern Wisconsin were investigated for human and bovine AdV and PyV using both previously validated and novel PCR assays. Subsequently, selected PCR methods were used to detect AdV and PyV in groundwater samples collected from private wells with demonstrated or suspected fecal contamination.

PROCEDURES AND METHODS

Excreta Sample Collection. Catch samples of dairy and beef cattle (*Bos primigenius taurus*) feces (n = 32) and urine (n = 21) were acquired opportunistically from individual animals between August 2008 and January 2010; eleven dairy cows provided paired fecal and urine samples. Eleven additional manure samples (i.e., mixed wastes, including feces and urine, from multiple cattle) were obtained: one sand-separated, dewatered manure sample, three bedding samples, two liquid manure lagoon samples, and five bedding-percolate samples. Waste samples from several additional animal species were examined for comparison. Five human sewage samples were collected from the 9-Springs wastewater treatment facility (Madison, WI). All excreta samples were collected in sterile containers, transported on ice, and stored for < 1 week at 4 °C or at -80 °C until analysis (except for one liquid manure sample, which was held at 4º C for approximately one year until analysis).

Dead-end Hollow fiber Ultrafiltration System. The HFUF system (Figure 1) employed a REXEED-21S hemodialysis filter (Asahi Kasei America Inc.) housing thousands of polysulfone hollow fibers (26.6 cm length, 185 µm inner fiber radius; 30-kDa molecular weight cutoff; 2.1 m^2 total surface area). The HFUF system was configured to accept flow directly from a common garden hose connection, allowing continuous concentration of an arbitrary sample volume from most private wells. During sample collection, the filter was positioned vertically and operated in the "dead-end" configuration (Leskinen and Lim, 2008; Smith and Hill, 2009) by keeping the filter outlet port capped. Groundwater fed by the home's water pressure into the filter inlet port was driven laterally through pores in the hollow fibers, achieving permeate flow rates of ~2 L min^{-1} at ~13 psi (controlled at the faucet). Platinum-cured silicone tubing was used (VWR International, no. 60985-730, 60985-738), and tubing-tubing connections were completed with interchangeable male/female polyethylene quick-disconnects (Bel-Art Scienceware, no. 197280000, 197290000). The male connectors in this series fit securely into the filter inlet and outlet ports and were used to equip the HFUF with a standard, leak-free barbed fitting for connecting tubing. To minimize microbe aggregation, a filter-sterilized (Corning, 430015) dispersant/chelating solution consisting of either (A) 10% sodium polyphosphate (NaPP, Sigma Aldrich), (B) 10% NaPP/7.5% EDTA or (C) 0.5 M EDTA was added continuously during filtration via syringe pump, operated at 2 mL min^{-1}. Considering a filtration rate of 2 L min^{-1}, the dispersant was diluted 1000-fold into the influent groundwater sample.

Groundwater Sample Collection by Hollow fiber Ultrafiltration. Between March 2010 and February 2011, 28 groundwater samples (~120 L, each) were collected by HFUF from twelve private wells; five of these wells were sampled on three to four separate occasions (Figure 2). Well selection was informed by state officials familiar with site histories. Samples were typically collected from an outdoor garden hose faucet, which was purged until electrical conductivity, temperature, pH and dissolved oxygen concentrations, measured with a YSI 556 multiprobe, stabilized (typically 10-15 min). The HFUF system was connected to the faucet with the filter outlet port open to purge the filter of storage solution. The filter outlet port was then capped, and the syringe pump feeding dispersant was activated. During filtration, system pressure was maintained at 13 ± 3 psi by adjusting the regulator on the home's faucet, and dispersant was refilled as needed. To reduce system pressure fluctuations, home owners were advised to limit water use during sample collection. Where water flow was poorly regulated by the home's existing fixture, a simple flow regulator was mounted to the faucet prior to initiating sample collection.

Following filtration of the first 60 L, 100 µL of PDR1 stock (strain D4; HER 23, Laval University) was suspended in 10 mL of ultrafiltered groundwater (collected from a tubing junction installed downstream of the permeate port) and injected (21G needle) through alcohol-swabbed tubing into the HFUF system upstream of the filter. PRD1 stocks were generated on *Salmonella enterica* serovar

Typhimuadditirium (strain LT2 pLM2 1217; Laval University), and the 100 µL addition was titered to 4 ± 2 × 10^8 genome equivalents (G.E.; see below) or 4 ± 2 × 10^7 colony forming units (cfu; USEPA Method 1602, 2001). To conclude filtration, water flow was stopped, and filter pressure was allowed to relax. Tubing was carefully disconnected (ensuring no loss of concentrate), filter caps were replaced, and the filter was placed in a plastic bag on ice for transport back to the laboratory, where concentrate was recovered. The time required for ultrafiltration of 120 L was consistently 60 minutes. Tubing was sterilized between uses with 10% bleach (≥ 30 min contact time); following disinfection, tubing was thoroughly rinsed (10-15 min) with distilled water or groundwater from the next sampling site. To assess the influence of concentrate recovery method (elution vs. back-flushing) on PRD1 recovery, paired groundwater samples were collected at three sites by splitting the influent water flow to two parallel HFUF systems.

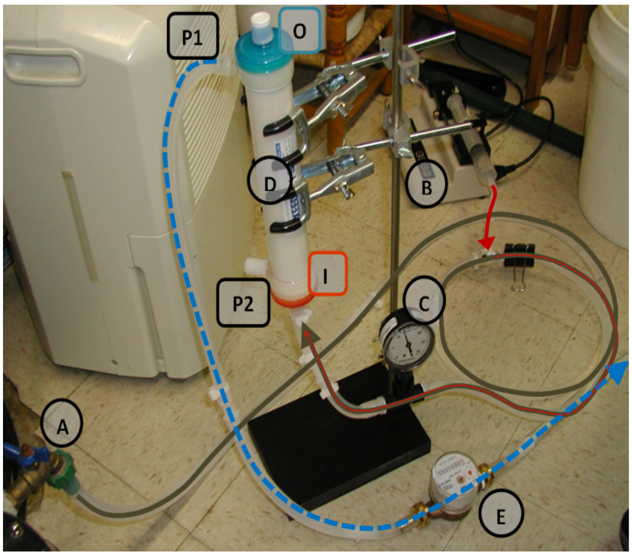

Figure 1. The HFUF was connected directly to a garden hose faucet (A), and sample water (gray, solid line) was fed into the filter inlet port (I) using the home's water pressure. HFUF system pressure was monitored with a liquid-filled pressure gauge (C) and maintained at ~13 psi by adjusting the tap (A). The HFUF system was operated in a dead-end configuration by leaving the filter outlet (O) and lower permeate (P2) ports closed. With port O closed, groundwater under pressure was driven laterally through 2.1 m^2 of hollow fibers contained within the filter housing; filtered water (blue dashed line) exited the open permeate port (P1) at ~2 L min^{-1}, verified using a flow totalizer (E). A dispersant solution (red solid line) was added continuously during filtration upstream of the filter via syringe pump (B), operated at 2 mL min^{-1}. The sampling event pictured occurred near Beloit, WI; the concentrated well sampled was positive for human AdV and PyV.

HFUF Concentrate Recovery and Secondary Concentration. Groundwater concentrate was recovered from the filter by back-flushing or elution 6-16 h after collection. Two concentrate recovery solutions (CRS) were used: (1) 0.01% NaPP + 0.1% Tween 80 and (2) 0.01% NaPP + 0.01% Tween 80. Concentrate recovery by back-flushing (Smith and Hill, 2009; Figure A1) involved reversing the direction of fluid flow through the filter relative to sample collection. To begin, both permeate ports were opened, and the permeate reservoir (i.e., the space within the filter housing *outside* of the hollow fibers) was purged with 500 mL of CRS1 using a peristaltic pump. The lower permeate port was then closed, the inlet port was opened, and 200 mL of CRS1 was pumped through the open permeate port and into the hollow fibers, displacing the sample concentrate into a 250-mL polypropylene centrifuge bottle. After 5-min contact time between the fibers and the CRS, the peristaltic pump was restarted and an additional 200-mL concentrate sample was collected. Filter elution was accomplished by opening the filter inlet and outlet ports and pumping 200 mL of CRS2 directly through the hollow fibers and into a 250-mL polypropylene centrifuge bottle. Following 5-min contact time, the peristaltic pump was restarted and an additional 200-mL concentrate samples was collected. The 400 mL of CRS recovered represents 3.6× the REXEED-21S filter priming volume (i.e., the volume of the full concentrate reservoir) of 112 mL.

Each 200-mL CRS sample was further concentrated by polyethylene glycol (PEG) precipitation. Briefly, CRS was supplemented to 3% beef extract, 0.3 M NaCl and 10% PEG 8000, pH 7.3. Following overnight incubation (4 °C, 120 rpm, ≥ 16 h), microorganisms were collected by centrifugation (60 min, 4550*g*, 4 °C); PEG supernatants were discarded, and PEG pellets from the first 400 mL of CRS were recovered with one 0.75 mL aliquot of Zymo Research Soil Microbe (ZRsm) DNA extraction kit lysis buffer. The third 200 mL was recovered with a separate 0.75 mL aliquot of ZRsm lysis buffer. All PEG pellets were stored at -20 °C until DNA extraction. Iron-rich samples from two households (both sampled repeatedly) were clarified (10 min, 4500*g*) prior to PEG precipitation in an attempt to remove iron solids.

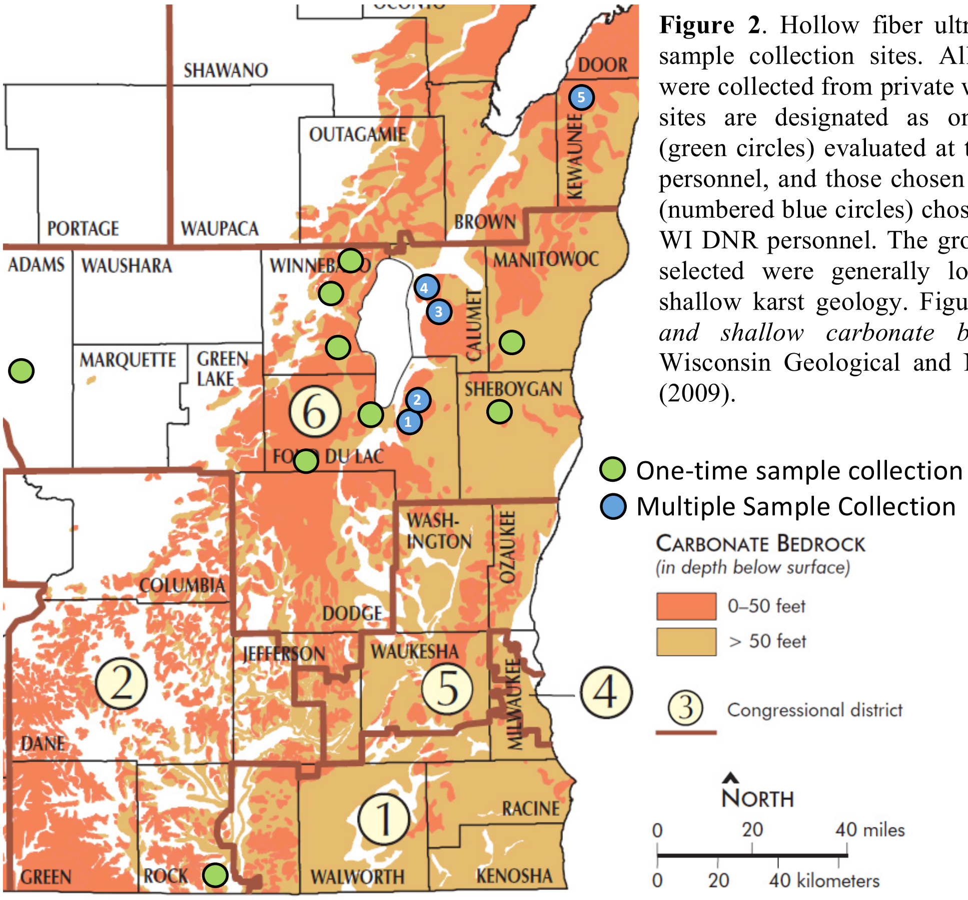

Figure 2. Hollow fiber ultrafiltration groundwater sample collection sites. All groundwater samples were collected from private wells. Sample collection sites are designated as one-time sampling sites (green circles) evaluated at the request of WI DNR personnel, and those chosen for repeated evaluation (numbered blue circles) chosen with the guidance of WI DNR personnel. The groundwater samples sites selected were generally located in regions with shallow karst geology. Figure adapted from, *Karst and shallow carbonate bedrock in Wisconsin*. Wisconsin Geological and Natural History Survey (2009).

Low-volume Groundwater Samples. Twenty-seven groundwater samples (200-600 mL), archived by the Wisconsin State Laboratory of Hygiene (WSLH), were concentrated by PEG precipitation and assayed by PCR for bovine BAdV-10 and BPyV-1. These samples were submitted to WSLH by the Wisconsin Department of Natural Resources for microbial source-tracking (MST) analysis in response to homeowner water quality complaints. The samples were investigated here to evaluate the utility of analyzing low-volume priority samples for viral markers of fecal contamination.

Bacteria and Virus Detection. Groundwater samples concentrated by HFUF were analyzed for coliform bacteria, *E. coli,* livestock and human AdV and PyV, and *Rhodococcus coprophilus*. Culturable *E. coli* and total coliforms in 100 mL of unfiltered groundwater (collected with 20 of 28 HFUF samples) and 1 mL of the first 400 mL of HFUF CRS (prior to PEG precipitation) were detected using the Colilert^{TM} reagent with the Quanti-tray^{TM} 2000 system (IDEXX Laboratories Inc.). Selected PCR methods were used to detect AdV, PyV and *R. coprophilus* and to quantify PRD1 in DNA extracted from PEG-precipitated HFUF groundwater sample concentrates. PRD1 was quantified by Taqman PCR against a $\log_{10}$ dilution series (10^2-10^7) of purified plamid DNA containing the target amplicon (TOPO TA, Invitrogen). Prior to PCR, the purified plasmid DNA concentration was quantified spectrophotometrically (Nanodrop ND 1000, Wilmington, DE). The cloned PRD1 amplicon was verified by sequencing. DNA extracted from PEG pellets of low-volume groundwater samples were assayed for BAdV-10 and BPyV-1. Primer sequences and the conditions employed in PCR assays are provided in Table A1.

DNA Extraction. All DNA extracts were prepared using the ZRsm DNA kit (Zymo Research Corp.). For livestock wastes, DNA was extracted directly from 0.5-g "solid" (feces, sand-separated manure and soil) or 0.5-mL liquid/slurry samples. Human sewage samples (100 mL) were clarified (4500*g*, 20 min, 4 °C) and PEG precipitated. For sewage samples and all groundwater concentrates, PEG pellets were extracted directly with the ZRsm kit, with minor modifications to the manufacturer's sample-lysis protocol: samples were suspended with ZRsm lysis buffer by vortexing and incubated at 70 °C (10 min) immediately prior to bead beating (2800 oscillations·min^{-1}, 1 min; Mini Beadbeater, BioSpec Products). Subsequently, DNA was extracted from 400 µL of clarified lysate (15,000*g*, 10 min for HFUF concentrates and 1 min for low-volume groundwater samples).

Oligonucleotide Selection and Design. Published primer sets for the specific amplification of BPyV-1 (Wang et al., 2005) and HPyV-BK plus HPyV-JC (McQuaiq et al., 2006) were adopted for this study without modification. Available complete capsid protein gene sequences for AdV (hexon gene) and PyV (VP1 gene) were obtained from GenBank and aligned by viral genus using ClustalW, executed in BioEdit (v.7.0.9.0). Broad-spectrum (BS) primers targeting atadenoviruses (AtAdV), mastadenoviruses (MaAdV) and polyomaviruses were designed to amplify an array of known and novel viruses. Primers were tested empirically for their ability to generate specific amplicons of the expected sizes from (i) DNA extracts of HAdV-41, BAdV-1, BAdV-2; (ii) purified plasmid DNA of BAdV-4, -6, -7 -8, and OdAdV (kindly provided by H. Lehmkuhl), and of HPyV-BK and simian (polyoma)virus type 40 (kindly provided by J. Mertz); and (iii) DNA extracts of AdV- and PyV-positive bovine manure and human wastewater samples. A BAdV-10-specific primer set targeting hexon gene hypervariable region 1 was designed using Primer3. A PRD1-specific Taqman PCR assay was designed by inspection of a multiple genome alignment of bacteriophages L17 (AY848684), PR3 (AY848685), PR4 (AY848686), PR5 (AY848687), PR772 (AY848688) and PRD1 (AY848689). Primer3 was used to verify the compatibility the primers and probe selected. The PDR1 Taqman assay was linear over six orders of magnitude, demonstrated 90% amplification efficiency (slope = -3.59), and exhibited no amplification when bovine (n = 3) and human waste samples (n = 6) were assayed. The expected target range and specify of all oligonucleotides used during this study was assessed *in silico* using the Specificity Check feature of Primer-BLAST (National Center for Biotechnology Information).

PCR. Conventional PCRs (50 µL) were prepared with GoTaq® Green Master Mix (Promega, Inc.) and 5 µL of DNA extract or 1 µL flanking PCR product (for nested and semi-nested reactions). All degenerate primers were included at a concentration of 300 nM × primer degeneracy (D), except MaAdF2 (D = 8), which was employed at 1600 nM total; non-degenerate primers were employed at 500 nM. Identical TD-PCR programs were used for both rounds of semi-nested amplification using BS AdV primer sets: 94 °C for 4 min, followed by 10 cycles of 94 °C for 30 s, 65 °C for 30 s (with a decrement 1 °C per cycle), and 72 °C for 1 min. An additional 30 cycles were completed as follows: 94 °C for 30 s, 55 °C for 30 s, and 72 °C for 1 min, finishing with a 72 °C (7 min) extension. All other conventional PCRs were completed using the following reaction conditions: 94 °C for 3 min, 40 cycles of 94 °C for 30 s, 55 or 58 °C for 30 s, and 72 °C for 1 min, followed by a final elongation at 72 °C for 7 min. All PCRs were prepared in a cooling block (4 °C) before placement in the preheated (94 °C) Eppendorf Mastercycler® Thermocycler. PCR products were detected under UV light after agarose gel electrophoresis (2%) and ethidium bromide staining. Quantification of PRD1 DNA was completed in 20-µL reactions (5 µl of DNA extract) using LightCycler® TaqMan® Master Mix on the LightCycler® 2.0 Real-Time PCR System (Roche Applied Science, Inc.). qPCR conditions were as follows: DNA polymerase activation at 95 °C for 10 min, followed by 45 cycles of DNA denaturation (95 °C, 15 s), primer annealing (58 °C, 40 s; 72 °C, 1 s), and polymerase extension (60 °C, 60 sec); the temperature ramp rate was 20 °C·s^{-1}. The oligonucleotides employed were synthesized by the University of Wisconsin-Madison (UW) Biotechnology Center or Integrated DNA Technologies (Coralville, IA); their sequences and PCR annealing temperatures are reported in Table A1.

RESULTS AND DISCUSION

Excreta Evaluation for AdV and PyV. We determined the prevalence of BAdV and BPyV in excreta samples from cattle to ascertain the utility of these viruses as fecal contamination indicators (Table A2). Using original, "broad-spectrum" PCR primer sets designed to detect an array of known and previously unidentified AdV and PyV, BAdV were detected in 13% of cattle fecal samples, 90% of cattle urine samples and 100% of cattle manure samples; 44% of BAdV-positive samples contained DNA from two genetically distinct AdV genera, *Atadenoviridae* and *Mastadenoviridae*. BPyV were detected less frequently than BAdV in these samples, at rates of 17% in cattle feces, 14% in cattle urine and 73% in cattle manure. BAdV excretion in urine was observed commonly during this investigation but had not been previously documented. Additionally, five previously unknown bovine viruses were detected and partially sequenced during this investigation, four BAdV and one BPyV, increasing the number of BAdV genotypes to 15 and BPyV genotypes to two.

Observed detection rates for two specific bovine viruses, BAdV-10 and BPyV-1 (e.g., 50% and 27%, respectively, in manure) supported targeting these viruses for fecal source attribution. BPyV-1 has been detected frequently in other investigations of bovine serum and excreta (Wang et al., 2005; Wong and Rose, 2009). However, no previous study has demonstrated prevalent, asymptomatic shedding of BAdV-10 by cattle. Based on this finding, we designed and validated a PCR assay for the specific detection of BAdV-10. Our assay targets a "hypervariable" region of the AdV hexon protein gene, making the PCR assay highly specific for BAdV-10. This attribute is critical, since knowledge of AdV (and PyV) genetic diversity across potential host species is incomplete. Therefore, PCR assays capable of detecting *multiple* viruses have an increased chance of detecting a previously unidentified virus with an unknown host, obscuring fecal source attribution.

We also evaluated all of our bovine excreta samples, plus five sewage influent samples, using a previously published PCR assay for HPyV (McQuaig et al., 2006). The specificity of the HPyV assay has been verified previously by testing 152 animal waste samples (from 13 species) (McQuaig et al., 2009). However, no information was available to validate its usefulness locally. In our hands, the assay showed no amplification of PyV in bovine samples and 80% HPyV detection in sewage (Table A2). The presence of HPyV at high concentration in sewage has been documented, and HPyV have shown higher prevalence in individual septic tanks than HAdV (Harwood et al., 2009; McQuaig et al., 2009). These factors encouraged our application of the HPyV PCR for fecal source tracking in domestic well water samples.

Hollow fiber ultrafiltration system configuration. Most previous laboratory and environmental investigations using HFUF to concentrate microorganisms employed a tangential-flow configuration. This method requires comprehensive operator training and is not conducive to rapid-response field sampling (Smith and Hill, 2009). We designed our HFUF system to operate in a dead-end configuration (Smith and Hill, 2009), which is permitted by the large surface area (2.1 m^2) of the hemodialysis filter. The streamlined system plumbing and sample collection routine associated with dead-end HFUF allows direct sample collection from a garden hose faucet. This simplification reduces the likelihood of sample contamination, since no intermediate vessel (e.g., a plastic garbage can) is employed during sample collection, and significantly reduces the operator training required for system operation. In addition, the dead-end HFUF is well-suited for rapid-response field implementation. Overall, the virus-concentration routine assembled here meets sample-processing criteria suggested for fecal source tracking investigations (Harwood et al., 2009): the method co-concentrates a variety of microbial targets using an affordable, commercially-available filter and co-purifies DNA using a commercially available extraction kit.

PRD1 recovery by dead-end HFUF. The efficacy of HFUF for concentrating microorganisms, including viruses, in controlled laboratory experiments has been demonstrated repeatedly, with optimized microorganism recoveries of 50 to 100% (Hill et al., 2005; Smith and Hill, 2009). However, as the chemistry of water samples becomes more complex, microorganism recoveries may diminish and/or become more variable (Leskinen and Lim, 2008; Knappett et al., 2011; Gibson and Schwab, 2011b); in these situations, significant correlations between marker recoveries and water chemistry parameters become more difficult to define (Hill et al. 2007). The expected site-to-site variability of groundwater chemistry challenges the utility of further (e.g., beyond Smith and Hill, 2009) laboratory optimization of dead-end HFUF. Therefore, to quantify the cumulative efficiency of our virus detection protocol, we spiked bacteriophage PRD1, an enteric virus surrogate, into the HFUF system during groundwater sample collection from domestic wells.

A large phage spike ($4 \pm 2 \times 10^8$ G.E.) was selected, anticipating that *in situ* microorganism recoveries from groundwater might be low and/or variable (Gibson and Schwab, 2011b), which was in fact, the case (Table 1). Considering 100% recovery of viruses from a groundwater volume of 115 L, our sampling and analysis protocol provides a theoretical concentration factor of $10^{5.5}$ (i.e., the 0.005 mL of concentrated "groundwater" DNA analyzed during PCR corresponds to an extrapolated native groundwater volume of 1500 mL). In practice, we observed an average PRD1 recovery of 16 ± 29% (*n* =

20), corresponding to an effective concentration factor of $10^{4.7} \pm 10^{4.9}$ and an average analysis of 250 ± 420 mL of groundwater by PCR.

Method recoveries varied widely for PRD1 among sample collection sites (Figure 3). The factor(s) promoting reproducibly strong PRD1 recoveries at Site 3 (31% ± 6%), but not the other sites, are unclear. Conversely, consistently low PRD1 recoveries observed at Sites 2 and 4 may be associated with the significant (> 5 mL) volumes of colloidal iron collected by HFUF at these locations. This iron appeared to have little impact on bacteria recovery (90% and 83% for Site 5), but was the most striking (though not statistically significant, $p = 0.12$) factor predictably associated with low PRD1 recovery. Of note, groundwater at these sites had detectable dissolved oxygen (0.7-5.6 mg L^{-1}) and low dissolved iron concentrations (<0.006-0.044 mg L^{-1}) (Walt Kelley, Illinois State Water Survey, personal communication). These observations (a) suggest that iron precipitation had occurred prior to sampling and exposure to atmospheric oxygen; and (b) appear responsible for negating the effectiveness of EDTA addition during HFUF sample collection as a method for reducing iron accumulation (Knappett et al., 2011).

In contrast with measured PRD1 recoveries, for sites where coliform bacteria were present in unfiltered groundwater and HFUF concentrates, the recovery of *in situ* coliform bacteria was impressive (46 ± 34%, $n = 9$). The higher recoveries estimated for bacteria are consonant with literature reports of stronger recovery of bacteria (than viruses) from environmental HFUF concentrates (Gibson and Schwab, 2011b). Unlike for PRD1, coliform recoveries by HFUF were determined without need for a secondary concentration or DNA extraction steps. Therefore, optimization of these methods could hold the key to improving virus detection in groundwater samples concentrated by ultrafiltration.

Paired samples were collected at three unique sites to determine if HFUF concentrate recovery methods could be adjusted to improve PRD1 recovery. For the three sites, groundwater concentrate was displaced from the HFUF by either elution or back-flushing. Consonant with published laboratory experiments (Hill et al., 2005) and our initial strategy, PRD1 recoveries for all three sites demonstrated stronger (though not statistically significant, $p = 0.16$) virus recovery by back-flushing compared with elution.

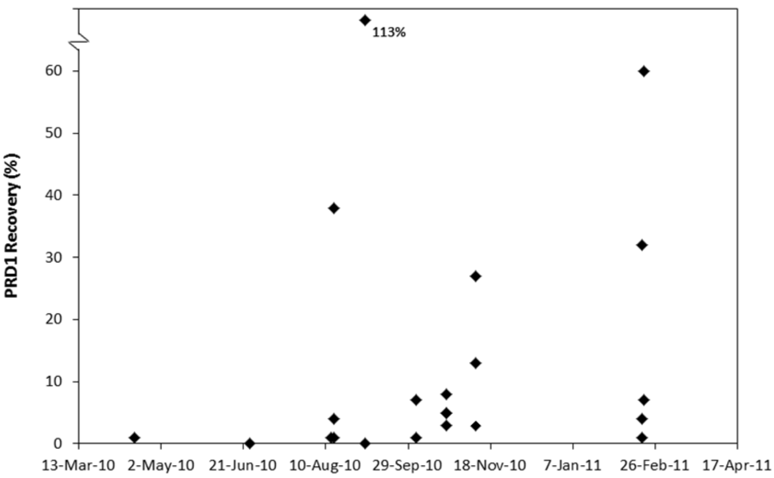

Figure 3. The recovery of exogenous bacteriophage PRD1 by HFUF from groundwater (115 ± 15 L) samples was highly variable. Average PRD1 recoveries (%) showed no statistical dependence on the factors (*a*) sampling site ($p = 0.43$), (*b*) dispersant (NaPP vs. EDTA solutions added during HFUF; $p = 0.75$), (c) colloidal iron (presence/ absence in HFUF concentrates; $p = 0.12$), or (*d*) collection month ($p = 0.50$). These results indicated a lack of predictable influence of changes in groundwater chemistry or variations in sample processing strategy on PRD1 recovery.

Fecal Source Attribution in Groundwater Samples: The primary motivation for this study was to evaluate the likelihood that AdV and PyV would be detected and prove useful for fecal source attribution in private groundwater samples deemed vulnerable to fecal contamination. Of the 24 groundwater samples collected by HFUF, 17 were positive for coliform bacteria, eight were positive for *E. coli*, six were positive for *R. coprophilus* and three were positive for at least one viral marker (AdV or PyV) of fecal contamination. A single viral marker was detected at two of the five sites targeted for repeated sample collection; of the six homes where groundwater was collected only once, one was positive for two viral markers (Site R, for Rock County). The detection of corroborating host-specific microbial markers is required for confident source attribution. Therefore, only for the latter site could an actionable contamination source, human, be reliably attributed. Subsequent site investigation by the WI Department of Natural Resources revealed a compromised pipe in the homeowner's septic system.

Table 1. PRD1 recovery and fecal indicator detection in domestic well water.

		PRD1 Recovery			Microbial Indicator Detection					Putative Source
	n	*n*[a]	Ave. (%)	SD (%)	Coliform Bacteria	*E. coli*	*R. coprophilus*	AdV or PyV		
Site 1	3	3	41	62	0/3	0/3	0/3	0/3	NA	Unknown
Site 2	5	4	18	28	3/5	0/5	1/5	0/4	NA	Unknown
Site 3	3	3	31	6	3/3	1/3	1/4	1/3	AtAdV[b]	Animal
Site 4	4	4	3	2	1/4	1/4	3/4	1/4	HPyV	Ambiguous
Site 5	3	3	5	8	3/3	2/3	1/3	0/3	NA	Unknown
Others	7	4	2	3	6/7	4/7	0/7	1/7	HAdV HPyV	Human[c]

[a] Number of HFUF samples collected that were spiked with PRD1.
[b] AtAdV detected showed 89% identity with BAdV-6.
[c] Source for Site R.

At Site 3, an AdV was detected with our AtAdV PCR assay. The expected target range for this assay comprises BAdV-4 through -8, plus ovine AdV-7 and goat AdV-1. During our investigation of bovine excreta, no AtAdV with less than 96% identity to prototype AtAdV genotypes were amplified using this assay. However, in this groundwater sample an AtAdV with only 89% identity with the closest known genotype (BAdV-6) was discovered. This novel AtAdV is predicted to have a livestock host, based on comparative phylogenetic analysis (Figure 4), and a livestock source of contamination is supported by the coincident detection in this sample of *R. coprophilus,* a bacterium that grows in the dung of herbivores and provides useful support for other ruminant fecal markers (Oragui and Mara, 1981; Savill et al., 2001; Gilpin et al., 2008). However, a wildlife host cannot be excluded. This scenario exemplifies one of the main problems with viral genetic markers of livestock contamination: potential host-ambiguity due to preponderance of unidentified genotypes. For that reason, PCRs that can amplify multiple livestock viruses require extensive validation prior to use in source tracking without confirmatory DNA sequencing. The detections of an HPyV and *R. coprophilus* at Site 4 were unsupported by corroborating host markers. Contamination at this site could be resulting from humans, grazing herbivores, or both.

In most cases, even the concentration of large sample volumes did not reveal sources or overcome the intermittent nature of groundwater contamination. For example, Sites 4 and 5 were sampled for bacteria by a research group from the Illinois State Water Survey one day prior to our February 2010 sampling trips. Using the same detection method (Colilert/Quantitray, IDEX), their results differed dramatically from ours: at Site 4, their 100 mL sample exceeded the upper detection limit of the Quantitray method (>2419 cfu) for coliform bacteria and was *E. coli* positive; conversely, our sample, collected 29 h later, showed *no* bacterial contamination. Nearly the opposite result was obtained for Site 5, where the IL group observed 5 cfu/100 mL coliform bacteria (*E. coli* absent) whereas *our* sample exceeded the Quantitray upper detection limit for coliforms and was *E. coli* positive (6 cfu/100 mL). These simple data highlight the significant challenge in "correctly" timing sample collection for fecal source tracking.

Large sample volumes are generally thought to be necessary when targeting viruses in groundwater. However, confident fecal source attribution was possible for several low-volume groundwater samples submitted to WSLH for microbial source tracking in response to homeowner water quality complaints. These samples were analyzed for BPyV-1 and BAdV-10, and frequently yielded positive results for these bovine viral indicators: eight of 28 samples analyzed were positive for BPyV-1, while four of these eight were also positive for BAdV-10. The effective groundwater volume analyzed by PCR for these low-volume groundwater samples was 1 to 10 mL for method recoveries ranging from 10 to 100%, respectively. Knappett et al. (2011), working in Bangladesh, recently detected human viruses in low-volume (250-mL) groundwater samples collected from shallow wells, supporting our findings.

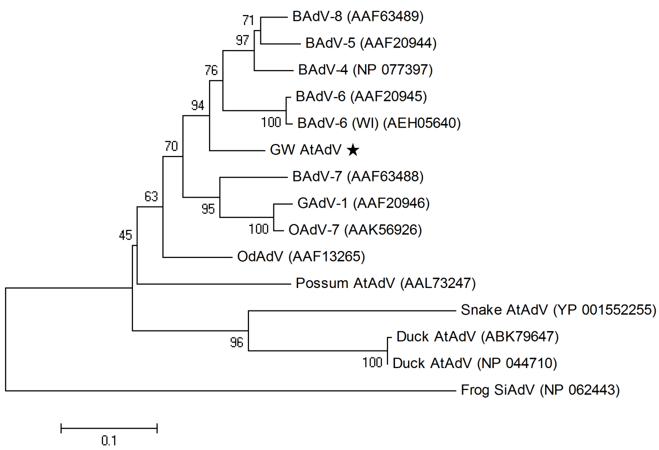

Figure 4. Neighbor-joining phylogenetic analysis suggested a livestock host for the AtAdV ("GW AtAdV") detected at Site 3. Prior to the analysis of this sample, the PCR assay employed had not amplified an AtAdV with less than 96% identity to known BAdV. This scenario is exemplary of one of the main problem with genetic markers for FST livestock contamination (and animal sources, more broadly): ambiguity when the sequence is identified due to preponderance of unidentified markers. For that reason, PCRs that can amplify multiple viruses (in particular livestock viruses) require extensive validation before they should be used for source tracking without DNA sequencing to identify the presumptive amplicon.

CONCLUSIONS AND RECOMMENDATIONS

Our detection of HAdV, HPyV, BAdV-10 and BPyV-1 in groundwater samples collected from private wells supports the utility of these viruses as fecal source indicators. In particular, our discovery of prevalent shedding of BAdV-10 by cattle is significant, and our implementation of a BAdV-10 PCR assay adds a highly cattle-specific marker to the toolbox of methods available to the source tracking community. Groundwater samples collected using HFUF showed large concentration factors (~10^4) and were often contaminated by coliform bacteria. However, in most cases, even the concentration of large sample volumes did not reveal contamination sources or overcome the intermittent nature of groundwater contamination by fecal material. On the other hand, low-volumes samples analyzed in response to immediate home-owner complaints frequently (and unexpectedly) yielded positive results for bovine viral indicators, resulting in definitive source attribution. Therefore, the analysis of these types of groundwater samples for AdV and PyV is recommended. Where potentially contaminated groundwater presents an immediate and unacceptable risk to human health (e.g., for vulnerable wells serving daycare facilities, nursing homes, or communities), the application of the dead-end HFUF method described here is also recommended. For example, at Site 4 and Site R, human viruses were detected in HFUF concentrate with low measured PRD1 recovery (0% and 1%, respectively) but were absent in a 400-mL sample collected and processed in parallel.

Strong *in situ* recovery of bacterial indicators (versus PRD1) suggests that improved virus recovery may be gained by further optimization of sample secondary concentration and DNA purification methods. For example, targeted treatment of CRS (e.g., incubation with EDTA for sample iron removal) or a reduction in the total volume of CRS collected may reduce the impact of method inhibitors. The use of beef extract as a CRS, and perhaps as a sample amendment immediately following filtration, would streamline sample processing and might result in improved virus recovery if virus attachment to the filter matrix is an issue.

Our results suggest that mobilizing a sampling effort to a particular site at the "right" time – which from a practical standpoint may be unknowable – is challenging. Alternatively, our successful detection of host-specific viral markers in low-volume groundwater samples suggests an alternative approach for site-dedicated source tracking: the homeowner could be enlisted in the collection of ~500-mL samples over a several day period; focusing on periods following large rain events or snow melts might improve the chances of fecal source attribution. Following the collection of a series of low-volume samples, the investigator could retrieve samples and perform source tracking following the methods described here.

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

Sibley, S.D. and J.A. Pedersen. 2011. Detection of Known and Novel Adenoviruses in Cattle Wastes via Broad-spectrum Primers. Appl. Environ. Microbiol., **77**:5001-5008.

"*Testing Well Water for Microorganisms*." Fall/Winter 2010, Aquatic Sciences Chronicle, University of Wisconsin Sea Grant and Water Resources Institute.

APPENDIX B:

TABLE A1. Oligonucleotides used for PCR. All assays, except for BPyV-1 and HPyV, were designed and validated during this investigation.

Assay	Direction	Oligo ID	Oligo Conc. (nM)	Annealing Temp (°C)	Sequences (5' - 3') [a]	Product size (bp)
MaAdV	Forward	MaAdF1		55	CAGTGGTCHTACATGCACATC	
	Reverse	MaAdR1		55	GCATAAGACCCGTAGCAWGG	599 – 725[b]
	Forward	MaAdF2		55	CATGCACATCGCSGGNCAGGA	588 – 714[b]
AtAdV	Forward	AtAdF1	500	55	CACATTGCGGGTAGAAATGC	
	Reverse	AtAdR1	600		TAAGCWGTTCCTCCATAAGG	323
	Forward	AtAdF2	500	55	GCGGGTAGAAATGCGAGG	
	Reverse	AtAdR2			TGTTGGAGCTACAAAAGGATCTC	114
BAdV-10	Forward	B10F	500	58	TTACGCCCAACTTCCTTTTG	
	Reverse	B10R			CCACGCGTCTACTCCGTATT	127
BPyV-1[c]	Forward	VP1F	500	58	GGTATTCGCCCTCTGCTGGTCAAG	
	Reverse	VP1R			GCTGGCAATGGGGTATGGGTTCT	527
	Forward	VP2F	500	58	ATT TCAAAGCCCCCTATCATC	
	Reverse	VP2R			GCCTACGCCATTCTCATCAAG	263
HPyV[d]	Forward	SM2	500	58	AGTCTTTAGGGTCTTCTACCTTT	
	Reverse	P6			GGTGCCAACCTATGGAACAG	176
R. c.[e]	Forward	RcF	200	58	GGGTCTAATACCGGATATGACCAT	
	Reverse	RcR			GCAGTTGAGCTGCGGGATTTCACAC	443
PRD1	Forward	PRD1F	500		AGCTTAATGACTACGCCAGT	
	Reverse	PRD1R		58	GGAAGATTCCGTTTGAACA	161
	Taqman	PRD1q	100		TAATGATTATTTGGCTTCACAAGCGGG	
PyV	Forward	PyV-F2900		46, 58	AATGAIAACACIAGRTAYTWTGG	
	Reverse	PyV-R4160	1000	46	GGTTGTITTTGARGATGTIAARGG	~1260
	Reverse	PyV-R0		58	CAIAGIGGICCMACNCCATTYTCAT	120

[a] H = C+A+T; W = A+T; B = C+T+G; S = G+C; degenerate positions are underlined.
[b] Amplification of hypervariable region, V1 (6) by MaAdV primers results in variably-sized products.
[c] Wang et al. (2005)
[d] McQuaig et al. (2009)
[e] *Rhodococcus coprophilus*; Savill et al. (2001)

TABLE A2. Summary of excreta and low-volume groundwater sample evaluations by broad-spectrum and virus-specific PCRs.

		Detection Rate					
Sample	Sample Info./Animal Age [a]	HPyV	MaAdV	AtAdV	PyV	BAdV-10	BPyV-1
Bovine Feces							
Dairy Calf	<14 weeks; AARS-DCU	0/9	0/9	0/9	1/8	0/9	2/8
Adult	1-10 years; UW-Dairy, AARS-BNC	0/21	4/23	0/23	3/22	0/9	0/22
Bovine Urine							
Beef Cow	AARS-BNC; ~ 15 months	0/3	2/3	3/3	2/3	2/3	0/3
Dairy Cow	UW-Dairy (*n* = 17); Farm A (*n* = 1); 2.5 to 9 years	0/18	13/18	11/18	1/18	13/18	0/18
Bovine Manure							
Dairy Lagoon Slurry	Two private dairies	0/2	2/2	2/2	2/2	1/2	1/2
Dairy Manure	Sand-separated	0/1	1/1	1/1	1/1	1/1	1/1
Bedding Percolate	Dairy Exposition	NA	5/5	5/5	4/5	NA	1/5
Beef Cattle Bedding	AARS-BNC; ~15 month cattle; moist, soiled hay	0/3	3/3	3/3	0/3	1/3	0/3
Environmental							
Field Mud [b]	Water station, Farm E	0/2	0/2	2/2	1/2	0/2	0/2
Field Runoff [c]	Drainage ditch, Farm E	0/1	1/1	1/1	1/1	1/1	0/1
Groundwater	≤ 600 mL; Archived by WSLH	NA	NA	NA	NA	4/28	8/28
Other							
Human sewage [d]	NSWTF, 24-h composites	4/5	5/5	0/5	5/5	0/5	0/5
Pig feces	AARS-P; 1 sow, 1 piglet	0/2	0/2	0/2	0/2	0/2	0/2
Pig wash water [e]	AARS-P; newborn to finished	0/1	1/1	0/1	0/1	0/1	0/1
Deer feces		0/4	0/4	0/4	0/4	0/4	0/4
Rabbit feces	One fecal pellet	NA	1/1	0/1	0/1	0/1	NA
Dog feces	3 to 4 year	0/2	0/2	0/2	0/2	0/2	0/2
Goose feces	10 scat composite	0/1	0/1	0/1	0/1	0/1	0/1

[a] Abbreviations: AARS, Arlington (WI) Agricultural Research Station; -DCU, Dairy Calf Unit; -BNC, Beef Nutrition Center; -P, Porcine Research Center; UW-Dairy, University of Wisconsin-Madison Dairy; NSWTF, Nine Springs Wastewater Treatment Facility (Madison, WI); NA, Not Analyzed.
[b] Collected approximately 3 and 6 meters from a water station.
[c] Collected from a muddy pool adjacent to a large cattle lot.
[d] Collected May, Jun and Oct 2009; Jan and Feb 2010. HAdV-31 detected once; HAdV-41-WI detected in all sample.
[e] Pen wash-water recirculated throughout the facility, sampling newborn to finished swine.

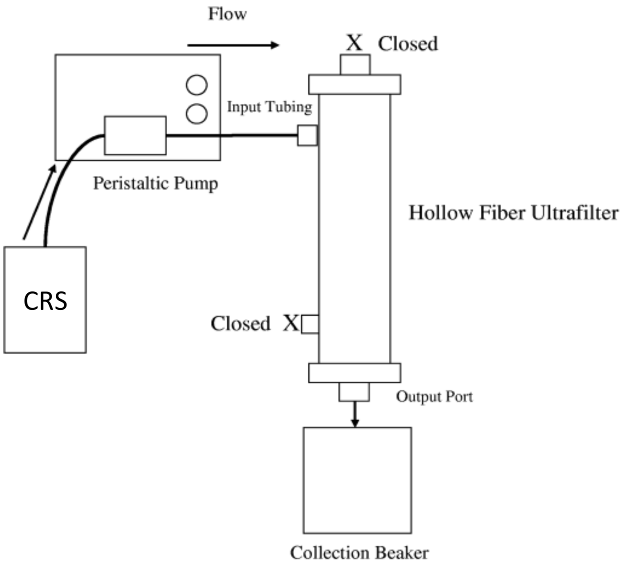

Figure A1. Configuration used for back-flushing the hollow fiber ultrafilter (from Smith and Hill, 2009). Four-hundred milliliters of a 0.01% sodium polyphosphate and 0.1% Tween 80 concentrate recovery solution (CRS) was used to displace and carry microorganisms collected within the filter's hollow fibers into two 250-mL centrifuge bottles for subsequent secondary concentration by polyethylene glycol precipitation.

Assessing the Effect of Pleistocene Glaciation on the Water Supply of Eastern Wisconsin

Basic Information

Title:	Assessing the Effect of Pleistocene Glaciation on the Water Supply of Eastern Wisconsin
Project Number:	2009WI310O
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End Date:	3/1/2011
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Congressional District:	WI 4th
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Quality, Hydrology, Groundwater
Descriptors:	
Principal Investigators:	Tim Grundl

Publications

There are no publications.

FINAL REPORT

ASSESSING THE EFFECT OF PLEISTOCENE GLACIATION ON THE SANDSTONE AQUIFER IN EASTERN WISCONSIN

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Funded by the
UW System Groundwater Research Program
Project #WR09R004

Introduction

Along the entire eastern portion of Wisconsin the primary municipal water supply aquifer is the confined Paleozoic sandstone aquifer. From a water supply/water planning perspective, it is important to know whether or not freshwater pumped from this aquifer is being replenished by modern recharge or whether it represents a finite resource emplaced during the Pleistocene. This project investigated the recharge history of the deep sandstone aquifer along the eastern edge of Wisconsin from Green Bay to Milwaukee. Knowledge of the recharge provenance is of paramount importance to developing strategies for long-term management. Pleistocene recharge would have been controlled by highly variable factors involving ice advance and retreat as well as permafrost formation and ice-induced pressure heads that likely drove recharge at rates that were much higher than at present.

Primary users of the information developed during this project will include water supply managers responsible for making long term water management decisions. In addition, the scientific community will be interested in the paleoclimatic information inherent to the noble gas temperature record and the companion $\delta^{18}O$ record. Information on subglacial meltwater recharge is also of critical importance to the understanding of glacial movement in general and the occurrence of periodic glacial surges especially in the context of global warming.

Approach

The current project builds upon the work of Klump, et al (2008) who provided clear evidence that deep groundwater in the southeast corner of the State was recharged during the Last Glacial Maximum (LGM). These authors sampled water from an east-west transect along the groundwater flow path in southeast Wisconsin near the terminus of the Green Bay Lobe of the Laurentide Ice Sheet (LIS). The current project collected groundwater along the flow path from similar transects located farther to the north near the center of the Green Bay Lobe and well removed from the LGM terminus. This yielded information on recharge conditions and timing as the ice advanced and retreated across the landscape.

Measurements of ionic composition (for basic geochemical modeling using PHREEQC (Parkhurst, 1995); $\delta^{2}H$ and $\delta^{18}O$ (for ice melt signal and Pleistocene temperature record);

$\delta^{34}S_{sulfate}$ (for determination of sulfate source); $\delta^{13}C$, ^{14}C (age of water); noble gas content and fractionation patterns (recharge sources and an independent measure of the Pleistocene temperature) were made in the groundwater of the confined sandstone aquifer along two northeast-southwest transects between the latitudes of Green Bay, WI (44.5˚ N) and Cedarburg, WI (43.3˚ N). Except in the Green Bay area this aquifer is actively pumped and municipal water supply wells were used as sampling points. In the Green Bay area existing municipal wells are maintained for emergency use and sampling was performed during test pumping (performed on a quarterly basis). All wells were completed solely within the Paleozoic aquifer starting in the recharge area and continuing downgradient along the flow path. The north transect, near Green Bay, consisted of nine wells. The Klump, et al. (2008) transect was taken near Milwaukee (43.0˚ N) and will be referred to in this report as the south transect. The center transect, between Fond du Lac and Cedarburg, consisted of 8 wells. The aquifer within the center transect displays highly variable thicknesses because of significant topography on the underlying basement rocks and the flow pattern is not uniformly west to east therefore center transect data could not be reliably interpreted was not included in this study. Raw data collected from center transect wells are given in the appendices. For reference, the locations of center transect wells are included in Figure 1.

Note that it is only along the western edge of the Michigan Basin (Wisconsin/Illinois) that the deep sandstone aquifer is a) accessible, b) contains fresh groundwater with the requisite residence times needed for finding water recharged during the Pleistocene LGM and c) has a relationship between location of the recharge area and ice lobe movement that allows the collection and dating of glacial recharge from positions near to and well back from the maximum terminus of a single ice lobe.

Background

During the LGM (~11- 26 k.a.), the LIS affected regional to hemispheric atmospheric circulation, climate patterns, and the isotopic composition of continental precipitation, due to changes in albedo, surface topography, and temperature (eg. Clark, Alley, et al. (1999)). While the climatic effects of the LIS have long since vanished, an influence of the LIS still persists through its impact on regional groundwater flow systems throughout the United States (e.g.

Boulton et al. (1995); Breemer et al. (2002); McIntosh and Walter (2006); Person et al. (2007)). There is compelling field evidence that injection of isotopically light, subglacial meltwater changed the salinity and geochemistry of groundwater in Wisconsin/Illinois (Siegel and Mandle (1984); Siegel (1990); Klump et al. (2008)).

Recent studies from different North American and European locations indicate that ice loading during the last glaciation strongly influenced groundwater flow patterns and origin (e.g. Filley (1984); Weaver and Bahr (1991a) (1991b); Young (1992); Clark et al. (2000); Edmunds (2001); Breemer et al. (2002); Person et al. (2003); Person et al. (2007); Hoaglund III et al. (2004); McIntosh and Walter (2006); Klump et al. (2008)), however the effects of the LIS may vary depending on the conductivity of the substrate (Carlson et al., 2007). Present-day water quality in southern Wisconsin and northern Illinois is evidently still affected by changes in the groundwater chemistry due to reversals of hydraulic gradients during glaciation and subglacial recharge (e.g. Siegel (1990), (1991); Siegel and Mandle (1984)). Breemer et al. (2002) demonstrated, using a 2-D groundwater model, that the LGM Lake Michigan Lobe probably reversed groundwater flow and increased groundwater velocity under Lake Michigan and in Illinois within ~1000 years of occupying its maximum position. Similarly drastic effects of the LIS on the underlying groundwater have been modeled at the continental scale (Lemieux et al. (2008a), Lemieux et al. (2008b)). Person et al. (2003) and Marksammer et al. (2007) showed that the LIS recharged aquifers along the New England Atlantic continental shelf explaining the disequilibrium between the freshwater/saltwater interface and modern sea level. In contrast, model simulations of the James Lobe of the LIS suggest that this lobe had little effect on groundwater flow in the western plains of North America because a poorly conductive Upper-Cretaceous shale layer occupies the upper layer of the bedrock and functioned as a regional aquitard (Carlson et al., 2007). These results were in close agreement with the isotopic spring data of Grasby and Chen (2005), which indicate reversal of groundwater flow in the aquifers only near surface exposures that were in direct contact with the James Lobe. Groundwater flow in glaciated regions underlain by more permeable bedrock like that of the Great Lakes region of North America was significantly influenced by the ice lobes whereas regions underlain by less permeable substrates such as the North American plains were not.

The geologic setting along the western coastline of Lake Michigan is ideal for studying the effects of Pleistocene glaciation on the underlying Paleozoic sandstone aquifer. The Paleozoic aquifer transitions from unconfined to confined conditions along a north-south line approximately 50 km inland from the coast of Lake Michigan (solid line in Figure 2). All stratigraphic units in the area dip eastward into the Michigan Basin and the Maquoketa Formation, a very effective aquitard ($K_z \sim 10^{-12}$ m/s), overlies the aquifer from this boundary eastward and serves as the confining unit. An extensive hydrostratigraphic framework developed for a hydrologic model of eastern Wisconsin near Lake Michigan (Feinstein et al., 2010) shows aquifer recharge occurring immediately west of the confined/unconfined boundary. Water moves slowly and continuously eastward in the confined portion of the aquifer since ice retreated out of Wisconsin ~11 k.a. (all ages calibrated, calendar years). This slow but continuous flow preserves a record of climatic conditions at the time of groundwater recharge.

In the region surrounding Green Bay, a veneer of Glacial Lake Oshkosh sediments overly the aquifer (red line in Figure 2) are draped over a variable bedrock surface and range in thickness from 150 m over bedrock valleys to as little as 5m in upland areas. These sediments are fine grained varve clays and display low vertical conductivities ($K_z \sim 10^{-9}$ m/s) using laboratory scale measurements (Moeller et al., 2007). Although field scale heterogeneities, especially in thinly covered upland areas will likely increase the vertical hydraulic conductivity, geochemical data support the notion that these sediments form an effective confining layer for the underlying sandstone aquifer. This has the effect of moving the recharge area to the western edge of the lake sediments.

Previous workers describe geochemical evolution from a $Ca\text{-}HCO_3$ character in upgradient areas to a $Ca\text{-}SO_4$ character downgradient, increasing salinity, dedolomitization reactions eastward along the flow path, ^{14}C groundwater ages, noble gas and stable isotope data (Grundl and Cape (2006); Klump et al. (2008)) that are all in agreement with these modeling results. In the south transect distinct pulses of water are delineated that were recharged before, during and after the LGM (Klump et al., 2008). Similar trends have been reported in the sandstone aquifer in Illinois (e.g. Perry et al. (1982); Gilkeson et al. (1984)) and in shallower dolomite aquifers (Ma et al. (2004); McIntosh and Walter (2006)) in other parts of the Michigan Basin.

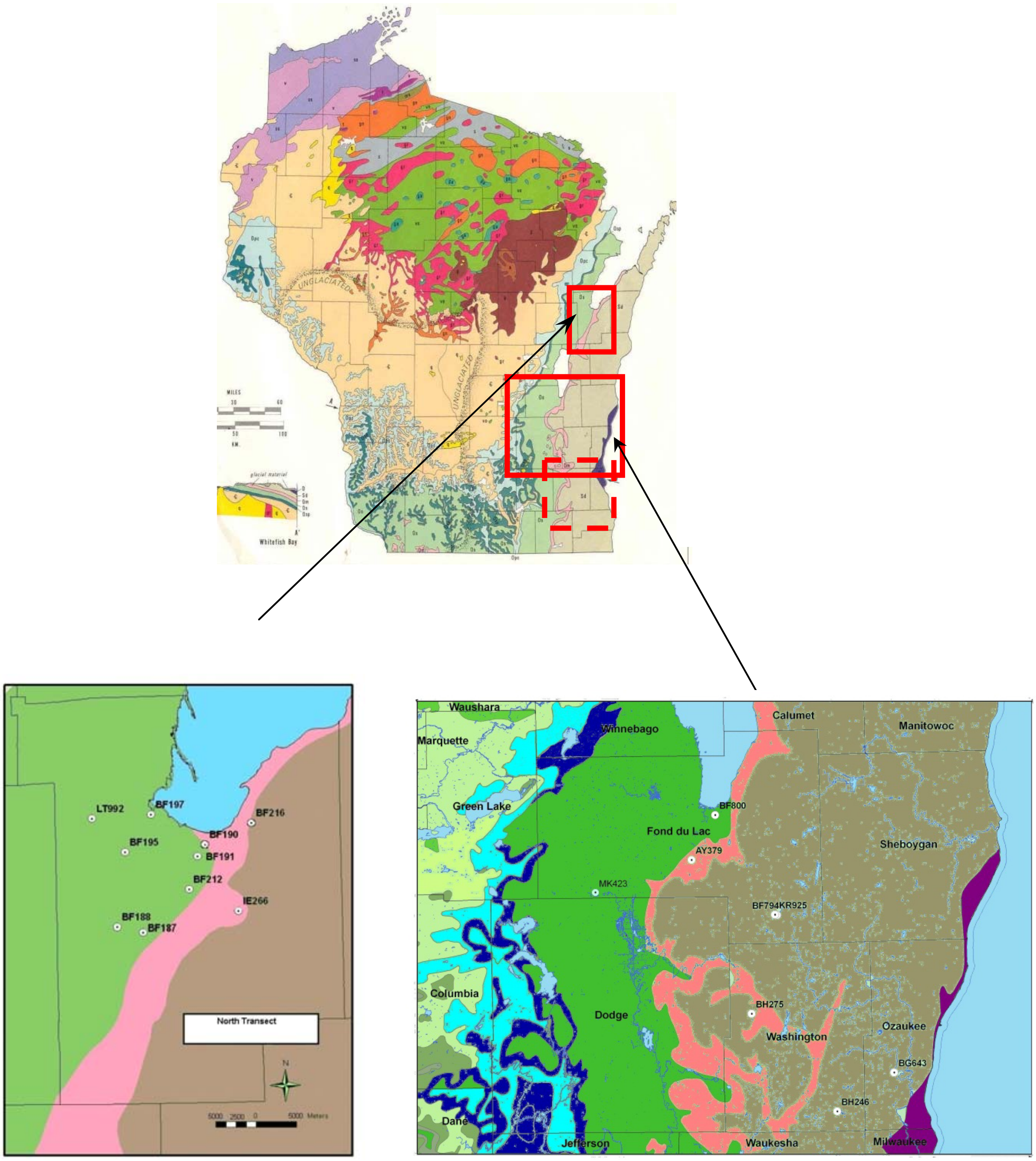

Figure 1: Wisconsin bedrock map with the north and central transect areas delineated. (modified from Mudrey et al. (1982) and Krall (2010)). Dotted square is the south transect of Klump, et al (2008). Colors on main map represent the following stratigraphic units: Purple = Devonian shales. Grey = Silurian dolomite. Pink = Maquoketa Shale. Green = Sinnippee Group. Dark green = St. Peter Formation. Light blue = Prarie de Chien Group. Tan = Cambrian sandstones.

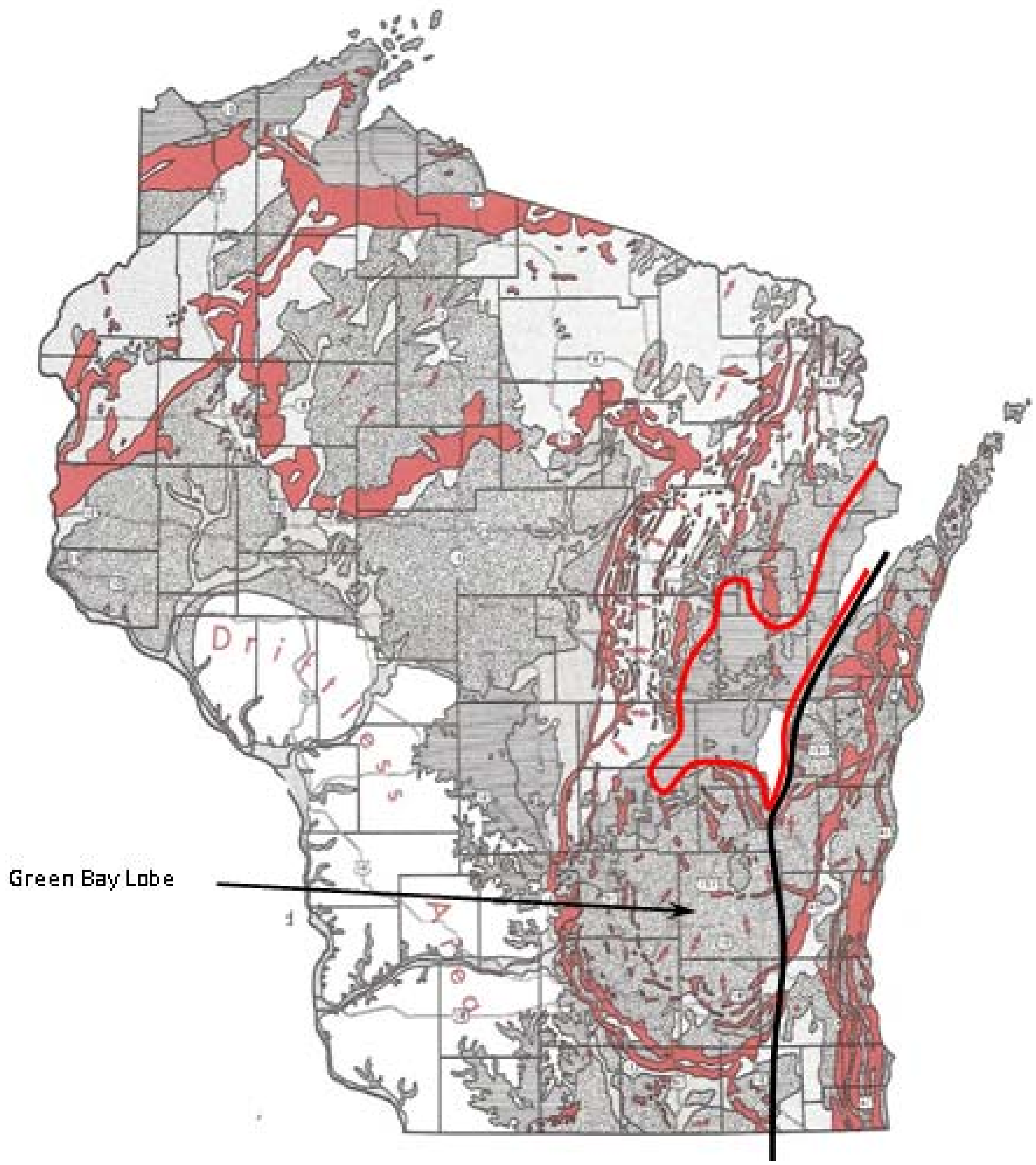

Figure 2: Ice age deposits of Wisconsin. Brown areas are moraines of the LGM (modified from Thwaites (1960)). The underlying Paleozoic sandstones become confined east of the thick black line. Areas inside the red line are confined by glacial Lake Oshkosh silts and clays (after Hooyer (2007)).

Methods

The Wisconsin Department of Natural Resources (WDNR) Drinking Water Database (http://www.dnr.state.wi.us/org/water/dwg/data.htm) and the associated Groundwater Retrieval Network (http://prodoasext.dnr.wi.gov/inter1/grn$.startup) were used to identify potential sampling wells. Potential wells had to satisfy the following criteria: a) the well was in active status b) the well had historical record of major ion composition c) the well was open only in the deep sandstone aquifer d) the well owner would grant sampling access. Candidate wells were sampled for major ions, sulfur isotopes in the summer of 2009. From this data, wells were selected for further study.

Wells were sampled at the raw water tap that exits the well before any water treatment occurs. Wells were pumped for at least one hour before sampling. Field measurement of temperature pH, conductivity, and dissolved oxygen (DO) were taken by electrodes in a flow through chamber. Portable colorimetric test kits (Chemetrics, Inc.) were used at the outlet tubing to measure sulfide, ferrous iron and an additional DO measurement. Electrode based and colorimetric DO analyses always coincided within the accuracy limits of the colorimetric method.

Samples for discrete analyses were collected after exiting the flow-through chamber. Major anion, $\delta^{18}O$ and $\delta^{2}H$ samples were collected after filtering through a 0.2um filter. Major cation samples were treated with trace metal grade nitric acid (4N) immediately after filtration. Alkalinity was determined immediately by titration with 0.02N HCl to pH 4.5. Sulfur isotope samples were collected with no headspace in 4L collapsible bladders. pH was adjusted with HCl to ~3.0 and barium chloride added to quantitatively precipitate dissolved sulfate as $BaSO_4$. Carbon isotope samples were also collected with no headspace in 4L collapsible bladders to which barium chloride was added. pH was adjusted with NaOH to ~9.0 in order to quantitatively precipitate dissolved carbonate as $BaCO_3$. $BaSO_4$ and $BaCO_3$ precipitates were filtered, dried and sent to the University of Waterloo Environmental Isotope Laboratory for $\delta^{32}S$ analysis or the University of Arizona AMS Laboratory for ^{14}C and $\delta^{13}C$ age dating analysis. $\delta^{18}O$, $\delta^{2}H$ analyses were also performed at the University of Arizona AMS Laboratory. Noble gas samples were collected in 1m long copper tubes attached directly to the raw water sample tap via clear Tygon tubing. Much care was taken to avoid bubble entrainment and the ends of the copper tubes pinched shut to collect the sample. Noble gas analysis was performed at the Environmental Isotope Group at ETH University, Zurich Switzerland. Major ion analyses were done in the author's laboratory via ion chromatography (anions) or flame atomic adsorption spectroscopy (cations).

Results

North transect wells show increasing total dissolved solids (TDS) content along the flow path from northwest to southeast. The four upgradient (northeastern) wells (LT992, BF195, BF197, BF188) average 407(±35) ppm TDS while the five downgradient (southwestern) wells (BF187, BF190, BF216, BF212, IE266) average 652(±153) ppm TDS. In addition, the overall chemical character transitions from Ca-HCO_3 to Ca-SO_4 dominated waters along flowpath. Upgradient wells display water that is strongly bicarbonate in nature with nearly equal amounts of calcium and magnesium as expected in a dolomite-rich aquifer. Increasing amounts of sulfate and to a lesser extent chloride from the dissolution of gypsum and halite are evident in downgradient wells (Figure 3). An additional differentiation between upgradient wells and downgradient wells can be seen in the sulfate isotopic signature. Downgradient wells not only contain more sulfate, but the sulfate is isotopically heavy as is typical for sulfate that originates from marine gypsum. A well-known layer of pyrite and arsenopyrite exists immediately to the west of the study area which can serve as the source of isotopically light sulfate (Gotkowitz et al., 2004). All major ion data is tabulated in the Appendices.

A more telling attribute of geochemical evolution along flow path is the presence of dedolomitization - at least within aquifer systems such as this one that contain abundant carbonate minerals. The prevalence of relatively soluble calcite in the aquifer causes it to be at saturation with calcite, continuing dissolution of gypsum along the flow path drives a series of sequential reactions (dedolomitization) that lead to the net dissolution of dolomite and net precipitation of calcite. These reactions are:

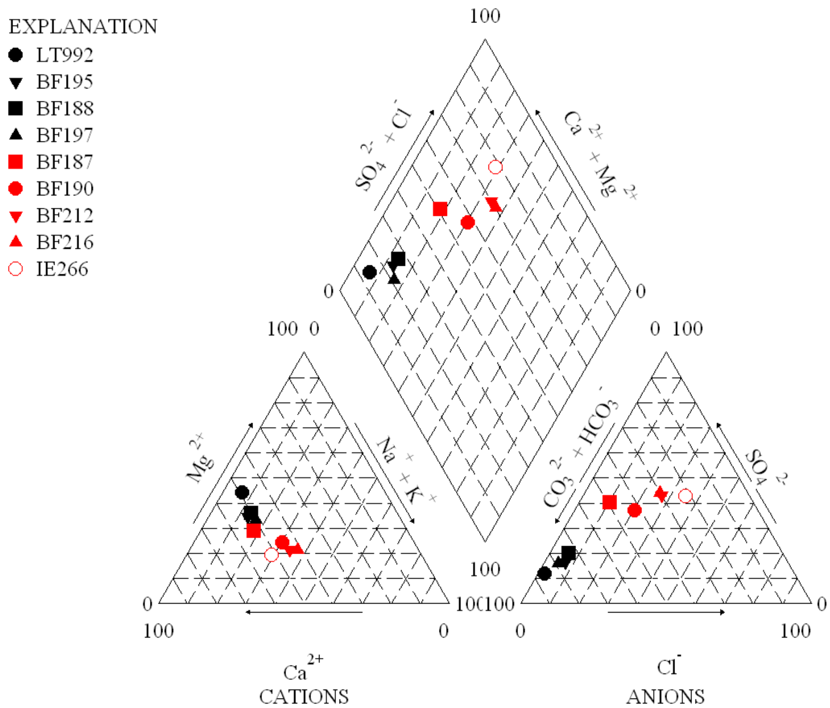

Figure 3: Piper diagram of north transect wells. Red symbols are older waters that were recharged during the LGM, black symbols are younger waters that were recharged after the LGM (see text).

1) Gypsum dissolution adds Ca^{2+} to the water

2) Additional Ca^{2+} causes calcite oversaturation and the resultant precipitation

3) Calcite precipitation removes CO_3^{2-} from the water causing dolomite under saturation and the resultant dolomite dissolution.

The overall reaction can be written as follows:

$$\underset{\text{(dolomite)}}{CaMg(CO_3)_2\,[s]} + \underset{\text{(gypsum)}}{CaSO_4\,[s]} + H_2O \rightarrow$$

$$\underset{\text{(calcite)}}{CaCO_3\,[s]} + Ca^{2+} + Mg^{2+} + SO_4^{2-} + HCO_3^- + OH^-$$

Wells in the north transect are all near saturation with calcite with calcite saturation indices averaging -0.19$\pm$ 0.16. Saturation indices within a few tenths of zero are considered to be at saturation. Saturation index data is tabulated in the appendices. Waters in which dedolomitization occurs plot along the charge balance derived from the overall reaction given above (Ca^{2+} + Mg^{2+} versus SO_4^{2-} + 1/2 HCO_3^- ; assume OH^- is very small). Strict dedolomitization requires that all sulfate is derived from sulfate minerals, primarily gypsum, however it has been demonstrated that within Green Bay and the surrounding environs, the oxidation of sulfide minerals, chiefly pyrite, are another source of dissolved sulfate (Gotkowitz et al., 2004). The $\delta^{34}S$ isotopic signature of pyrite-derived sulfate is isotopically light, displaying values that range from +10‰ to -15‰ (CDT) whereas sulfate derived from the dissolution of marine gypsum displays values that exceed +20‰ and can reach as high as +30 ‰ in early Paleozoic evaporates. (Clark and Fritz, 1974). The $\delta^{34}S$ isotopic content of measured sulfate was used to adjust for the portion that arises from gypsum dissolution by setting $\delta^{34}S_{pyrite}$ to the lowest measured value (4‰) and $\delta^{34}S_{gypsum}$ to the highest measured value (34‰).

Dedolomitization results are shown in Table 1 and Figure 4. The three farthest downgradient wells (BF212, BF216, IE266) fall close to the charge balance line and display cation and anion sums of 3.0 or greater indicating more extensive dedolomitization than in the remaining wells (cation and anion sums between 2.0 and 3.0)

Well #	Ca^{2+} (mMol/L)	Mg^{2+} (mMol/L)	HCO_3^- (mMol/L)	$SO_4^{2-}{}_{(total)}$ (mMol/L)	$\delta^{34}S$ (‰)	$SO_4^{2-}{}_{(gypsum)}$ (mMol/L)	$SO_4^{2-}{}_{(gypsum)}$ (%)	Ca^{2+} + Mg^{2+}	1/2HCO_3^- + SO_4^{2-}
BF187	1.55	0.84	3.49	0.61	16.9	0.26	43	2.39	2.36
BF188	1.27	0.90	4.32	0.15	11.9	0.04	26	2.17	2.31
BF190	1.49	0.79	3.11	1.13	29.0	0.94	83	2.27	2.68
BF195	1.18	0.78	3.74	0.07	9.3	0.01	18	1.96	1.94
BF197	1.22	0.82	4.28	0.12	12.2	0.03	27	2.04	2.26
BF212	2.11	1.00	3.25	1.97	29.4	1.66	85	3.11	3.60
BF216	2.02	1.02	3.26	2.37	33.9	2.37	100	3.05	4.00
IE266*	2.94	1.10	2.87	2.38	29.2	2.00	84	4.04	3.81
LT992	1.33	1.19	5.07	0.02	5.6	0.00	5	2.52	2.55

Table 1: Dedolomitization analyses for north transect wells. IE266 is an anomalous well – see text.

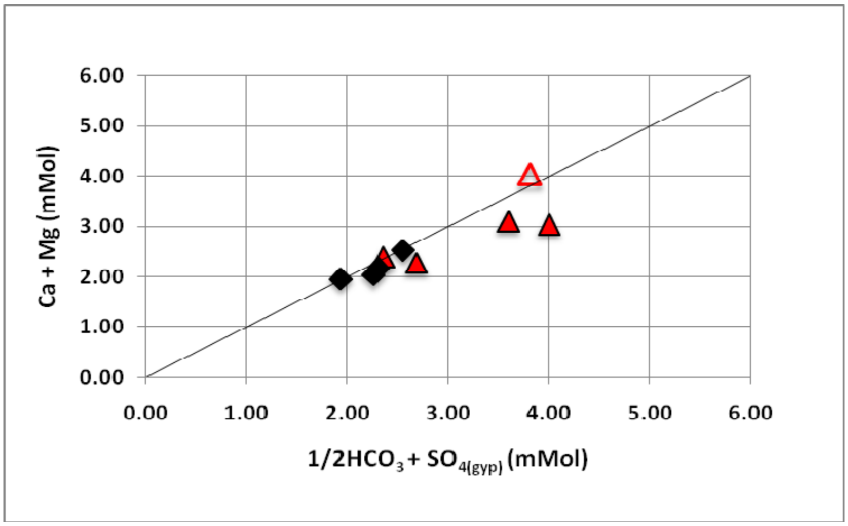

Figure 4: Dedolomitization charge balance plot in north transect wells. Sulfate concentrations are adjusted to reflect the portion that is derived from gypsum dissolution. Red triangles are wells recharged during the LGM, black diamonds were recharged post LGM. Open red triangle is IE266.

Two wells exhibit anomalous behavior, BF191 and IE266. BF191 in particular is anomalous in that it shows the lowest measured TDS of any well, a strong Ca-HCO_3 character and little dedolomitization in spite of its location near the middle of the flow path. In addition its ^{14}C age is negative, its isotopic signature is extremely heavy (resulting in an impossibly warm $\delta^{18}O$ temperature) and the noble gas data could not be rectified by the fitting program. All of these data are indicative contamination with another water source likely through a compromised well casing or localized faulting. Raw data for BF191 is listed in the appendices and it is located on the base map for reference (Figure 1) however it has been excluded from any further interpretation (data plots or contour maps). IE266 is anomalous only in its isotopic composition (and the resulting $\delta^{18}O$ temperature) and ^{14}C age with respect to its position in the flow path; major ion data agrees with other wells in the transect. The noble gas sample was lost for this well. This is also likely to be caused by a compromised well casing or localized faulting that allows mixing of the aquifer with younger, warmer water within the well bore. IE266 data is included on all data plots and contour maps.

The increasing age of these samples with distance downgradient was confirmed by ^{14}C age dating (Table 2). The ^{14}C ages and errors are averages and ±1 standard deviations obtained by using three different correction models for calculating the initial activity A^0 of radiocarbon (Fontes and Garnier (1979); Pearson and White (1967); Tamers (1967)). Figure 8 contains a map of the same data. The ^{14}C data confirm that the eastern portion of this transect contains groundwater that was recharged during the time when the ice sheets of the Michigan and Green Bay Lobes last covered the area (Mickelson and Colgan, 2004). A clear demarcation between water older and younger than ~10 k.a. (LGM and post-LGM recharge respectively) is seen in the center of the transect roughly parallel to the modern day Fox River. Two analogous demarcation lines were observed in the south transect that separate pre-LGM from LGM wells and LGM from post-LGM wells (Klump et al., 2008). There are no municipal wells far enough eastward along the flowpath in the north transect to encounter pre-LGM water.

Well	δ^2H (‰)	$\delta^{18}O$ (‰)	^{14}C (pmC)	$\delta^{13}C$ (‰)	A^0 (pmC)	^{14}C age (yr)	$\delta^{18}O$ temperature (°C)
BF187	-110.30	-15.40	12.76(±0.15)	-10.9	47(±6)	10752(±1048)	-2.6
BF188	-88.96	-12.72	21.36(±0.20)	-12.6	54(±6)	7601(±887)	1.3
BF190	-125.65	-17.47	8.73(±0.15)	-11.1	48(±6)	14055(±1075)	-5.6
BF195	-84.70	-11.71	29.34(±0.20)	-11.6	50(±7)	4389(±1053)	2.7
BF197	-90.99	-12.75	18.31(±0.17)	-12.5	51(±2)	8528(±394)	1.2
BF212	-120.68	-16.85	4.43(±0.12)	-10.4	46(±8)	9326(±1430)	-4.7
BF216	-127.66	-17.31	4.52(±0.12)	-11.5	49(±5)	19684(±896)	-5.3
IE266*	-74.36	-10.35	28.25(±0.21)	-8.1	42(±16)	2801(±2964)	4.7
LT992	-78.10	-11.02	32.34(±.022)	-12.8	53(±3)	4051(±443)	3.7

Table 2: Stable isotope and radiocarbon analyses for north transect wells. ^{14}C ages and errors are average values and ±1 standard deviation as determined by making use of three different correction models for calculating the initial activity (A^0) of radiocarbon. IE266 is an anomalous well – see text.

Stable isotope data also support the observation that Pleistocene age water is present in this aquifer. All wells exhibit isotopic values that lie along the global meteoric water line with no indication of isotope exchange with aquifer solids (Figure 5). Meteoric water is isotopically lighter if it evaporated in a cold climate and this systematic relationship between isotopic content and temperature can be used to estimate the average annual temperature at the time of recharge from the relationship: $\delta^{18}O$(‰) = 0.695*T(°C)-13.6 (Dansgaard, 1964). A plot of $\delta^{18}O$ temperature versus ^{14}C age is shown in Figure 6. Also shown is the equivalent data for the south. Data from south transect wells transect (from Klump et al. (2008)) is tabulated in the Appendices. A minimum age is given for the oldest well in the south transect because this well has very little ^{14}C activity (0.07 ± 0.2 pmC) and is at the edge of reliable ^{14}C dating. Both temperature trends are consistent with modern day average annual temperatures of 6.4 °C in Green Bay and 8.5 °C in Milwaukee (data available at http://www.aos.wisc.edu/%7Esco/clim-history/index.html).

Obvious temperature minimums occur in both transects that broadly coincide with available literature dates for LIS advance and retreat. LIS chronology is not well constrained, largely due to a paucity of available radiocarbon dates (Attig et al., 2011). It is generally presumed that ice moved into the Wisconsin area about 26,000 years ago (Mickelson and Colgan (2004), Winguth et al. (2004)) and completely retreated out of northern United States by 9,800 years ago (Mickelson and Colgan, 2004). Estimates for the timing of the initial ice retreat of the Green Bay Lobe from its maximum position center around 22,000 years ago (Hooyer (2007); Winguth et al. (2004)) although more recent estimates have ice remaining at the maximum position for another 3500 years; until 18,500 years ago (Attig et al., 2011). The ice margin near the latitude of Fond du Lac (midway between the north and south transects) has been dated as early as 19,000 years ago although small re-advances occurred at 16,500 and 13,700 years ago (Hooyer (2007), Hooyer et al. (2009)). The Two Rivers terminal moraine is close to the north transect and has been dated at 13,700 years ago (Winguth et al., 2004). The south transect lies at a latitude midway between the Johnstown and Green Lake moraines which have been dated at 22,200 and 17,000 years respectively (Winguth et al., 2004). In Figure 6, ice presence is depicted as ~19,000-26,000 years ago in the south transect and ~13,000-26000 years ago at the north transect although the timing of retreat could be as much as 3500 years later.

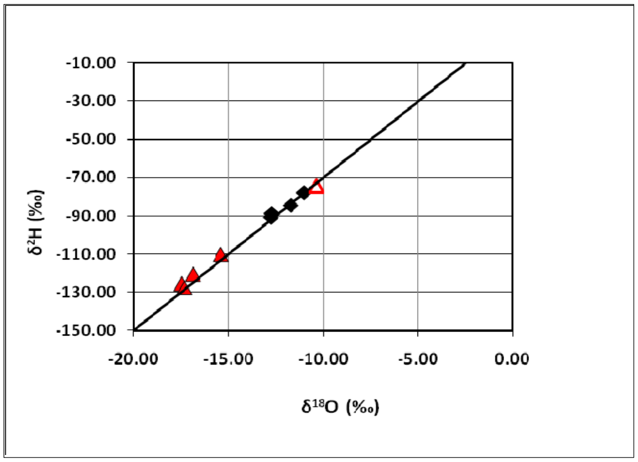

Figure 5: Stable isotope data for north transect wells. Solid line is the global meteoric water line: $\delta^2H = 8 \times (\delta^{18}O) + 10$. Red triangles are wells recharged during the LGM, black diamonds were recharged post LGM. Open red triangle is IE266.

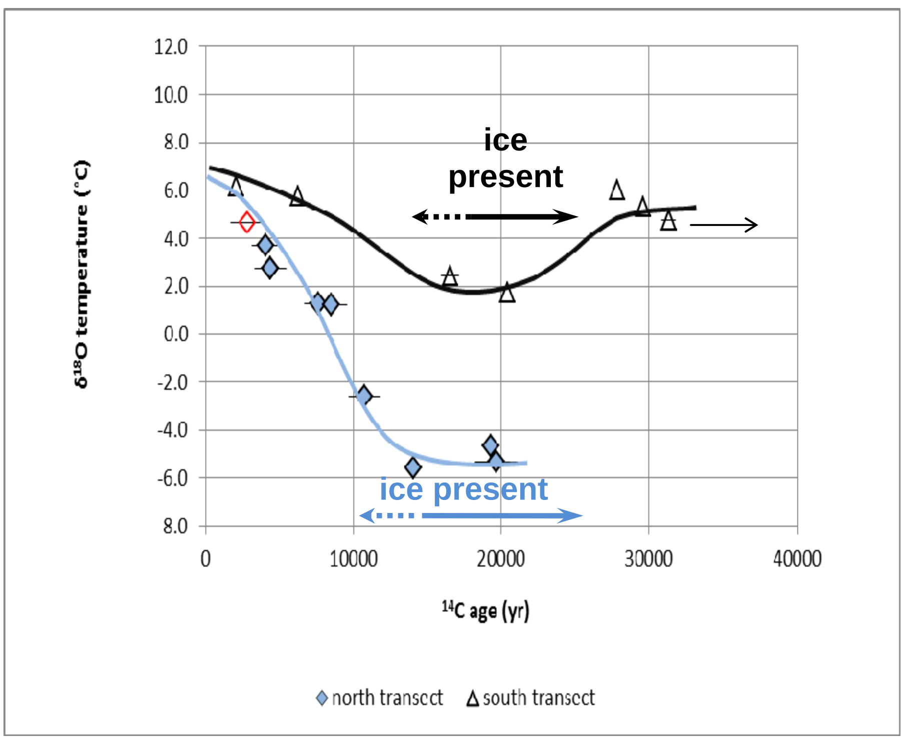

Figure 6: Oxygen isotope temperature versus corrected ^{14}C ages for north and south transects. South transect values taken from Klump et al. (2008). A minimum age is given for the oldest well in the south transect because this well has very little ^{14}C activity (0.07 ± 0.2 pmC) and is at the edge of reliable ^{14}C dating. Error bars are ±1 standard deviation as determined by making use of three different correction models for calculating the initial activity (A^0) of radiocarbon. Open red diamond is IE266.

Analysis of noble gas temperatures and the amount and fractionation of excess air are also consistent with a glacial origin for groundwater in the north transect. Both environmental parameters were calculated using the closed-system equilibrium (CE) model (Aeschbach-Hertig et al., 2000) which assumes that residual bubbles of air are trapped in groundwater as the water table rises during a recharge event. The air in these bubbles reaches a closed-system equilibrium with the surrounding water that is a direct function of the amount of air dissolved and hydrostatic head during equilibration and is an inverse function of soil temperature. Under these conditions the heavy noble gases preferentially dissolve and the aqueous noble gas content differs from atmospheric content. This fractionation of the different noble gases upon dissolution is described by the fractionation factor F, which ranges from 0 to 1 with complete dissolution of entrapped air, i.e., unfractionated excess air, represented by F = 0. This fractionation results in a Ne → Xe enrichment pattern in which successively heavier gases are preferentially dissolved. The pressure parameter q is the ratio of dry gas pressure in the entrapped gas to that in the free atmosphere and thereby is a measure of the hydrostatic pressure exerted on the entrapped air. The reader is referred to Kipfer, et al., (2002) for a detailed description of the process of excess air generation.

Groundwater almost universally contains dissolved air in excess of atmospheric equilibrium because of the extra pressure exerted on bubbles trapped during recharge. Normally recharged groundwater contains excess air, as defined by Ne in excess of atmospheric equilibrium (ΔNe), of 10-50% (Kipfer et al., 2002). Pure glacial meltwater is known to contain as much as several hundred percent ΔNe (Vaikmae et al., 2001). Excess air in glacial meltwater has very minimal fractionation because it originates as air trapped in firn – a process that does not significantly fractionate air (Severinghaus and Battle (2006); Huber et al. (2006)).

Noble gas data (Table 3) are unusual in several respects. The amount of excess air (ΔNe) ranges from ~60 to ~107% which is higher than is seen in normal groundwaters, but not as high as expected from pure melted glacial ice. Additionally, the pressure factor (q) is very high for normally recharged groundwater. Each 0.1 increment in q above 1.0 is equivalent to a recharge head of 1 meter (Aeschbach-Hertig et al., 1999) implying recharge heads of as much as 8 meters (Figure 7). Lastly, noble gas temperatures all lie between 1.6 and 3.2 °C. There is no agreement between $\delta^{18}O$ and noble gas temperatures; in particular there is no trend of decreasing.

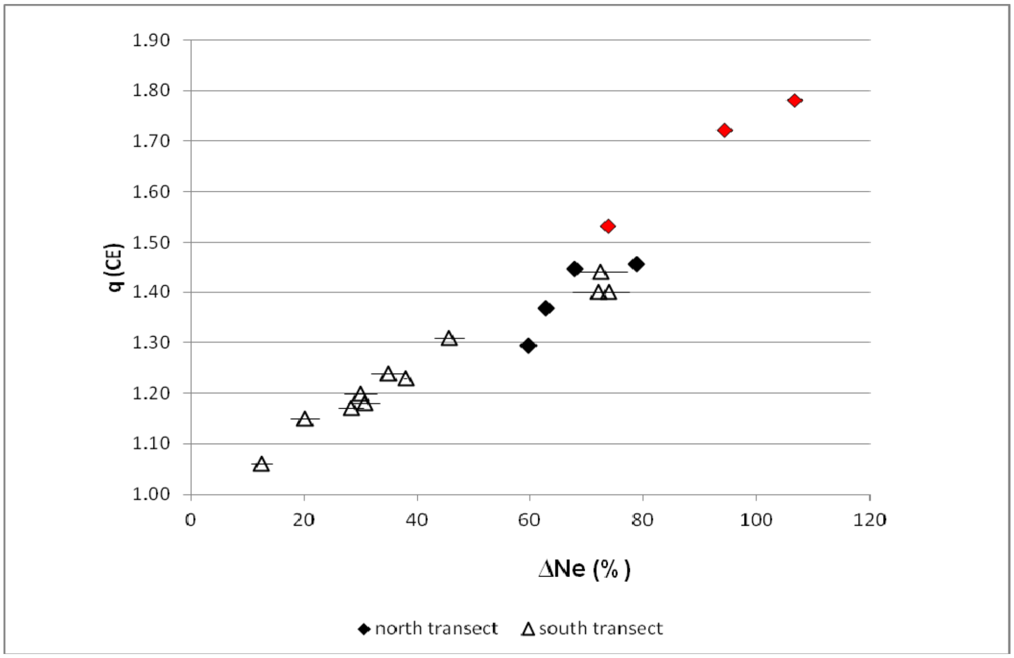

Figure 7: Plot of excess air (ΔNe) versus pressure factor (q) as calculated from the CE model. South transect values taken from (Klump et al., 2008). Black diamonds are post-LGM recharge wells; red diamonds are LGM recharged wells. Typical ΔNe values seen in normally recharged groundwater lie between 10% and 50%. ΔNe uncertainties are determined from the covariance matrix in the least squares fitting algorithm (Aeschbach-Hertig et al., 1999).

well #	noble gas temperature (°C)	Δ Ne (%)	q (CE model)	F (CE model)	$\delta^{18}O$ temperature (°C)	^{14}C age (yr)
BF187	3.1(±0.6)	73.8(±1.4)	1.53	0.47	-2.6	10752(±1048)
BF188	3.2(±0.4)	67.8(±1.4)	1.44	0.43	1.3	7601(±887)
BF190	gas sample lost				-5.6	14055(±1075)
BF195	1.6(±0.3)	59.6(±1.4)	1.29	0.12	2.7	4389(±1053)
BF197	2.8(±0.4)	78.8(±1.4)	1.46	0.29	1.2	8528(±394)
BF212	3.2(±0.6)	106.8(±1.4)	1.78	0.37	-4.7	9326(±1430)
BF216	3.1(±0.8)	94.3(±1.4)	1.72	0.44	-5.3	19684(±896)
IE266*	gas sample lost				4.7	2801(±2964)
LT992	4.1(±0.4)	62.8(±1.4)	1.37	0.35	3.7	4051(±443)

Table 3: Noble gas data for north transect. ΔNe and noble gas temperature uncertainties are determined from the covariance matrix in the least squares fitting algorithm (Aeschbach-Hertig et al., 1999).

temperature in older, downgradient wells in the noble gas data. This is in contrast to the south transect in which $\delta^{18}O$ and noble gas temperatures largely agreed with each other (Klump et al., 2008).

Discussion

The confined nature of the deep sandstone and the resulting long flow paths are supported by the observed geochemical trends including increasing TDS, the transition from Ca-HCO_3 to Ca-SO_4 dominated water, and a well-developed dedolomitization pattern and increasing ^{14}C age. This is consistent with eastward flow in a confined aquifer that is recharged to the west of the transect. Both the thick sequence of glacial lake clays and the Maquoketa Shale serve as confining units (cf. Figure 1).

$\delta^{18}O$ data, in conjunction with ^{14}C ages, display a cooling paleotemperature record that coincides with the LGM (Figure 6). Water recharged during the LGM displays $\delta^{18}O$ derived temperatures that indicate average annual temperatures as low as -5.3 °C; a temperature that is 12 °C cooler than the modern average annual temperature of 6.4 °C. This is much larger than previous estimates of -5 to -9 °C of cooling in North American paleogroundwaters (Clark et al. (1997); Stute et al. (1995); Aeschbach-Hertig et al. (2002); Ma et al. (2004)), and Europe (Andrews and Lee (1979); Stute and Deak (1989); Beyerle et al. (1998)). There could be no meteoric recharge in a climate this cold because of the presence of extensive permafrost and the lack of liquid water. This water must contain a large proportion of glacial ice that precipitated in a very cold climate and maintains its isotopic signature during later recharge. As such it does not reflect the climatic conditions prevailing during the time of recharge but it does indicate that water was injected into the aquifer during the LGM and that a large proportion of it originated as glacial meltwater. The demarcation between LGM and post-LGM recharged wells occurs at an age less than 10 k.a. and a $\delta^{18}O$ temperature above 0° C (Figure 8). The demarcation between LGM and post-LGM wells can also be seen in the major ion signature (Figure 3), and the extent of dedolomitization (Figure 4).

Glacially recharged water is a function of the hydrology of drainage above (supraglacial), within (englacial) and beneath (subglacial) glaciers. This is highly complex system that is a function of temporally variable supraglacial water supply, the direction and intensity of internal stress within the glacier and the existence of high conductivity zones (fractures and debris filled crevasse traces) (Gulley et al., 2009). The vast majority of supraglacial water that drains to the

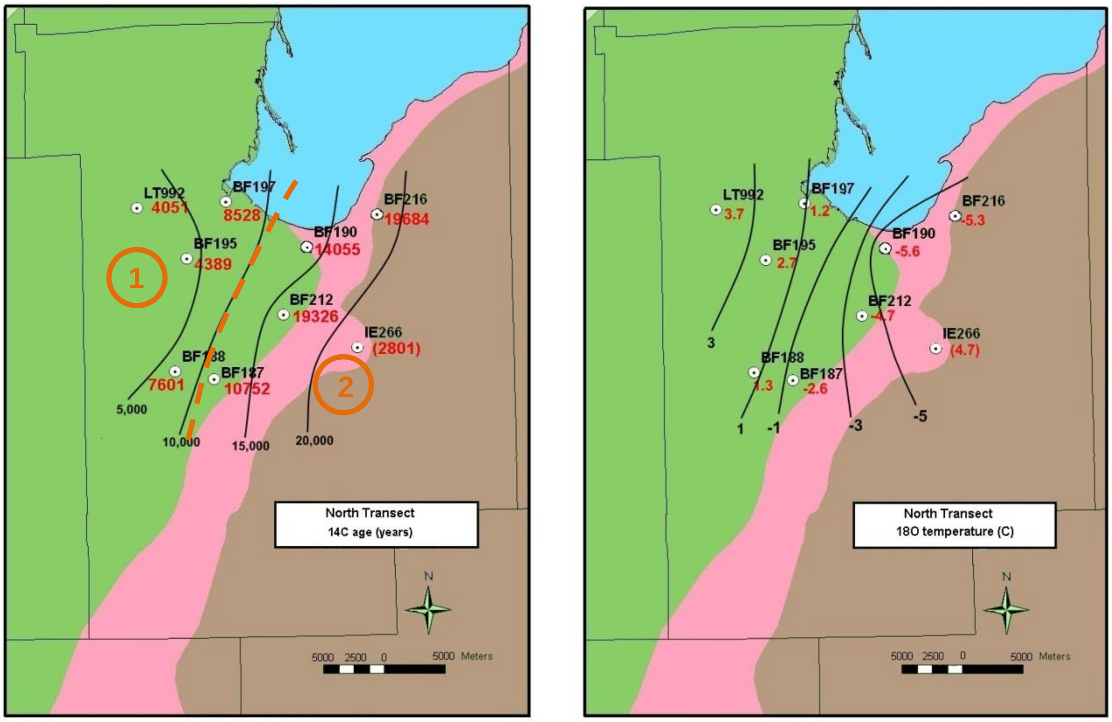

Figure 8: Maps of north transect wells showing ^{14}C ages and $\delta^{18}O$ temperatures. Bedrock units are shown using the color scheme of Figure 2. Dotted orange line (on ^{14}C age map) denotes the demarcation between post-glacially recharged water (1) and glacially recharged water (2). Well IE266 is not included in the contouring.

base of the glacier is transported by a system of large (meter scale diameter), irregularly spaced moulins that preferentially occur in fast moving portions of the glacier where ice fracturing is prevalent (Gulley et al., 2009). Within alpine glaciers, water levels in these moulins can vary by hundreds of meters in as little as a day (Badino and Piccini (2002); Vieli et al. (2004)). A network of small interconnected fractures is also present that operates as a spatially extensive drainage system that transmits a much smaller volume of water. These two drainage systems are hydraulically connected with the rapidly fluctuating, high volume moulin system inducing transient pressure gradients in the less transmissive fracture network. Beneath continental glaciers, direct basal melting is also a component of subglacial water. The relative proportion of basal met to surface drainage is specific to each ice sheet and is a function of the overall temperature regime, ice thickness and flow dynamics of the glacier (Bell, 2008). Although it is clear that two interconnected englacial drainage systems plus basal melting all contribute to subglacial water, the spatial and temporal variability of this complicated hydrologic system is poorly understood. Effects on the underlying aquifers are even less understood because most subglacial drainage studies focus solely on the effect that subglacial water has on the speed of ice movement.

The north transect is ~100 miles north of the maximum glacial extent but below the equilibrium line (where melting/ablation exceeds snowfall). As such, supraglacial lakes and streams containing a mix of meteoric water and glacial meltwater would have formed. The entire englacial drainage system began filling up early in the melt season when the moulins were still closed at the base by ice creep during the preceding winter and supraglacial influx began increasing. This was a very dynamic system with partially filled, frozen off sections of moulins and small fractures both of which contained water and pressurized air that acted like the pressurized bubbles of the closed system equilibrium model. As the melt season continued, the moulin-based drainage system re-opened and the englacial system was efficiently drained via surface water outlets at the terminus. As winter approached, supraglacial flux slowed, the moulins re-closed and the water table elevation became a function of slow drainage through relatively low conductivity subglacial sediments.

The contrast between the noble gas and isotopic data collected from the north transect and that reported for the south transect (Klump et al., 2008) contains information that indicates the physical mechanisms responsible for subglacial recharge at different positions within the glacier. In the north transect, the observed normal fractionation patterns (Ne → Xe enrichment), pressure factors (q) indicating recharge heads of as much as 8 meters in the LGM recharged wells, ΔNe values in excess of normal recharged groundwater (Figure 7) and noble gas temperatures that are all above 0 °C with no spatial trend (Table 3), are all consistent with recharge that was dominated by supraglacial melt and b) occurred at a water table that was in effect within the ice sheet. Recharge within the dynamic englacial system allows for the observed high pressure factors and the associated large ΔNe values. Because the physics of pushing excess air into the water are the same in pressurized moulins as in the pore spaces of partially saturated sediment, the Ne → Xe enrichment pattern is identical to normally recharged groundwater. A significant amount of direct basal melt recharge is not possible because direct recharge of melted ice would lead to a very small Ne → Xe enrichment pattern. Noble gas temperatures reflect the air temperature within the moulins and this was just above freezing. $\delta^{18}O$ temperatures reflect the isotopic signal of the ice itself which does not get re-set when it melts. Note that in this case neither the δ18O nor the noble gas temperatures reflect local climate. The conclusion is that recharge in the north transect is mostly supraglacial melt with lesser amounts of local meteoric water. This is a close analog to the modern day Greenland ice sheet in which surface melt drains completely to the subglacial hydrologic system. In contrast, modern day Antarctic ice sheets display little connectivity between surface meltwater and the base of the glacier but instead rely on basal melting to supply subglacial water (Bell, 2008).

In the south transect aquifer recharge occurred under conditions where the annual pressure change was approximately 0.5 to 4 meters and ΔNe values ranging from 12%-72% both of which are within the typical range for meteoric waters (Figure 7). The south transect was at the very edge of the ice sheet and the recharge was dominated by meteoric water. Recharge occurred through a water table that was not subject to the dynamic conditions of englacial hydrology but was at the base of the ice or just below within the sediment. Any supraglacial lakes/streams had a large component of local meteoric water and moulins either did not freeze shut (it was too warm at this latitude) or the ice decayed so rapidly that active moulins did not form at all. Since most of the recharge in the south transect was meteoric water (less was supraglacial melt), the $\delta^{18}O$ temperatures and the noble gas temperatures match because they were set at the same time/place. In this case, both temperature records reflect the local climate at the time of recharge. The Ne → Xe enrichment pattern remains normal therefore contributions from direct basal melt were small. Figure 9 is a diagrammatic representation of recharge mechanisms occurring along the axis of the Green Bay lobe.

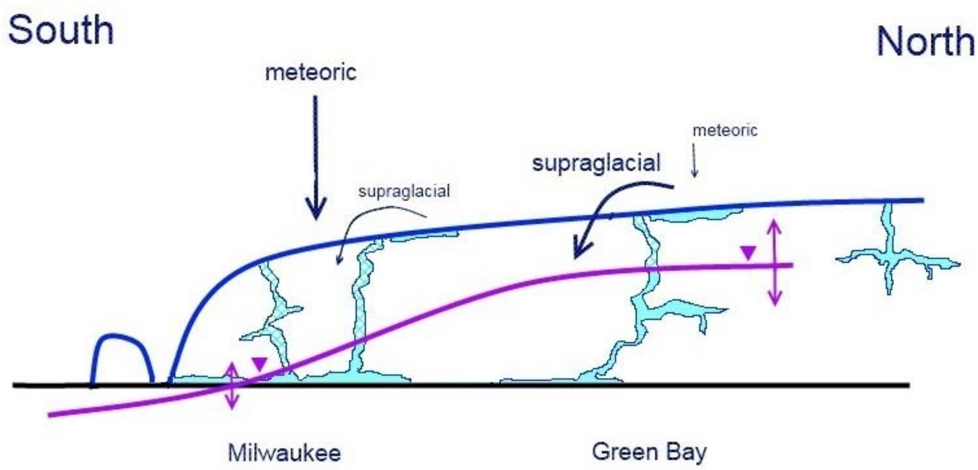

Figure 9: Schematic of glacial recharge mechanisms as seen in the Green Bay lobe. In the south transect (Milwaukee) englacial hydrology is minimal and the water table resides at or just beneath the base of the ice. Recharge is dominated by meteoric water (recharge heads, pressure factors and fractionation are normal, $\delta^{18}O$ and noble gas temperatures reflect local climate). In the north transect (Green Bay) the water table resides within the glacier and englacial dynamics prevail. Recharge is dominated by supraglacial melt (recharge heads and pressure factors are high, fractionation is normal, $\delta^{18}O$ temperatures reflect moulin air temperature at time of recharge, noble gas temperatures reflect isotopic signature of the ice itself). See text for full explanation.

Conclusion

This study, in conjunction with earlier work (Klump et al., 2008), provides a better understanding of the paleohydrology of aquifers in the upper Midwest and by extension, in other glaciated parts of the world. It demonstrates the presence of glacially recharged water in the deep sandstone aquifer along the entire eastern coastline of Wisconsin. It is clear that Laurentide Ice Sheet did not seal off the aquifer but instead injected large volumes of glacial meltwater into the aquifer. This information is of use to water supply managers responsible for making long term water management decisions throughout eastern Wisconsin. For instance, the results of this study indicate that the majority of the water pumped from both the Green Bay and the Milwaukee areas has been Pleistocene in age and is not being replenished on a time scale relevant to human activities.

This research also indicates that the LIS was analogous to the modern day Greenland ice sheet with subglacial water being primarily derived from supraglacial melt instead of basal melting. To the author's knowledge, this study is the first to use noble gas and isotopic data to deduce the provenance of water being delivered to the base of glaciers. Data of this sort can aid in determining potential forcings behind the rapid margin fluctuations that characterized the deglaciation of the southern LIS. In addition to addressing important water resource issues, our research on the ice-water system may lead to new insights regarding ice-stream and fast-ice behavior, of great significance not only for understanding the southern lobes of the LIS, but also for predictions of the response of the remaining ice sheets (Greenland and Antarctic), with attendant effects on sea level, to present and future climate change.

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APPENDIX A

North and Central transects: Physical well data, major ion and isotopic composition.

North Transect (Brown County)

General Information							
Well #	High Capacity #	Location (County, City)	Depth (ft)	Closed to (ft)	Contact	Elevation (masl)	static water level (mbgs)
BF187	75557	Brown, DePere	863	265	Dan Carpenter	195	43
BF188	75558	Brown, DePere	787	500	Dan Carpenter	191	--
BF190	75560	Brown, Preble	950	311.5	Tom Landwehr	179	36
BF191	75561	Brown, Preble	973	341	Tom Landwehr	182	27
BF195	75565	Brown, Green Bay	777	235	Tom Landwehr	197	--
BF197	75567	Brown, Green Bay	815	269.5	Tom Landwehr	178	46
BF212	75582	Brown, Bellevue	855	547	Bill or Glen	180	52
BF216	75586	Brown, Scott	1235	646	Mel Deprey	232	89
IE266	1717	Brown, Bellevue	1130	605	Bill or Glen	230	96
LT992	2895	Brown, Hobart	785	487	Rick Kinney	207	29

Center Transect (Fond du Lac, Washington & Ozaukee Counties)

General Information							
Well #	High Capacity #	Location (County, City)	Depth (ft)	Closed to (ft)	Contact	Elevation (masl)	static water level (mbgs)
AY379	1064	FdL, Byron	1150	373	Kathy Scharf	258	52
BF794	78463	FdL, Campbellsport	1200	585	Mark Grueber	303	61
BF800	78469	FdL, Fond du Lac	835	579	Kathy Scharf	229	18
BG643	83701	Ozaukee, Cedarburg	1210	718.7	Tim Martin	242	33
BH246	87902	Washington, Germantown	1282	531	Jim Driver	267	57
BH275	87931	Washington, Allenton	735	440	Tom Gurecki	301	52
KR925	1745	FdL, Campbellsport	1245	649	Mark Grueber	323	97
MK423	2313	FdL, Waupun	866	326	Steve Schramm	271	16

APPENDIX A continued

North Transect (Brown County)

	Chemical and Isotope Data (mg/L unless otherwise denoted)																					
Well #	Temp (°C)	Spec. Cond. (mmhos/cm)	pH (sU)	DO	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Fe^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	HS^-	$\delta^{34}S$ (‰)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	Alkalinity (mEq/L)	measured TDS	calcite SI	Dolomite SI	Gypsum SI
BF187	11.8	0.689	7.48	1.6	62.1	20.4	22.3	4.5	0.25	213.2	27.0	136.2	0	0	16.89	-15.40	-110.30	3.5	427	-0.02	-0.97	-1.53
BF188	11.2	0.551	7.02	1.3	50.9	22.0	14.0	4.2	0.1	263.4	13.9	55.8	0	0	11.87	-12.72	-88.96	4.32	305	-0.45	-1.12	-1.96
BF190	11.9	0.552	7.35	1.1	59.5	19.1	43.4	5.2	0.4	189.9	54.5	130.0	0	0	28.97	-17.47	-125.65	3.11	421	-0.22	-0.77	-1.57
BF191	9.5	0.314	7.03	12.7	34.3	19.5	7.1	1.3	0.0	127.2	13.4	24.1	1.2	0	4.21	-5.85	-42.24	2.1	163	-0.9	-1.94	-2.41
BF195	10.7	0.252	7.19	2.0	47.3	18.9	12.3	3.0	0.0	227.9	12.2	37.8	0.34	0	9.35	-11.71	-84.70	3.8	239	-0.36	-0.99	-2.13
BF197	11.2	0.513	7.48	2.2	48.9	19.9	16.3	4.5	0.1	261.4	10.0	41.5	0	0	12.19	-12.75	-90.99	4.28	264	0	-0.25	-2.09
BF212	11.6	1.040	7.31	0.7	84.4	24.4	71.9	6.3	0.3	198.5	103.7	223.7	0	0	29.36	-16.85	-120.68	3.27	639	-0.14	-0.67	-1.26
BF216	14.3	1.036	7.34	0.7	81.1	24.9	78.2	7.7	0.3	199.1	99.8	228.5	0	0	33.94	-17.31	-127.66	3.26	647	-0.09	-0.49	-1.28
IE266	12.9	1.250	7.04	1.7	117.8	26.7	73.2	7.9	0.3	174.9	166.6	271.8	0	0	29.22	-10.35	-74.36	2.9	786	-0.33	-1.12	-1.08
LT992	10.6	0.543	7.31	0.9	53.4	28.9	6.6	3.4	0.4	309.6	4.9	33.0	0	0	5.57	-11.02	-78.10	5.08	300	-0.08	-0.29	-2.17

Center Transect (Fond du Lac, Washington & Ozaukee Counties)

	Chemical and Isotope Data (mg/L unless otherwise denoted)																					
Well #	Temp (°C)	Spec. Cond. (mmhos/cm)	pH (sU)	DO	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Fe^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	HS^-	$\delta^{34}S$ (‰)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	Alkalinity (mEq/L)	measured TDS	calcite SI	Dolomite SI	Gypsum SI
BF794	10.0	0.834	7.19	4.5	90.9	26.5	10.8	4.2	0.6	372.5	10.7	121.9	0	0	15.98	-9.25	-62.80	6.11	474	0.05	-0.31	-1.46
BF800	11.2	1.139	--	3.5	92.3	35.3	40.3	4.4	0.0	247.0	102.8	192.1	0.34	0	19.57	-12.88	-89.98	4.05	671	0.04	-0.19	-1.30
BG643	10.4	0.758	7.06	1.4	72.0	34.8	12.0	1.4	0.0	358.1	29.6	44.6	2.3	0	1.60	-8.98	-61.51	5.9	411	-0.16	-0.52	-1.96
BH246	11.9	0.737	7.23	0.5	68.7	26.0	4.3	1.3	0.4	387.2	2.6	69.4	0	0	20.75	-9.12	-59.66	6.3	404	0.04	-0.19	-1.78
BH275	11.1	0.762	6.98	1.0	72.6	24.6	6.9	2.2	0.3	350.5	3.8	104.3	0	0	19.43	-9.22	-60.70	5.75	448	-0.25	-0.83	-1.59
KR925	13.0	0.948	7.2	0.8	101.0	30.8	23.2	5.9	0.9	299.8	34.3	216.2	0	0	19.41	-11.19	-79.21	4.94	587	0.02	-0.29	-1.21
MK423	10.0	0.661	7.18	1.3	69.0	31.3	3.8	1.5	1.5	381.9	4.9	21.0	0	0	n/a	-9.88	-66.01	6.26	365	-0.03	-0.28	-2.29

APPENDIX B

North and central transects: radiocarbon and noble gas data. ΔNe and noble gas temperature uncertainties are determined from the covariance matrix in the least squares fitting algorithm. Uncertainties in corrected ^{14}C age are ±1 standard deviation as determined by making use of three different correction models for calculating the initial activity (A^0) of radiocarbon. Uncertainties in percent modern ^{14}C are analytical error as reported by the University of Arizona AMS analytical laboratory.

North Transect

well #	^{14}C (pcm)	^{13}C (‰ PDB)	uncorrected ^{14}C age (yr)	corrected ^{14}C age (yr)			avg. corrected ^{14}C age (yr)	noble gas temperature (°C)	Ne (equ) (ccSTP/g)	Ne (m) (ccSTP/g)	Δ Ne (%)	q (CE model)	F (CE model)
				Tamers	Pearson	F. & G.							
BF187	12.8 (±0.2)	-10.9	16539	11962	10158	10137	10752 (±1048)	3.1 (±0.6)	2.10E-07	3.66E-07	74 (±1.4)	1.53	0.47
BF188	21.4 (±0.2)	-12.6	12400	8626	7097	7082	7601 (±887)	3.2 (±0.4)	2.10E-07	3.52E-07	68 (±1.4)	1.44	0.43
BF190	8.7 (±0.2)	-11.1	19588	15296	13445	13424	14055 (±1075)	gas sample lost					
BF191	105.0 (±0.4)	-4.6	-391	-4521	-14396	-14495	-11137 (±5730)	--	2.13302E-07	1.71E-07	--	--	--
BF195	29.3 (±0.2)	-11.6	9850	5605	3789	3773	4389 (±1053)	1.6 (±0.3)	2.1395E-07	3.42E-07	60 (±1.4)	1.29	0.12
BF197	18.3 (±0.2)	-12.5	13638	8984	8304	8298	8529 (±394)	2.8 (±0.4)	2.1116E-07	3.78E-07	79 (±1.4)	1.46	0.29
BF212	4.4 (±0.1)	-10.4	25037	20978	18515	18487	19327 (±1430)	3.2 (±0.6)	2.10E-07	4.34E-07	107 (±1.4)	1.78	0.37
BF216	4.5 (±0.1)	-11.5	24875	20719	19180	19154	19684 (±896)	3.1 (±0.8)	2.10E-07	4.09E-07	94 (±1.4)	1.72	0.44
IE266	28.3 (±0.2)	-8.1	10154	6223	1133	1046	2801 (±2964)	gas sample lost					
LT992	32.3 (±0.2)	-12.8	9068	4562	3798	3792	4051 (±443)	4.1 (±0.4)	2.08008E-07	3.39E-07	63 (±1.4)	1.37	0.35

Center Transect

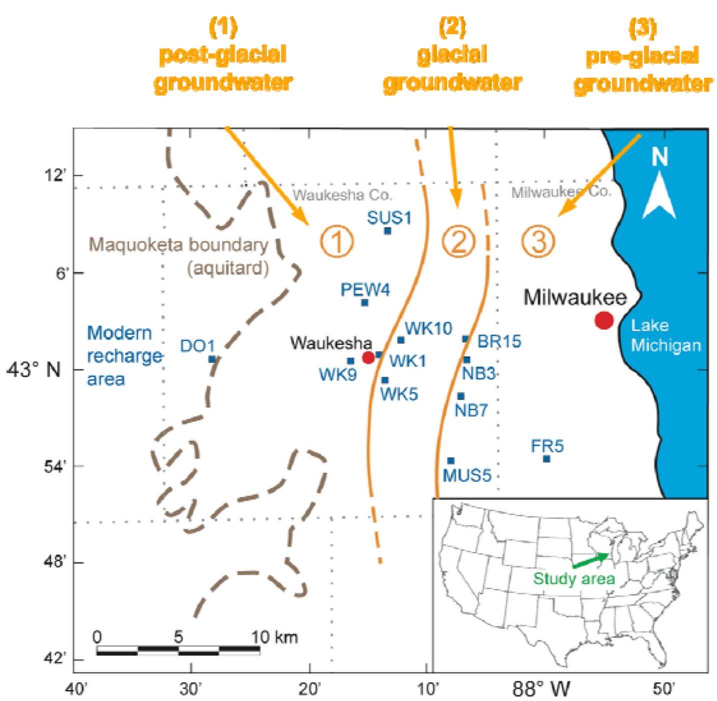
well #	^{14}C (pcm)	^{13}C (‰ PDB)	uncorrected ^{14}C age (yr)	corrected ^{14}C age (yr)			avg. corrected ^{14}C age (yr)	noble gas temperature (°C)	Ne (equ) (ccSTP/g)	Ne (m) (ccSTP/g)	Δ Ne (%)	q (CE model)	F (CE model)
				Tamers	Pearson	F. & G.							
AY379	7.6 (±0.1)	-9.9	20722	16253	13667	13636	14519 (±1502)	0.8(±0.3)	2.16145E-07	3.82E-07	77 (±1.4)	1.38	0.10
BF794	19.1 (±0.2)	-11.7	13319	9190	7430	7418	8013 (±1019)	5.7 (±0.4)	2.04368E-07	5.98E-07	193 (±1.4)	2.07	0.09
BF800	42.6 (±0.3)	-11.8	6849	1319	842	838	999 (±277)	4.4 (±0.5)	2.07395E-07	2.87E-07	39 (±1.4)	1.28	0.62
BG643	69.3 (±0.3)	-13.5	2948	-1185	-2060	-2066	-1770 (±507)	1.8 (±0.5)	2.13538E-07	3.32E-07	55 (±1.4)	1.38	0.52
BH246	46.9 (±0.3)	-10.9	6084	1622	-601	-628	131 (±1291)	8.8 (±0.4)	1.98021E-07	2.39E-07	21 (±1.4)	1.13	0.59
BH275	28.8 (±0.2)	-11.2	9997	6262	3650	3623	4512 (±1516)	8.1 (±0.4)	1.99435E-07	2.38E-07	19 (±1.4)	1.12	0.68
KR925	22.5 (±0.2)	-12.3	11972	7722	6457	6439	6873 (±736)	4.2 (±0.4)	2.07798E-07	3.03E-07	46 (±1.4)	1.30	0.51
MK423	34.5 (±0.2)	-12.0	8560	4314	2742	2731	3262 (±911)	6.4 (±0.7)	2.02989E-07	2.69E-07	33 (±1.4)	1.26	0.68

APPENDIX C

South transect: Location map, noble gas and ^{14}C age data as reported by Klump, et al. 2008.

South Transect (Milwaukee and Waukesha counties)

well #	avg. corrected ^{14}C age (yr)	noble gas temperature (°C)	δ18O temperature (°C)	Δ Ne (%)	q (CE model)	F (CE model)
BR15		2.9 (±0.5)	3.2	72.4 (±4.7)	1.44	0.35
DO1	2065 (±828)	8.1 (±0.4)	6.2	12.5(±1.8)	1.06	0.00
FR5	27851 (±478)	3.4 (±0.4)	6.2	73.8 (±3.7)	1.40	0.2
MUS5		4.1 (±0.6)	7.7	20.1 (±2.5)	1.15	0.8
NB3	54974 (±23619)	3.3 (±0.6)	5.4	34.8 (±3.1)	1.24	0.62
NB7	29606 (±583)	2.6 (±0.2)	5.7	37.9 (±0.3)	1.23	0.51
PEW4		3.5 (±0.5)	5.3	30.6 (±2.9)	1.18	0.51
SUS1		4.5 (±0.6)	4.6	30.0 (±2.9)	1.20	0.65
WK10	20403 (±245)	1.4 (±0.5)	1.9	72.0 (±4.6)	1.40	0.29
WK5	16534 (±371)	2.3 (±0.5)	2.3	45.7 (±2.7)	1.31	0.57
WK9	6277 (±150)	5.5 (±0.5)	5.5	28.3 (±2.2)	1.17	0.58
WK1	8274 (±780)					



Forecasting Impacts of Extreme Precipitation Events on Wisconsin's Groundwater Levels

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Forecasting impacts of extreme precipitation events on Wisconsin's groundwater levels

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Final Report
University of Wisconsin Water Resources Institute
Project Number WR09R005

Project Summary
Forecasting impacts of extreme precipitation events on Wisconsin's groundwater levels

Project I.D.: WR09R005

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Period of Contract: July, 2009 - June, 2010

Background/Need: Large precipitation events in southwest Wisconsin during 2007 and 2008 caused water table rise and flooding of about 4,400 acres several kilometers away from the flood plain of the Wisconsin River. The long-lasting flood caused $17 million in property and crop damage, and drew interest to impacts of climate change on ground water recharge and rapid water table rise.

Objectives: To evaluate potential effects of climate change on temporal and spatial patterns of groundwater recharge in a humid region. The likelihood of groundwater inundation of low-lying areas is also considered.

Methods: We applied a series of climate and hydrologic models to a study area in Spring Green, Wisconsin, for two 20-year periods in the 21st century (2046-2065 and 2081-2100). Statistically down-scaled climate forecasts (50 kilometer resolution) from eight Global Circulation Models (GCMs) were applied to a grid-based soil water balance model (SWB). Daily estimates of deep infiltration from the SWB model were applied as recharge to the water table in a three-dimensional groundwater flow model. Results include estimates of recharge, water table rise and groundwater flooding.

Results and Discussion:

Precipitation: The average of the annual precipitation rates among the eight climate models in both future periods, 886 mm, is 7% greater than simulated for the "base case" period (1981-2000). The range in average annual precipitation for future periods is wider than the base case, varying from 706 to 1,030 mm for 2081-2100. All of the climate models predict an increase in temperatures for all months relative to the base case, coinciding with the increase in CO_2 concentrations in the emissions scenarios.

Recharge: SWB model results show a trend of decreasing average annual recharge in the mid- and late-21st century. Over all eight GCMs, mean annual recharge for 2046-2065 decreased 4% (15 mm) from the base case (358 mm), but three models predict no change or an increase in recharge during this period. By the end of the century, average annual recharge decreases 25% from the base case, and none of the eight models predict an increase compared to the base case.

Although the SWB simulations are predicated on the increase in precipitation forecast by the climate models, the temperature increase common to all eight climate models results in more water partitioned to ET, which reduces recharge to groundwater. The SWB model results are sensitive to plant type, which is represented in the SWB by the soil depth parameter. An increase in this parameter effectively increases soil storage capacity, allowing evapotranspiration to occur at a high rate for a longer period of time. In this application of the SWB model, the soil depth controls partitioning between recharge and evapotranspiration.

Model results suggest that although recharge declines on average, high recharge years will occur more frequently in the future. The variability in annual recharge increases substantially in both future periods. By the late-century, recharge ranges from 41 mm to 701 mm per year, with a mean of 302 mm.

Water table conditions: Under the highest and lowest simulated recharge rates, average groundwater levels in the study area declined compared to the base case. However, both recharge scenarios produced some years of very high water table elevations, similar to those observed in 2007 and 2008. The model shows up to 3 meters in water table fluctuation during years with extreme recharge events, which is sufficiently large to cause groundwater-related flooding in the study area if antecedent conditions include above average water table conditions.

We applied the climate record for 2007 and 2008 to the SWB model to compare simulated water table response to recharge to conditions observed in 2007 and 2008. The SWB annual recharge depths for 2007 and 2008, 653 and 638 mm respectively, are among the highest values simulated for either future period. The 21st century simulations generated only one such instance of successive high-recharge years (693mm and 660 mm).

Conclusions/Implications: This series of models suggest that years of extremely high water table conditions may still occur but will remain relatively rare in the 21st century. Water resource managers should expect to see some years of high recharge amongst overall less recharge on average. This SWB model indicates warmer climate conditions will increase ET, resulting in a reduction in recharge under certain crop types or land cover.

The series of models may be applied to various settings to determine likely fluctuation in water table elevation. In the Spring Green region, the water table fluctuates 3 meters, and this estimate can be used to plan suitable development (for example, basement and foundation depths, road construction, or design of on-site wastewater treatment systems). This finding may also inform mapping of land susceptible to water table rise to the ground surface, or to evaluate the utility of crop insurance or drainage systems for agricultural lands.

The eight statistically downscaled GCMs produce a wide range and high variability in annual recharge estimates. This may limit the utility of these forecasts for water resources engineers concerned with climate change.

Recommendations: Future research should investigate partitioning of rainfall between ET and deep infiltration using more robust methods to estimate ET.

Related Publications:

Gotkowitz, M.B., Attig, J.W., McDermott, T. and Saines, M., In Review. Groundwater Flooding of a River Terrace in Southwest Wisconsin.

Key Words: climate change, recharge, evapotranspiration, groundwater flooding

Funding: Wisconsin Water Resources Institute through the State of Wisconsin's Groundwater Research and Monitoring Program

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1. Introduction

In the summer of 2008, the region near Spring Green, Wisconsin, experienced flooding of 4,378 acres (1772 ha) several kilometers away from the flood plain of the Wisconsin River, outside areas currently designated as floodplain by the Federal Emergency Management Agency. Field investigation and modeling showed that surface runoff was captured in closed topographic depressions and was unable to infiltrate due to water table rise to the land surface (Gotkowitz et al., In Review). This water table rise followed record snowfall the preceding winter and unusually high summer precipitation in 2008 – including a record 432 mm in an 8-day period in early June. The floods were sustained for nearly six months, causing $17 million dollars in damage and the condemnation of 29 homes.

The extensive damage to agricultural crops and residential and commercial properties brought heightened interest to the potential impacts of climate change on ground water recharge and rapid water table rise. Concerns include the need to alter or adapt current emergency response systems, infrastructure design, building standards, and land use to these potential effects of changes in the frequency and magnitude of precipitation events. Several hydrologic analysis tools now available lend themselves to testing potential impacts of climate change in various hydrologic settings. This project was undertaken as a proof of concept wherein a series of climate and hydrologic models is applied to the Spring Green study site to predict the likelihood of significant water table rise and groundwater flooding in humid regions with a shallow water table.

Due to an increase in fossil fuel consumption over the last century and accompanying increase in concentrations of atmospheric greenhouse gases, local- and global-scale climate change is expected throughout this century (IPCC, 2007). Climate change may include changes to the intensity, magnitude, and frequency of precipitation events, daily minimum and maximum temperature, and relative humidity. Many global climate models (GCMs) have been produced to predict these changes to climate, but the models differ significantly on the degree to which precipitation and temperature will be affected in humid regions of the Midwest. While some models predict wetter conditions and others predict drier conditions, most predict more common extreme precipitation events. Additionally, increasing winter temperatures changes are expected impact the volume and timing of snowmelt. These factors are likely to impact groundwater recharge.

Groundwater recharge is of particular interest where it may cause rapid water table rise to the land surface. Groundwater flooding is defined here as ephemeral rise of the water table above land surface. Such conditions can occur in areas with poorly developed surface drainage when climatologic and hydrogeologic conditions cause rapid water rise. For this condition to occur, recharge must exceed the aquifer storage capacity and the rate of discharge to established surface water bodies. Where this condition persists or is a frequent occurrence, the surface water is more likely considered a wetland, rather than an instance of groundwater-related flooding. Groundwater flooding appears to be a rare occurrence that has received little attention in peer-reviewed literature. One exception is extensive and long-lasting flooding in 2001 of the Chalk aquifer in northern France (Negrel and Petelet-Giraud, 2005) and southeast England (Adams et al., 2010).

1.1 Project scope and objectives

This project was undertaken as a proof of concept wherein a series of climate and hydrologic models were used to assess potential changes in groundwater recharge in a temperate climate. Output from regional scale (50 kilometer resolution) climate forecasts were applied a grid-based soil water balance model (SWB), which yielded daily estimates of deep infiltration through the soil column. The infiltration was applied as recharge to the water table in a three-dimensional MODFLOW (Harbaugh 2005) model of the region. This modeling sequence tested the utility of the downscaled climate projections in assessing future groundwater recharge patterns, and examined the vulnerability of the selected landscape to recurring episodes of groundwater inundation. The modeling approach was supplemented with a modest field investigation to determine the suitability of the existing hydrogeologic conceptual model to the study area.

Our objectives included evaluating the effects of climate change on groundwater recharge and water table elevation in a humid region with a shallow water table. We examined the likelihood of groundwater inundation of low-lying areas at the Spring Green study site under these climate forecasts, producing a series of water table hydrographs for the period studied. An additional objective of the work was to examine potential effects of alternative cropping on evapotranspiration rates and subsequent groundwater levels. This is of interest because enhanced evapotranspiration offers a potential benefit of lessening the frequency or extent of groundwater inundation.

1.2 Study Site

Most of the area flooded in the summer of 2008 is within the town of Spring Green, in southwest Sauk County (figure 1). Climate in this region is typical of the midwestern United States, with average annual precipitation of about 840 mm, most of which occurs from April through September. Average daily temperatures vary from -8.2 °C in January to 22 °C in July (National Climate Data Center, 2004).

Spring Green is in the “driftless area” of Wisconsin, a region extending into Minnesota, Iowa, and Illinois, that is free of Pleistocene glacial sediments present throughout much of the Midwest (Heyl et al., 1959). The landscape is characterized by steep hillslopes that separate river valleys from narrow, flat-topped uplands. In the study area, the Wisconsin River traverses a broad expanse of glacial outwash deposited by meltwater streams flowing from Quaternary glaciers. The 2008 flooding occurred on the upper of two terraces in the area, which lies about 7.4 m above and 4 km north of the floodplain of the river (figure 2). Extensive deposits of wind-blown sand on the terrace create about 11 m of topographic relief. A bedrock escarpment flanks the terrace to the north, rising to an elevation of 335 m. The lower parts of some stream valleys, such as Big Hollow, that cut the bluffs are lined with fine-grained sediment deposited in ancient (late-glacial) lakes.

The outwash deposits form an unconfined aquifer consisting of coarse-grained sand and gravel over 50 m in thickness (figure 2) (Gotkowitz et al. 2005). These deposits are underlain by a thick, regionally-extensive Cambrian sandstone aquifer. The uplands are capped by dolomite of the Ordovician Prairie du Chien group. Groundwater in the study site generally flows from north to south from the uplands to the Wisconsin River. Hydraulic conductivity of the sand and gravel deposits is 49 m/day on average, while the sandstone aquifer hydraulic conducitvity is about 2.4 m/day. Crystalline PreCambrian rock undelies the Cambrian units and forms the base of the deep aquifer.

The uplands are relatively well-drained with a number of ephemeral streams capable of removing surface water and high groundwater from the system. These streams generally become perennial on downstream reaches near the Wisconsin River. However, the terraces that experienced flooding in 2008 contain internally-drained closed depressions and lack any perennial streams. Rainfall runoff forms ponds; this water either infiltrates or evaporates.

2. Methods

The primary components of this project included compilation and formatting of GCM output, running a soil water balance (SWB) model, and refining and running a three-dimensional transient groundwater flow model of the study area (Figure 3). A limited field investigation added to the existing hydrogeologic characterization of the study site.

2.1 Climate Models

The Climate Working Group of the Wisconsin Initiative on Climate Change Impacts (WICCI) statistically down-scaled results from 15 of 20 GCMs submitted to the Coupled Model Intercomparison Project (CMIP3). We used eight of these GCMs (Table 1) for the years 2046-2065 and 2081-2100. All employ the A2 carbon emissions scenario, which is considered a high-end emissions scenario representing the most realistic emissions trajectory (IPCC, 2001).

Table 1. Eight down-scaled GCMs

Canadian Center for Climate Modeling and Analysis's CGCM 3.1	CCCMA
Australian Commonwealth Science and Research Organization's Mark 3.0	CSIROMK30
Geophysical Fluid Dynamics Laboratory's Climate Model 2.0	GFDL
Max Planck Institute for Meteorology's ECHAM5	MPIM_ECHAM5
Centre National de Recherches Meteorologiques Climate Model 3	CNRM
Australian Commonwealth Science and Research Organization's Mark 3.5	CSIROMK35
Model for Interdisciplinary Research on Climate 3.2 medium resolution	MIROC32
Meteorological Research Institute's CGCM2 3.2	MRI_CGCM2

The GFDL simulation for 1981-2000 provides a "base case" for comparison. All GCMs are de-biased in this early period and are constrained to produce similar results, so output from the other GCMs for this period were not analyzed. Comparison of actual and modeled monthly precipitation and monthly temperature showed that the GFDL results reasonably match observed conditions for 1981-2000.

2.2 Soil Water Balance Model

Daily precipitation, minimum temperature, and maximum temperature estimates from the downscaled GCMs drive the SWB model (Westenbroek et al., 2009) which produces spatially-varying estimates of deep infiltration. The SWB uses a daily time step and was applied to a 30m x 30m grid of the study site. The SWB requires site-specific land use, soil type, available soil water capacity, and flow direction information, which were obtained from widely available GIS datasets. For the purpose of this project, output from the SWB model was compiled as a deep infiltration (that is, recharge) depth for each grid cell for each day, for each twenty-year simulation. Ultimately, the two GCM datasets that resulted in highest and lowest average annual recharge were carried forward to the groundwater flow model.

The model estimates daily infiltration at each grid cell based on daily precipitation, antecedent soil moisture, land use, and soil type using the SCS Curve Number approach (United States Department of Agriculture, 1986). This is an empirical method that estimates the amount of runoff generated for a specified area and a precipitation event of a known magnitude. In the SWB, if effective precipitation (P) exceeds potential evapotranspiration (PE), infiltration occurs and soil moisture increases up to a maximum water-holding capacity (roughly equal to the field capacity). Any infiltration beyond this maximum value becomes deep drainage that travels below the root depth of vegetation. For the purposes of this project, this "deep infiltration" is considered recharge to the groundwater system. If PE exceeds P, the model removes water from the soil using an accumulated potential water loss value that limits evapotranspiration based on the number of consecutive days in which P < PE. Soils yield water to ET more easily when soils are relatively wet, as is typical during the days immediately following rainfall events (when P > PE).

The model routes runoff to downslope grid cells (flow direction data is obtained from a digital elevation model); runoff may then infiltrates in a downslope cell. This runoff/infiltration process continues until the water infiltrates, reaches a surficial water body, or reaches the edge of the model domain. The Spring Green area lacks surficial drainage outlets and contains many internally-drained closed depressions. To simulate these conditions, the maximum daily infiltration parameter in the SWB is set to a very high value (25.4 cm). This ensures that runoff captured in closed depressions is ultimately simulated as infiltration, rather than being routed out of the model.

In the SWB model, the "soil depth" parameter is analogous to rooting depth, and it must be specified for each grid cell. Increasing or decreasing the magnitude of soil depth alters the model's partitioning of precipitation into evapotranspiration, infiltration, and surface runoff under a specific vegetation type. Generally, a large soil depth produces more ET as roots penetrate deeper, and more infiltration is required to produce deep drainage or recharge. The SWB model contains default soil depth parameters for each soil and land use type. These vary from 0 m open water and perennial ice and snow to between 0.6 and 1.4 m for most vegetation (including agricultural, grassland, and forested vegetation). Additional detail on the SWB is provided by Westenbroek et al. (2009).

2.3 Groundwater Flow Model

SWB-generated estimates of deep infiltration were applied to a refined version of a Spring Green MODFLOW model (Gotkowitz et al., 2002). The refined model grid consists of 372 rows and 445 columns, with a spatial resolution of 30m x 30m in the vicinity of the flooded area (figure 1). Cell size increases to a maximum of 500m x 500m at the model boundaries. The resolution provides greater accuracy near the flooded region, with decreasing resolution with distance from the site to allow for reasonable model run times. The model was then checked to ensure it maintained a good calibration.

Table 2. Hydraulic conductivity and specific yield

Area	Horizontal hydraulic conductivity (m/day)	Vertical hydraulic conductivity (m/day)	Specific Yield
Layer 1: uplands alluvium	15.2	1.52	0.15
Layer 1: valley alluvium	76.2	7.62	0.1
Layer 2: Sandstone bedrock	0.582	0.0582	0.001
Layer 2: Upland interbedded sedimentary bedrock	0.0582	0.00582	0.0001

The two-layer model contains two hydraulic conductivity zones per layer (Table 2, Figure 2). Boundary conditions consist of specified heads on the west, north, and east edges of the domain, derived from simulated conditions obtained in previous modeling of the area (Gotkowitz et al., 2002). The Wisconsin River is assumed to be fully penetrating and is the southern model boundary. Streams high in elevation are treated as MODFLOW drains. This approach is useful because many upland reaches of these streams are ephemeral, and the drain feature simulates groundwater discharge only if the simulated water table exceeds the modeled stream elevation.

2.4 Field Investigation

Using direct-push methods, we collected sediment cores and installed monitoring wells at the locations and depths shown in Figures 1 and 4. Fine-grained sediments were encoutnered in Big Hollow, north of the flooded area. No fine-grained sediment was observed within the outwash deposits on the terrace. These points provided measurements of vertical hydraulic gradients in the study area.

3. Results
3.1 Climate Predictions

Seasonal and daily precipitation data generated by the GCMs were averaged for the base case period, 1981 – 2000, and mid- and late- 21st century time periods. The mean annual precipitation forecast for the area is 886 mm for 2046-2065 and 2081-2100, an increase of about 7% from the average for the base case period (828 mm per year). As illustrated in Figure 5, the range in average precipitation increases in both future period increases from the base case. Six of the eight models predict that conditions in 2081-2100 will be similar or wetter than 1981-2000. Comparison of the GFDL base case with the 21st century results suggests that on average, seasonal differences may include drier summers with wetter spring and autumn (Figure 6). Winter precipitation increases slightly by the end of the century.

All eight GCMs predict an increase in temperatures for all months relative to the base case period, coinciding with increasing CO_2 concentrations in the IPCC emissions scenarios (2007). On average, the simulated monthly temperatures rise from the base case average of 7.9°C by 2.9 °C by 2065 and by an additional 2.8 °C at the end of the century (Figure 7). Predicted mean annual temperatures range from 10.4 °C (CSIROMK30) to 12.4 °C (MIROC32) in 2046-2065, with a larger range predicted for 2081-2100, from 10.6 °C (CSIROMK35) to 16.7 °C (MIROC32).

3.2 Recharge Estimates

The SWB model provides spatial estimates of recharge over the model domain. The pattern of recharge in the study area includes higher values in the Wisconsin River valley, where coarse-grained sandy soils and the lack of streams and drainage enhance infiltration (figure 8). Recharge in the uplands to the north is generally lower with the exception of the forested slopes. Recharge averaged across the model domain for the base case period is 358 mm. This is consistent with SWB results in neighboring Dane County, WI, which indicate about 350 mm of recharge in the western, unglaciated areas in the county (Hart et al., 2009). The mean annual recharge distribution for the base case period was slightly negatively skewed, indicating years of low recharge were more likely than years of high recharge. Annual recharge during this period ranged from 190 to 510 mm per year.

Mean annual recharge simulated from the eight GCMs for 2046-2065 was 343 mm (table 3), a 4% decrease (15 mm) from the base case. These simulations have a positively-skewed frequency distribution, indicating that the likelihood of high recharge years increases compared to the base case (figure 9). The range varies from about 100 mm to up to 752 mm per year. Mean annual recharge varies from 101 mm under the MIROC32 scenario – a decrease of 25% from the base case, compared to 389 mm under GFDL, which is an increase of 8.5% from the base case. Some models, such as MIROC32, have a positively skewed distribution, while the CNRM model yields a distribution close to normal.

Mean annual recharge simulated for the late century, 2081-2100, was 302 mm. The frequency distribution was also positively skewed (figure 9); overall, these simulations predict a decrease in average annual recharge but an increase in the number of years that fall above average. Figure 10 shows a greater range in recharge in the late-century period than the mid-century. Model ECHAM5 results in the greatest annual recharge of 701 mm, while MIROC32 produces the lowest year, of 41 mm. Several of the models yield an average annual recharge near that of the base case (358 mm). The MIROC32 model produces an average recharge almost 50% lower (170 mm).

Table 3. Annual recharge by GCM for future climate periods. All values are in centimeters.

	2046-2065					2081-2100				
	Min	Max	Mean	Change from Base	Skew	Min	Max	Mea n	Change from Base	Skew
CCCMA	19.3	72.0	37.5	+1.6	0.97	21.1	64.6	35.8	-0.05	1.31
CNRM	18.3	46.3	31.5	-4.3	0.09	8.30	35.6	20.5	-15.3	0.03
CSIROMK30	13.9	75.3	35.7	-0.15	0.74	11.3	61.8	34.0	-1.8	0.28
CSIROMK35	12.7	61.8	35.0	-0.8	0.33	12.7	61.6	35.0	-0.84	0.33
GFDL	17.5	61.5	38.8	+3.0	0.15	16.7	48.3	30.9	-4.9	0.38
MIROC32	9.88	65.0	26.9	-8.9	1.17	4.11	50.9	16.8	-19.0	2.17
MPIMECHAM5	14.8	59.4	34.3	-1.6	0.20	10.7	69.2	35.5	-0.30	0.56
MRICGCM2	22.8	54.6	34.3	-1.5	0.48	13.1	50.9	33.9	-1.9	-0.30
ALL GCMs	***16.1***	***62.0***	***34.2***	***-1.6***	***0.97***	***12.2***	***55.4***	***30.3***	***-5.5***	***0.53***

Figure 11 compares the proportion of average annual recharge, evapotranspiration, and precipitation for each model during both future climate periods. The CNRM model illustrates the case where increased precipitation produces an increase in ET and a decrease in recharge. The SWB model simulates an average of 452 mm of ET annually in the base case period; this value rises to 510 mm in 2046-2065 (average of 8 GCMs) and 549 mm for the late 21st century. These models indicate that a higher proportion of rainfall is partitioned into ET, decreasing recharge.

3.2.1 Evapotransipiration and the soil depth parameter

The SWB model applies a user-specified soil depth parameter (roughly analogous to rooting depth) to calculate ET at each model cell. Model sensitivity to this parameter was evaluated by doubling soil depths from base case values and generating five years of SWB output with CCCMA (2046-2050) climate data. Total annual ET increased between 45 mm and 51 mm, decreasing recharge by about 10% (between 45 to 59 mm). This decrease in simulated recharge indicates that the SWB model is sensitive to plant type. Soil depth is an important determinant in the model’s partitioning between recharge and evapotranspiration because it increases soil storage capacity and allows ET to occur at a maximum potential rate for a longer period of time.

One of the most poorly-understood aspects of climate change is potential changes in ET, which is highly dependent upon vegetation type and soil water availability. Doubling the SWB soil depth parameter, as described above, simulates a change in dominant vegetation from relatively shallow- to deep-rooted plants (for example, switching from corn to poplar trees). This suggests that a change in cropping patterns could exacerbate changes to the hydrologic system resulting from an increase in temperatures, increasing the proportion of precipitation that is evapotranspired.

3.2.2 MODFLOW Model under Observed Climate in 2007 and 2008

We evaluated the ability of the SWB recharge estimates to simulate observed water table response to recharge using 2007 and 2008 climate data from Spring Green (Automated Weather Observation Stations, 2010). Annual precipitation totaled 1240 and 1070 mm in 2007 and 2008, respectively, with a record 430 mm during an 8-day period in June, 2008. With this precipitation record as input, the SWB model simulates 653 mm of recharge in 2007 and 638 mm in 2008. These values are similar to the maximum recharge depths predicted under the eight GCMs during the mid- and late-century periods (Figure 10).

The simulated daily recharge for 2007 and 2008 was applied to the MODFLOW model. Figure 12 illustrates the match obtained between the simulated water table and observations from Peck's well, located in Spring Green. A second comparison (Figure 13) between daily measurements from a monitoring well in Mazomanie, Wisconsin (located about 20 km east of Spring Green) and model results shows that the model reproduces large peaks as well as gradual increases and decreases in water table elevation during 2007 and 2008. The simulated magnitude of water table fluctuation is greater at Spring Green than in the record observed at Mazomanie, which is attributed to differences between actual recharge in Mazomanie and the simulated recharge applied to the model in Spring Green.

3.3 Water Table Response to Recharge

The effect of changing recharge in the 21st century was investigated by applying the highest and lowest recharge records from the GCMs (CCCMA and MIROC32 respectively) to the MODFLOW model. The head distribution generated from a dynamic-equilibrium run-up period provided the initial conditions for this transient simulation. Hydrographs (Figure 14) were compiled for two locations in the model domain; Peck's well, which was flooded in 2008, and SG2, which did not experience flooding.

These model results indicate that groundwater rising to the land surface may re-occur, but will remain a rare event. In simulations of the mid-21st century, high recharge conditions result in a relatively steady water table, at about 216.6 meters, with annual fluctuations of up to three meters in extreme cases. Low recharge conditions result in an average water table elevation of 215.2 meters by 2055, with annual fluctuations of about 1.5 meters. Both the wet and dry models predict one instance of groundwater flooding (defined as the water table reaching the land surface elevation of 219 meters). The model shows numerous instances of the water table rising to within one meter of the land surface.

By the late 21st century, both high- and low-recharge models suggest about a 0.5 meter decrease in the average water table elevation from the mid-century, about 216.0 and 214.8 m respectively. The water table rises to within one meter of the land surface once under high-recharge conditions and not at all under the low-recharge model.

Results at well SG2A are similar with respect to the absolute change in the water table. The high-recharge model causes a water table decline of about 0.6 m by the end of the century, and low-recharge conditions yield a similar decline, from about 215.4 meters in 2055 to 214.8 meters at the end of the century. Because this location has a higher elevation and a greater initial depth to water, it is not susceptible to water rise to the ground surface in any of the simulations.

4. Discussion

The eight GCMs and the SWB model applied to the study area indicate that on an annual basis, recharge will be more variable under future climate conditions. Figures 9 and 10 are perhaps most illustrative in portraying the potential ranges in annual recharge; some of the GCMS suggest that average conditions may not change, but low- and high-recharge years may occur more frequently. These graphs show a general downward trend in average recharge by the late-21st century, and three of the GCMs indicate that average recharge may fall below the 25th quartile of that seen in the 20th century. During the mid-21st century, recharge is expected to drop about 4% from the base case. However three models predict no change or an increase in recharge during this period. By the end of the century, the drop in recharge increases to 25% from the base case, and none of the models predict an increase from the base case.

The changes in recharge predicted by the SWB model are driven by the magnitude of precipitation and changes in temperature in the down-scaled GCM results. MIROC32, for instance, predicts the lowest annual precipitation and the highest temperatures (figures 5 and 7), resulting in both the lowest average and the lowest range of annual recharge (figure 10). CCCMA predicts the highest precipitation, resulting in high average recharge. The large difference in simulated recharge generated from these eight GCMs indicates the importance of using more than one GCM to examine potential hydrologic conditions under changes in climate in this region. Additionally, the importance of increasing temperature in the recharge estimates is driven by the partitioning of soil water between ET and recharge in the SWB model. Minimum, maximum, and average daily temperatures are employed in a Thornthwaite-Mather approach to estimate ET. The importance of ET to these recharge estimates suggests additional, robust methods to estimate ET could be useful to further investigate the impact of temperature and vegetation type on the fate of water in the vadose zone.

Applying the highest and lowest estimates of recharge from the SWB to the groundwater model causes water table decline *under both conditions* during the late 21st century (Figure 14). The high recharge case, the CCMA model, undergoes a large increase in ET from mid- to late- 21st century (Figure 11). This change in the soil water balance drives the decrease in recharge to the water table. By 2100, both high- and low-recharge conditions result in water table elevations at Peck's well area that are well below the land surface, suggesting that rising temperatures and their affect on ET will alter the hydrologic cycle.

High groundwater conditions may be a recurring issue during the mid-21st century. Both high-and low-recharge scenarios produce years of water table elevations as high as those experienced in 2007 and 2008, generating one instance of groundwater flooding at Peck's well. The high-recharge simulation causes several instances of water table rise to within a meter of land surface. By the late-21st century, these two models do not generate years of such high water table conditions. However, as described below, such a result would likely have occurred had the late-century recharge estimates from MPIM_ECHAM5 been carried forward to the groundwater model.

To compare future recharge and water table response to actual conditions in 2007 and 2008, we applied daily climate observations from Spring Green to the SWB model. This produced annual recharge of 65.3 and 63.8 cm, respectively, among the highest values generated by the eight GCMs for future periods (Figure 10). The combination of two high recharge years in succession likely played a role in the occurrence of flooding. Successive years of high recharge are rare in the GCM results. The MPIM_ECHAM5 model generated 69.3 and 66.0 cm of recharge in 2094 and 2095, respectively. This analysis also provides a sense of the annual depth of recharge that may be required to raise water table elevations above the land surface.

5. Conclusions and recommendations

This series of models suggests that while years of extremely high water table conditions may occur, they are likely to remain relatively rare events in the 21st century. The highest estimated recharge rates for the study area cause a 3-meter fluctuation in water table elevation, and this information may be of interest for planning residential and commercial development in similar climatic and hydrogeologic settings. Construction of buildings and infrastructure (basement and foundation depths, road construction, and design of on-site wastewater treatment systems) should consider the upper range of potential water table elevations to avoid problems such as the extensive damage from water table rise in Spring Green.

These findings may also inform efforts to map flood-prone or fully-saturated regions, or to evaluate the costs and benefits of long-term mitigation strategies, such as surface water detention basins, drainage systems, and crop insurance.

The analysis of the Spring Green area was intended as a proof-of-concept for this modeling approach. The eight statistically downscaled GCMs produce a wide range in estimates of annual recharge, which may ultimately limit the utility of these forecasts for water resources engineers concerned with climate change. However, general findings may prove more useful. For example, the range of simulated recharge constrains potential impacts of climate change, given the aquifer storage capacity in this setting. Based on this work, a reasonable range of recharge to apply to flow models incorporating different hydrogeology is vary the calibrated recharge value by a decrease of 25% and an increase of about 8%. As demonstrated for the study area, a time series of recharge based on the ranges from each GCM could be developed for transient simulations.

Future research in this area should investigate partitioning of rainfall between ET and deep infiltration. More robust methods to estimate ET should be compared to those generated from this application of the SWB.

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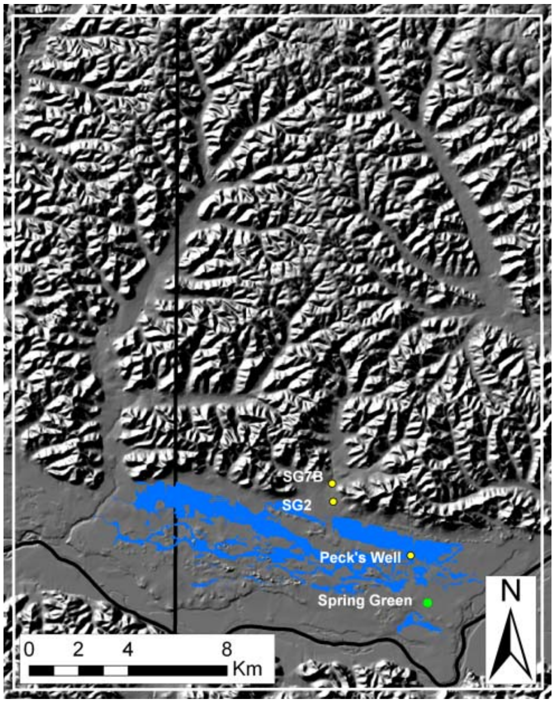

Figure 1. Study area in Sauk and Richland Counties (above) and topography (left). Blue shaded area indicates extent of flooding in 2008. White border is the extent of the MODFLOW model domain.

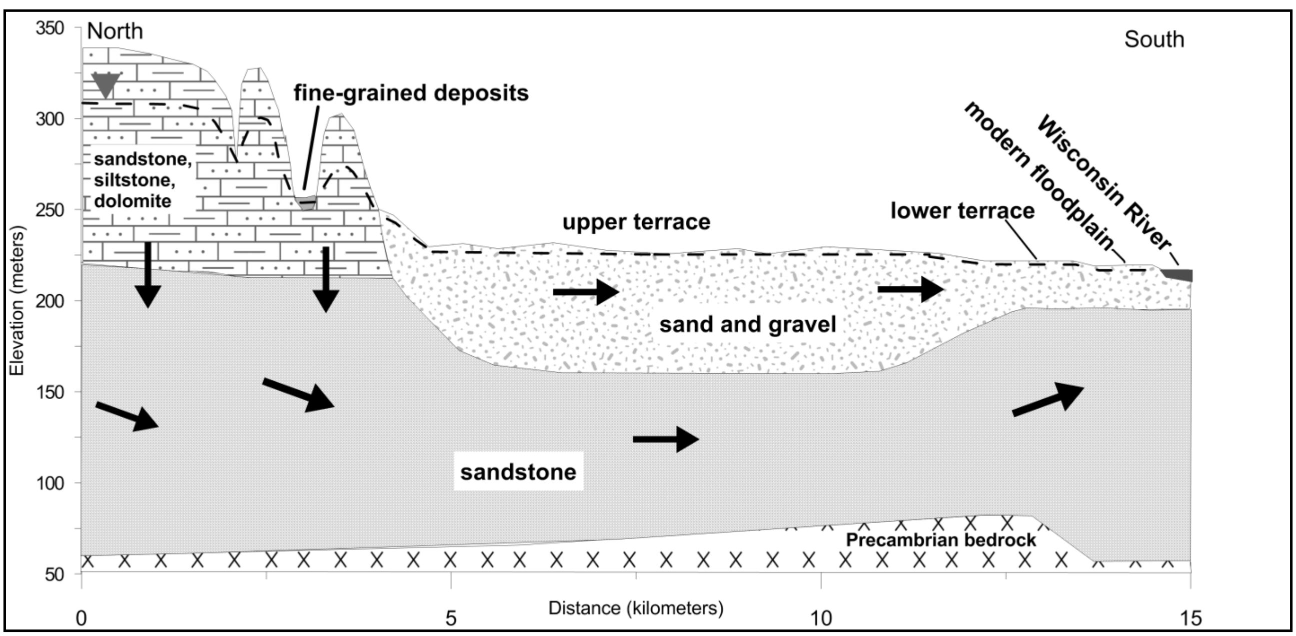

Figure 2. Spring Green hydrostratigraphy

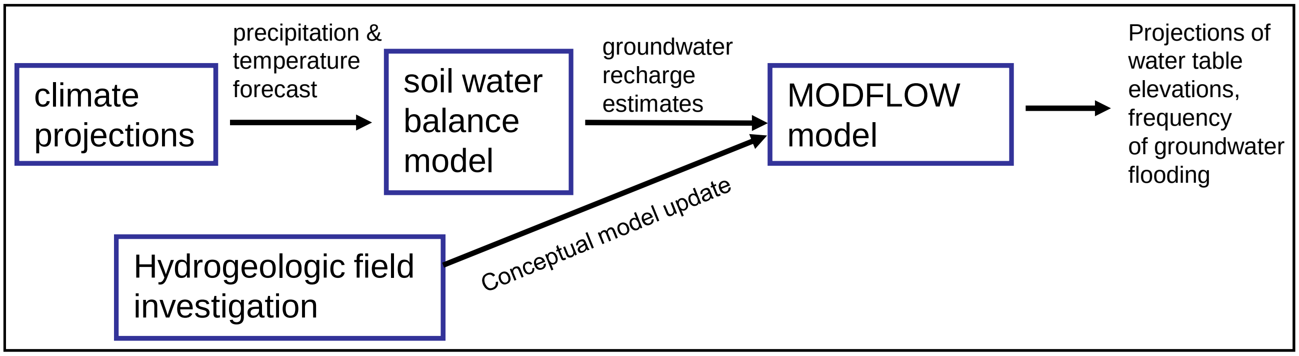

Figure 3. Project sequence.

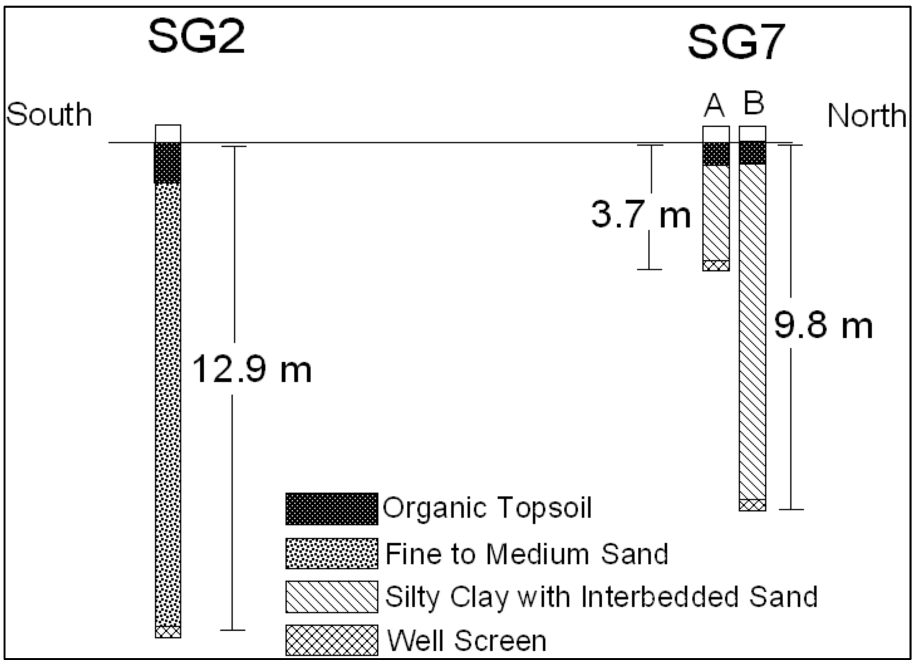

Figure 4. Boring depths and material (not to scale).

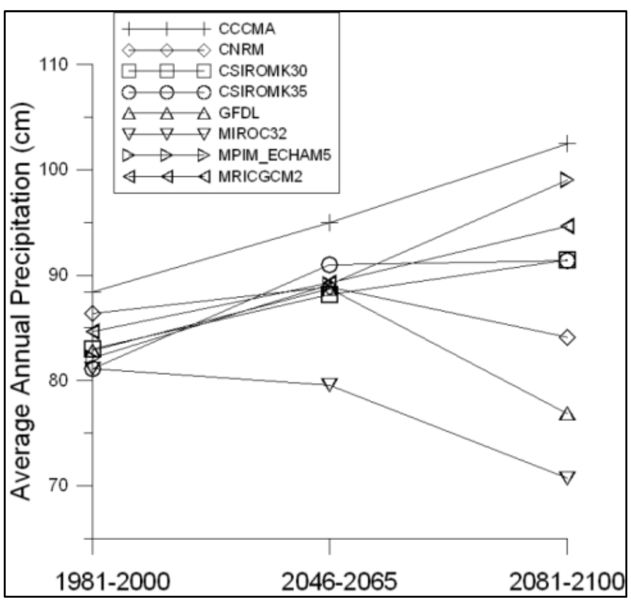

Figure 5. Average annual precipitation by GCM for three time periods.

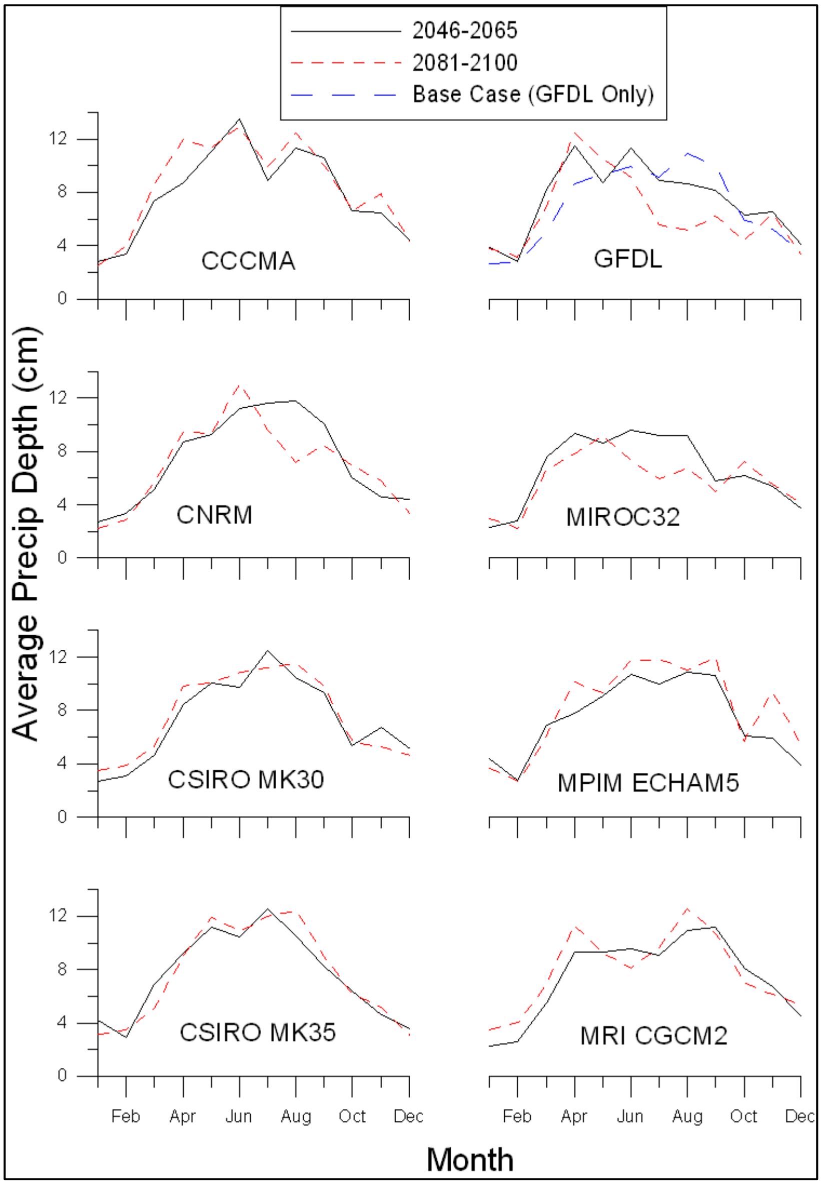

Figure 6. Average monthly precipitation, 2046-2065 and 2081-2100. The base case period is shown for GFDL only. Precipitation is the water equivalent depth for snowfall.

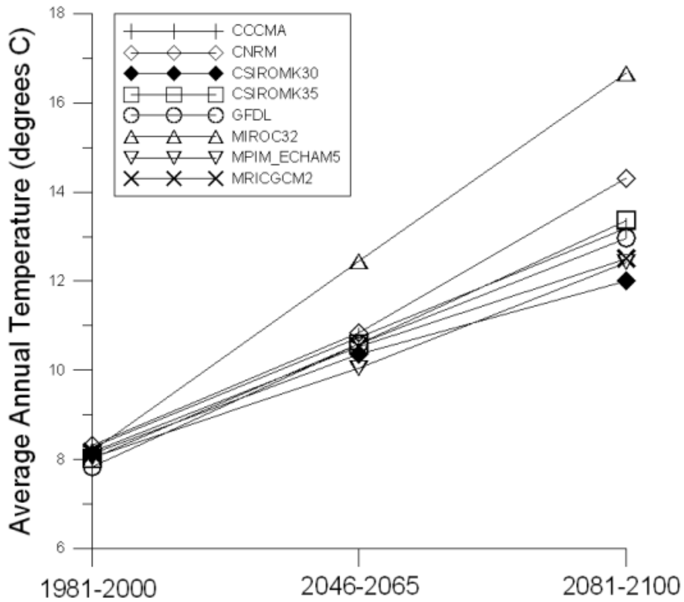

Figure 7. Average annual temperatures simulated by GCMs.

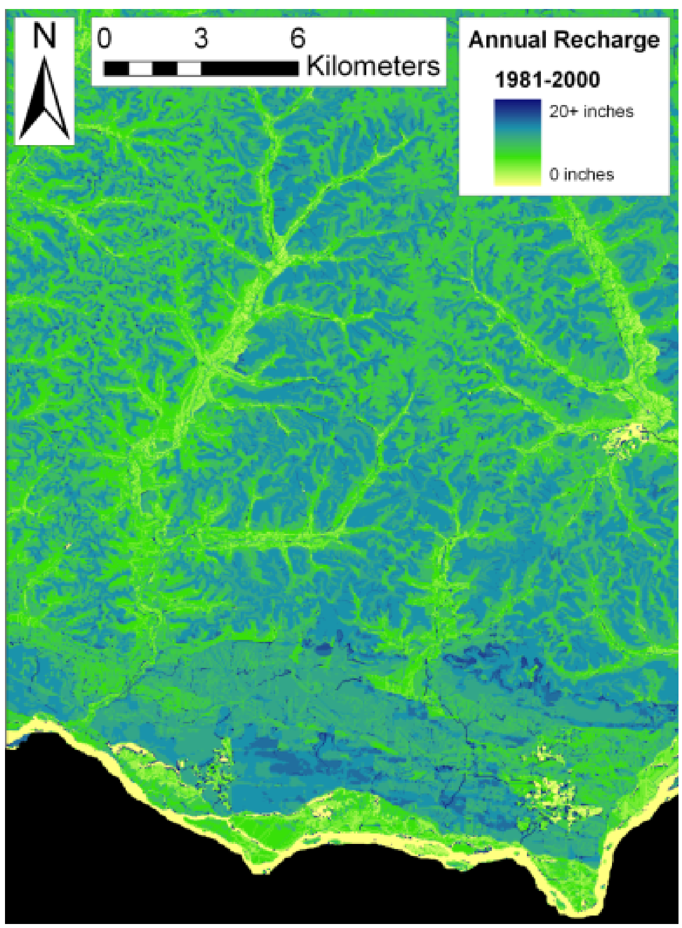

Figure 8. Base case simulated average annual recharge (from GFDL), 1981-2000.

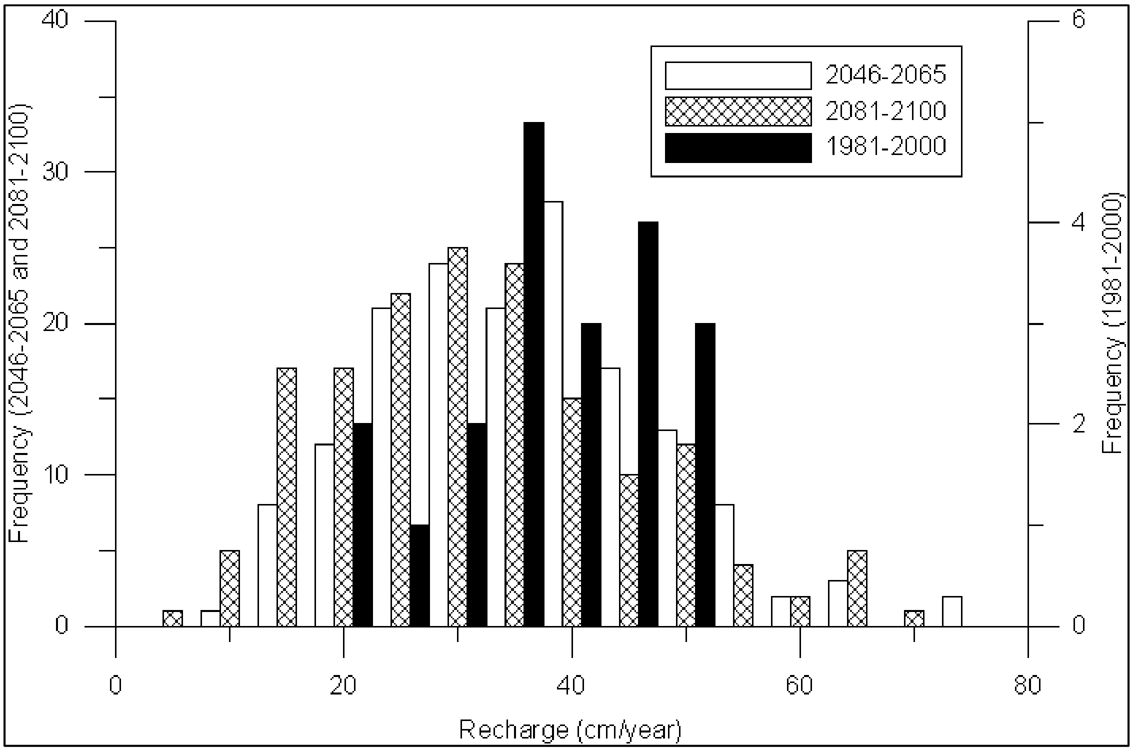

Figure 9. Annual recharge frequency distribution under two future climate periods (left axis) and the base case (GFDL only; right axis).

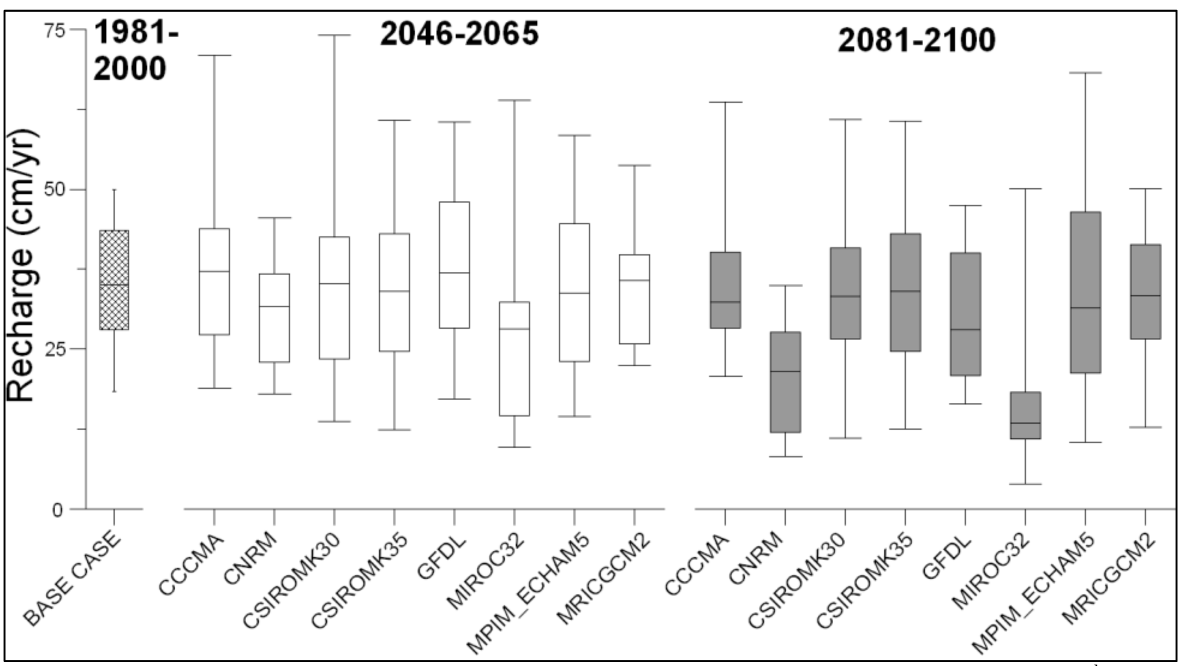

Figure 10. Recharge distribution for each GCM during future climate periods. Maximum, 75th quartile, mean, 25th quartile, and minimum are shown.

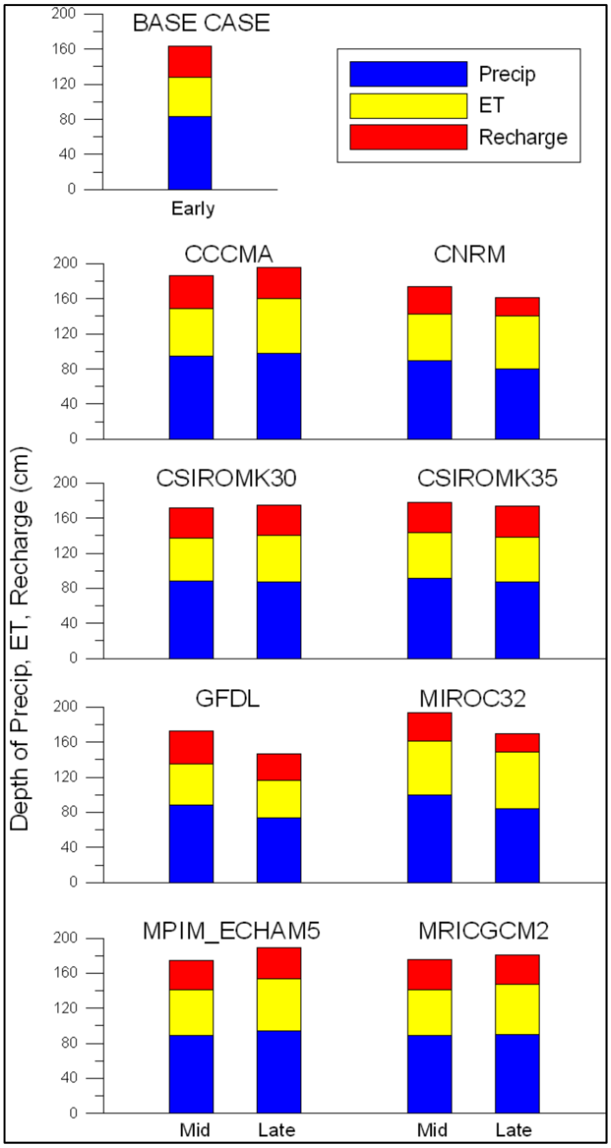

Figure 11. Annual average precipitation, evapotranspiration, and recharge (cm). Eight GCMs are compared to the base case.

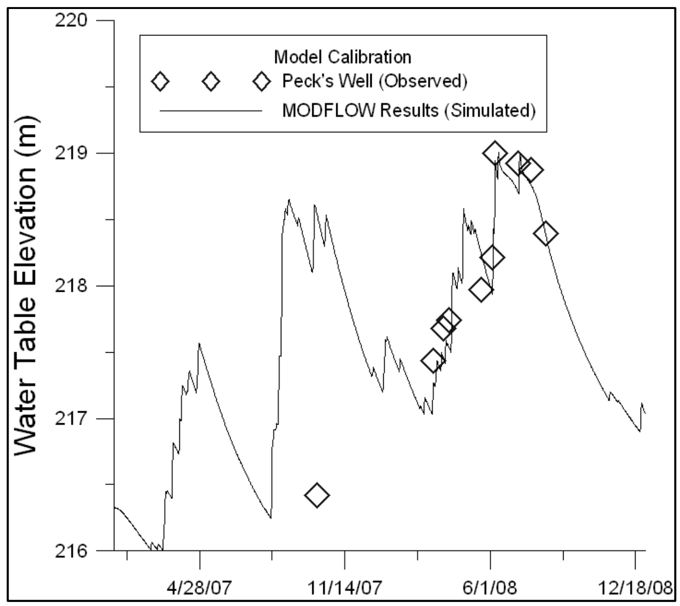

Figure 12. Observed and simulated water table elevation, 2007 – 2008. See Figure 1 for location of Peck's Well.

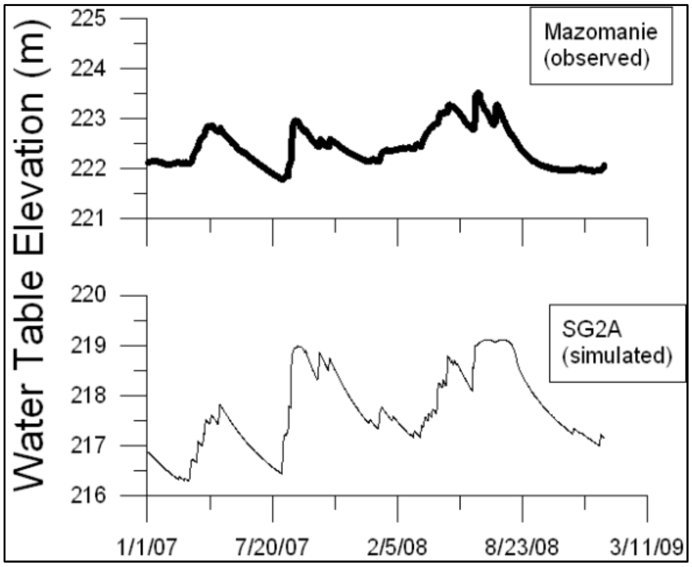

Figure 13. Observed and simulated water table, at Mazomanie well and Spring Green, respectively.

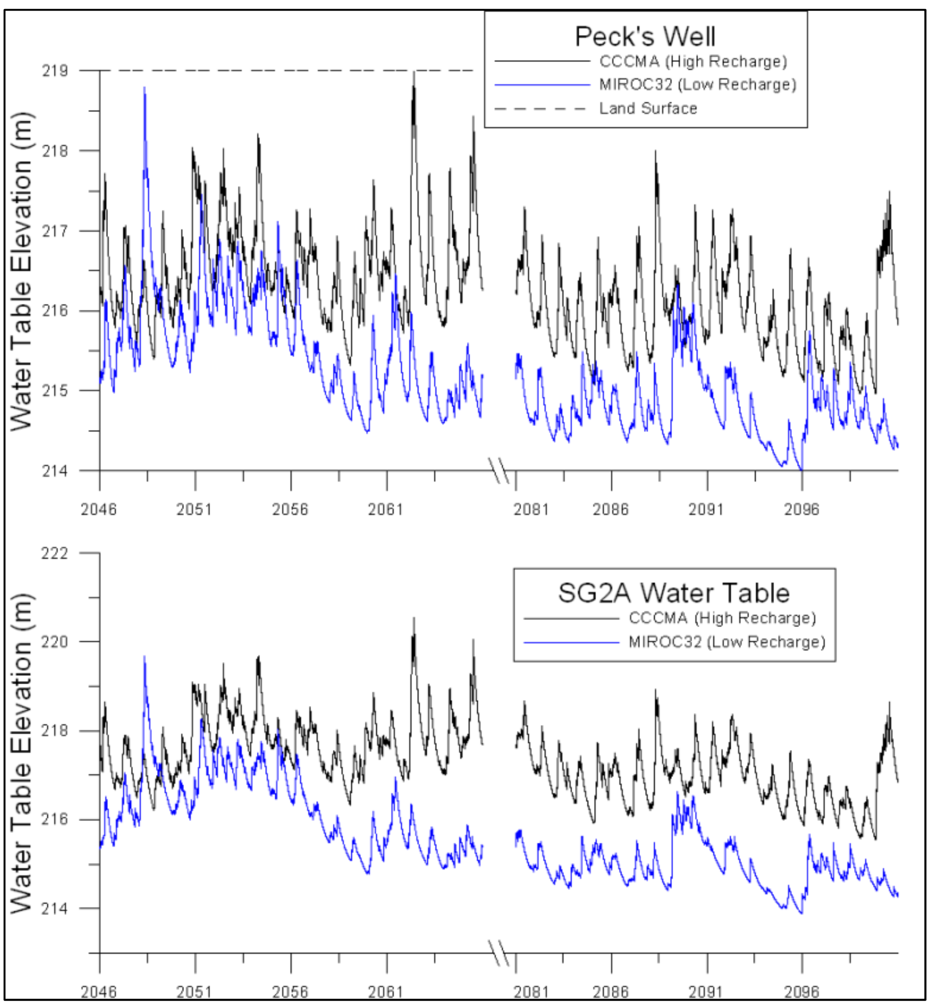

Figure 14. Water table hydrographs under high- and low-recharge conditions.

DTS as a Hydrostratigraphic Characterization Tool

Basic Information

Title:	DTS as a Hydrostratigraphic Characterization Tool
Project Number:	2009WI312O
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DTS AS A HYDROSTRATIGRAPHIC CHARACTERIZATION TOOL

Project Completion Report

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Project Summary

Title: DTS as a hydrostratigraphic characterization tool

Project ID: WR09R006

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Period of Contract: July 01, 2009 – June 30, 2010

Background/Need: Subsurface heterogeneity in hydraulic properties and processes is a fundamental challenge in hydrogeology. Most hydrogeologic problems are complicated by uncertainty in permeability, which is often difficult or impossible to fully characterize. The usefulness of heat as a tracer has been limited by thermometry that only records temporal changes in temperature at a single fixed or moving point. Distributed temperature sensing (DTS) is a powerful new method that allows for the nearly continuous measurement of temperature in time and space along fiber-optic cables. The fine spatial and temporal monitoring ability of DTS is creating new and unprecedented opportunities to study hydraulic heterogeneity at a wide range of scales. Despite numerous recent applications of DTS applications in surface water investigations, down-hole uses in hydrogeology have been limited. Recent studies on the Sandstone Aquifer system of Wisconsin have shown preferential flow through laterally continuous bedding plane fractures to be a defining characteristic of sandstone units that were traditionally assumed to be homogeneous and isotropic. The implication of these findings is that more detailed characterization efforts are necessary to adequately assess flow and transport problems in these units.

Objectives: The purposes of this study were to develop DTS as a down-hole groundwater monitoring and aquifer characterization tool, and to use its novel monitoring capabilities to gain new information on hydraulic heterogeneity in the Sandstone Aquifer system. This study builds on previous work by using DTS to monitor ambient and artificially-stimulated temperatures for the purpose of detailed hydraulic characterization at the borehole scale. In addition, DTS was used to investigate the effects of borehole flow processes on temperatures measured in wells. Finally, the novel monitoring capabilities of DTS allow hydraulic heterogeneity in the Sandstone Aquifer system to be studied at an unprecedented level of detail.

Methods: Investigations were conducted at three sites. At a former Aquifer Storage and Recovery (ASR) site in Oak Creek, WI, a 550 m deep monitoring well was instrumented with DTS. Temperatures were measured under ambient conditions, and during a week of pumping from an identical well located 55 m away. Subsequent geophysical logging and modeling studies were used to identify the processes affecting measured temperatures. Active, single-well thermal tracer experiments were conducted in two naturally flowing multi-aquifer wells near Madison, WI. Borehole water was circulated through an above-ground heat exchanger system, which was closed to the atmosphere. The system produced heating of up to 10 °C above ambient at flow rates of approximately 8 to 13 l/min. Heated water was returned to the wells using a depth-adjustable rubber garden hose outlet. The migration of the heated water in the borehole was monitored using DTS. Outlet depths and injection times were varied.

Results/Discussion

At Oak Creek, DTS data collected in the monitoring well recorded transient well-bore flow induced by pumping in the neighboring ASR well. Accompanying modeling studies showed that early-time decreases in temperatures signified downward flow, and that a reversal in this trend signified a transition to upward flow at steady-state. Geophysical logging provided an improved site conceptual model, and valuable information on the Sandstone Aquifer system under the Milwaukee area. In the two wells near Madison, WI, DTS data collected during active thermal tracer experiments characterized the ambient borehole flow regimes, revealing intervals of fracture-dominated and intergranular flow in the Sandstone Aquifer system. In comparison with geophysical logging, the DTS data showed diverging flow in both wells to be emanating from bedding plane fractures at stratigraphically similar locations in the Wonewoc sandstone.

The results of this study show wells to be complex conduits that are affected by, but do not necessarily represent, conditions in the aquifer, especially in hydraulically heterogeneous settings. Diverging flow in the Wonewoc Formation emanating from bedding plane fractures in stratigraphically similar positions suggests regional-scale fracture flow. This finding is significant in light of recent investigations that have characterized the Wonewoc as dominantly intergranular, and warrants further investigation

Conclusions/
Recommendations:

The active thermal tracer experiments demonstrated the effectiveness of DTS as a tool for detailed aquifer characterization. As a tool for measuring borehole flow, DTS has an effective operating range that exceeds that of conventional heat pulse and spinner flow meter techniques, which were previously unable to adequately characterize the ambient flow regime in DN-1440. In addition, DTS effectively integrates measurements over the entire width of the borehole, in contrast to heat pulse and spinner flow techniques, which may respectively be affected by leakage around the diverter or turbulence near the edge of the borehole. As a tool for measuring temperatures, DTS is superior to conventional wireline tools in its response time, which is on the order of seconds rather than minutes, and its ability to profile temperature synoptically without disturbing the fluid column.

Future work could use DTS methods to characterize aquifer heterogeneity in other wells open to the Sandstone Aquifer system. As shown respectively in the May 19 and May 28 experiments, both constant source and finite-pulse heating techniques can provide useful information. The latter provides the most unambiguous results as a stand-alone technique. An electric resister may provide a superior heat source in comparison to the heat exchanger used in this study.

Keywords: DTS, heat, temperature, tracers, hydrostratigraphy, Cambrian-Ordovician Aquifer System, Sandstone Aquifer, groundwater, Wisconsin

Funding: Wisconsin Groundwater Research and Monitoring Program through the University of Wisconsin Water Resources Institute.

Introduction

DTS is a powerful new method that allows for the rapid profiling of temperature along fiber optic cables. A thorough review of DTS theory can be found in Tyler et al. (2009), Selker et al. (2006a) and Hurtig et al. (1994). DTS is based on the transmission of pulsed laser light down an optical fiber and observation of the backscattered (reflected) signal. A small portion of the backscattering (Raman scattering) returns to the instrument at two characteristic wavelengths: one longer (anti-Stokes signal) and one shorter (Stokes signal) than the incident. The intensity ratio of the anti-Stokes and Stokes signals is an exponential function of the fiber temperature.

DTS was developed in the early 1980s (Dakin et al. 1985), and first applied to the Earth sciences in 1992 by Hurtig et al. (1993), who used it to profile ambient temperatures in shallow boreholes at the Grimsel Test Site in Switzerland. Following recent improvements in cost and instrument design (Selker et al. 2006a), the last several years have seen an explosion of DTS applications in hydrologic investigations. Most of these have been in surface water (e.g. Tyler et al. 2009; Mofffet et al. 2008; Westoff et al. 2007; Selker et al. 2006) and surface water/groundwater interactions (e.g Vogt et al. 2010, Henderson et al. 2009; Lowry et al. 2007; Selker et al. 2006b). Although DTS is now widely used by the oil and gas industry for down-hole production monitoring (e.g. Simonits and Franzen 2007), down-hole uses in hydrogeology have been limited.

This study builds on previous work by using DTS to monitor ambient and artificially-stimulated temperatures for the purpose of detailed hydraulic characterization at the borehole scale. In addition, DTS was used to investigate the effects of borehole flow processes on temperatures measured in wells. Finally, the novel monitoring capabilities of DTS allow hydraulic heterogeneity in the Sandstone Aquifer system to be studied at an unprecedented level of detail.

The Cambrian-Ordovician Aquifer System (hereafter referred to as the "Sandstone Aquifer system") is an areally extensive, multi-aquifer sequence of mature, quartzose "sheet" (Runkel et al. 1998) sandstones, interbedded with dolomites, siltstones and shales.

At Oak Creek, WI, the Sandstone Aquifer system extends from approximately 180 m below ground surface (bgs) to more than 550 m bgs. In ascending order, the major units are the Mt. Simon, Eau Claire, Wonewoc, Tunnel City, St. Peter, and Sinnipee. The Sinnipee and overlying Maquoketa Shale act as a regional aquitard. Following extensive overpumping in the mid-twentieth century, Oak Creek and most other communities along Lake Michigan switched their water supply from the aquifer to the lake.

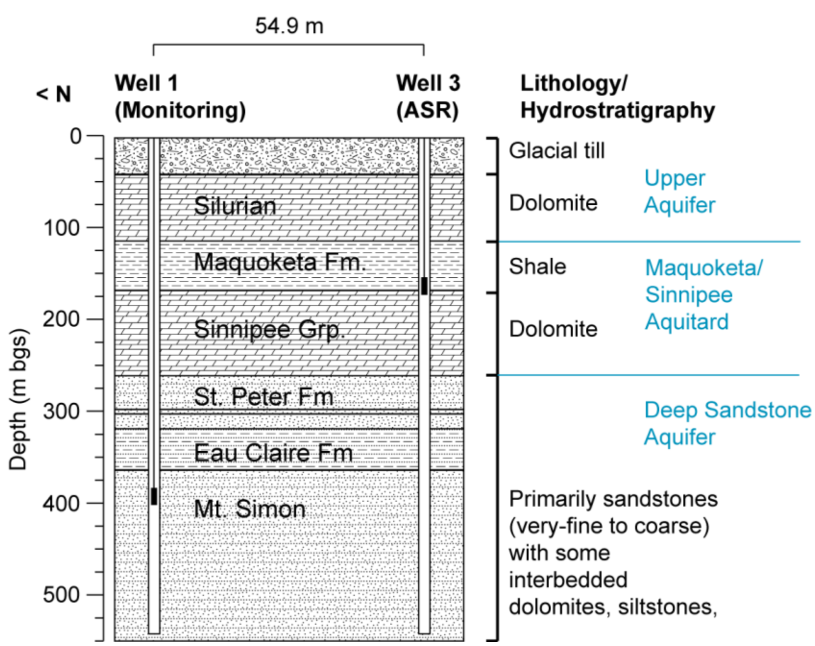

Figure 1: Schematic of the Oak Creek ASR site.

An Aquifer Storage and Recovery (ASR) operation at Oak Creek sought to use the Sandstone Aquifer system as a reservoir for the temporary storage of treated Lake

Michigan water, which would provide an auxiliary supply source of peak summer water demand, thereby reducing the necessary treatment plant design capacity. Two 550 m deep former municipal wells were retrofitted for ASR use (Figure 1). Well 3 was converted an ASR well, with the capability to inject or extract water at rates exceeding 3,800 l/min (1,000 gpm). Well 1, located 55 m away, was set up as a monitoring well, with a 57 l/min (15 gpm) sampling pump installed at a depth of 405 m bgs. Eight ASR "pilot" cycles were conducted between 1999 and 2007. Treated water from Lake Michigan was injected into Well 3, stored for a period of time, and then recovered (Miller 2001). An original objective of this study was to use DTS to monitor an injection cycle at Oak Creek. It was thought that DTS in Well 1 could potentially detect the breakthrough of the injection water, which was typically initially 10 °C colder than the native groundwater. Despite the cancelation of further ASR cycling due to water quality problems, the large open interval (370 m) and thermal history of ASR cycling at Oak Creek provided a unique opportunity for DTS in the Sandstone Aquifer system (Leaf 2010).

The bedrock units in the Madison area are the same as those at Oak Creek, but were less deeply eroded along the Cambrian-Ordovician unconformity. In addition to a thicker Tunnel City Group, the overlying Trempealeau and Prairie du Chien groups are also present. Hydrostratigraphically, the sequence can be divided into an upper and lower aquifer separated by the Eau Claire aquitard. Municipal pumping in the Madison metropolitan area has lowered water levels in both bedrock aquifers. This has substantially altered the natural flow system, creating vertical hydraulic gradients that are complex in both space and time. The Madison lakes, which previously received regional groundwater discharge, now lose water to the lower aquifer over much of their area (Bradbury et al. 1999). Although this has buffered declines in water levels, it presents a potential long-term threat to water quality in the lower aquifer. An exception to this reversal is the northern end of Lake Mendota, which lies near the margin of the cone of depression. In this area (which includes well DN-1440), vertical hydraulic gradients are sufficiently small to allow for periodic flow reversals in response to municipal pumping cycles (Bradbury et al. 1999; Anderson 2002).

Vertical hydraulic gradients in the Sandstone Aquifer system near Madison are also produced by natural phenomena. The unglaciated Driftless Area, which lies directly west of Madison, is characterized by a relatively high topographic relief and shallow depths to bedrock. This results in high rates of recharge (Hart et al. 2009) occurring at differing elevations. In the heterogeneous Sandstone Aquifer system, this produces vertical variations in head at downgradient locations. This is thought to be the primary reason for vertical hydraulic gradients at IW-512.

Several recent investigations have found laterally continuous bedding plane fractures to have a dominating effect on flow in the Tunnel City Group (e.g. Swanson 2007; Swanson et al. 2006; Runkel et al. 2006). This finding may also extend to other units in the Sandstone Aquifer system. In the initial characterization study of DN-1440, Anderson (2002) noted significant borehole flow from fractures in the Wonewoc Formation (see below). Similar investigations by Hart and Luczaj (2010) have observed fracture-dominated borehole flow in wells open to other units of the Sandstone Aquifer system. Some question remains as to the lateral continuity, and therefore regional significance, of these features.

Procedures and Methods

DTS measurements were collected in Well 1 at Oak Creek from November 13-16, 2009 under ambient conditions (using 30 min integrations) and from November 16-21 (using 15 min integrations) with Well 3 pumping at approximately 3,800 l/min (1,000 gpm). Pairs of reference coils at each end of the DTS cable were kept in icewater and circulating ambient temperature baths, which were also instrumented with Solinst Barologgers. The reference temperatures recorded by the Barologgers were used to calibrate the DTS data. A similar experiment was performed in June of 2008. A complete description of the 2008 experiment, and additional details on the 2009 experiment at Oak Creek can be found in Leaf (2010).

Following a hang-up of the DTS cable on the Well 1 sampling pump apparatus, the sampling pump and piping were removed from Well 1. This allowed for geophysical logging. In early February of 2010, natural gamma, caliper, normal resistivity, temperature, and fluid conductivity logs were collected. Heat-pulse logging of ambient well-bore flow was conducted in March of 2010. In addition to improving the conceptual model of the Oak Creek site, the geophysical logging results (Appendix B) provide a valuable addition to the limited pool of information on the Sandstone Aquifer system under the Milwaukee area.

Two numerical models were used to investigate the potential processes controlling the temperatures observed in Well 1 at Oak Creek. A three-dimensional transient MODFLOW (Harbaugh et al. 2000) simulation examined borehole flow in Well 1 induced by pumping in Well 3, by simulating Well 1 as a column of high conductivity (10^6 m/d) cells. An 11-year, two-dimensional transient simulation of radial groundwater flow and heat transport using the code HYDROTHERM (Kipp et al. 2009) examined the long-term thermal effects of ASR cycling on temperatures in the aquifer. A complete description of these models can be found in Leaf (2010).

Two research wells near Madison, WI were selected for active thermal tracer experiments. Well DN-1440 is situated in the Pheasant Branch Conservancy, which is located north of Middleton, WI near Lake Mendota. The open interval of DN-1440 intersects both the upper and lower aquifers, allowing for flow between the units in the presence of vertical hydraulic gradients. Packer head testing by Anderson (2002) showed a periodic reversal in the vertical gradient between the two aquifers that correlated with pumping schedules for Middleton Wells 4 and 5, which are located approximately 1.5 and 3 km from DN-1440, respectively.

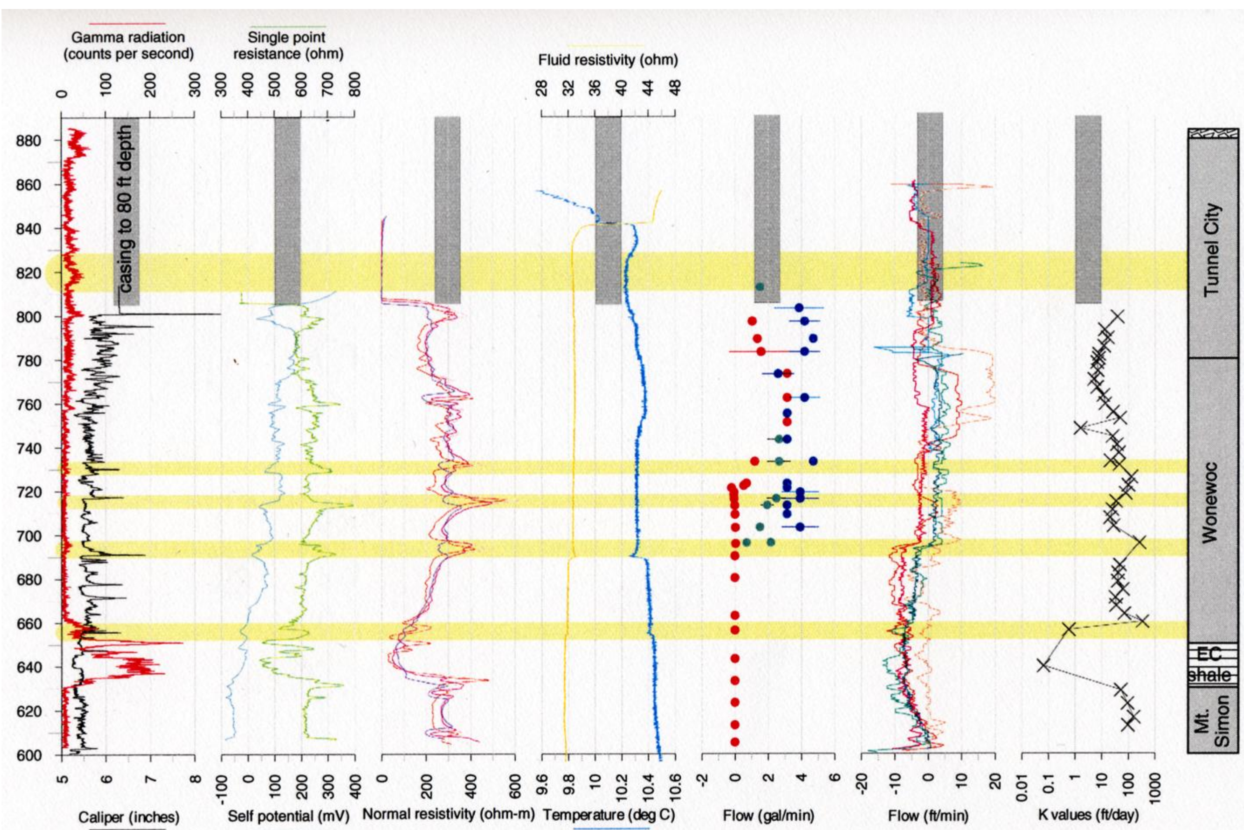

Figure 2: Borehole geophysics for DN-1440 (from Anderson 2002). Elevation is in ft. above sea level.

Figure 3: Snapshot from downhole video log of DN-1440 showing hydraulically active fractures at 58 m depth.

Figure 2 suggests that flow in DN-1440 is significantly influenced by fractures. Numerous secondary porosity features were detected in the Tunnel City and Wonewoc during the drilling of DN-1440, some of which correlate to anomalies in the geophysical logs (e.g. changes in resistivity, temperature and flow) that are consistent with hydraulically active bedding plane fractures. The locations of these features are denoted in Figure 2 by the yellow bands. The fractures at elevations of 657 and 693 feet (58.5 and 69.5 m bgs) appear to be important, as evidenced by abrupt transitions in temperature and flow, and high values of hydraulic conductivity, obtained through closed-interval packer testing (Anderson 2002). These features are also evident in a television log (Figure 3), which suggest that they represent clusters of bedding plane fractures.

Well IW-512 is located in a quarry off of Iowa County Highway A near Hollandale, WI. The well intersects at least three aquifers: the Mt. Simon, the Wonewoc/Tunnel City, and an upper aquifer consisting of a thin layer of sandstone (possibly the Jordan) and fractured dolomite in the Praire du Chein Group. As in DN-1440, there is significant hydrostratigraphic and hydraulic heterogeneity in portions of this well. Previous geophysical investigations by Hart and Luczaj (2010) have documented numerous fractures in the upper 100 m and diverging flow in the Wonewoc Formation.

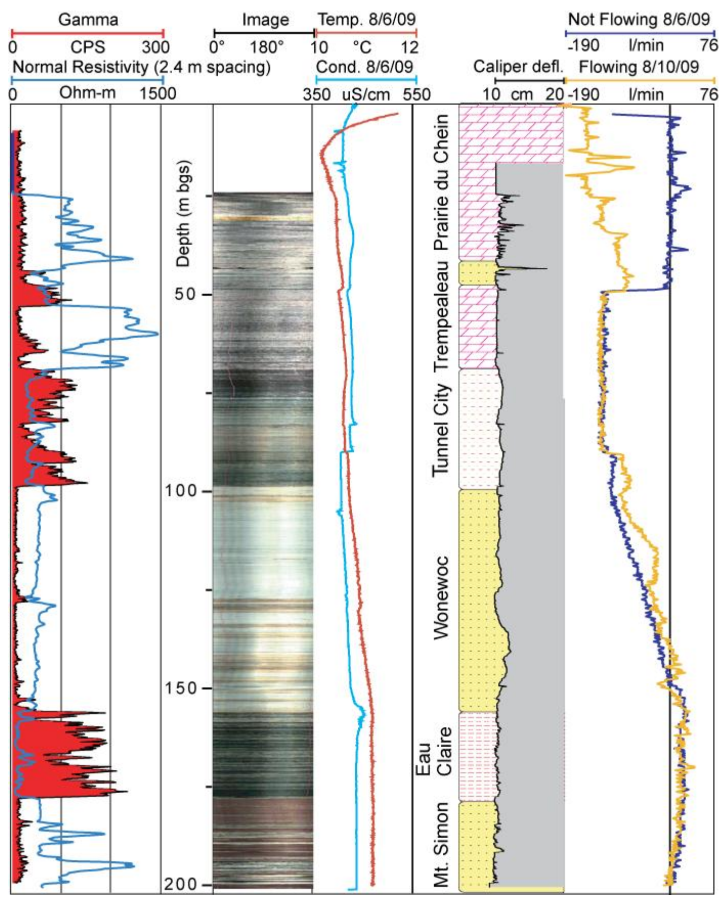

Figure 4: Borehole geophysics for IW-512.

In this well, heads in the Wonewoc/Tunnel City aquifer are above the land surface. Under ambient conditions, flow out of the casing can reach 180 l/min (45 gpm). This artesian flow can be stopped by installing a standpipe on the casing that allows the water level to rise to hydrostatic conditions (~1 to 2 m above the land surface). This causes all upward flow in the borehole to exit into the sandstone unit at about 45 m bgs, shown by the dark blue flowmeter curve in Figure 4. The normal configuration for IW-512 is with outflow stopped by a large PVC ball valve installed on the top of the casing. To ensure steady-state conditions with the well flowing, the valve was removed two days before the thermal tracer experiment.

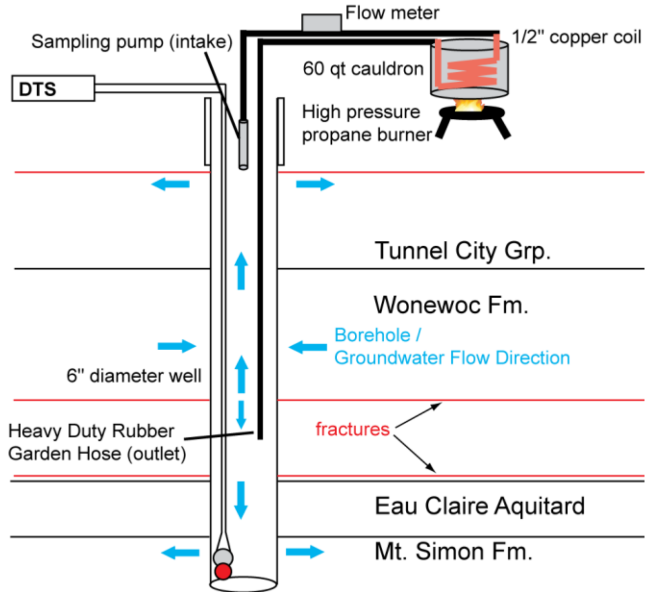

Figure 5: Heating system setup at DN-1440.

A system was developed for heating groundwater with minimal disturbance (Figure 5). A low-flow, submersible Grundfos pump situated in the cased portion of the borehole delivers well water at adjustable rates of ~4 to 13 l/min (1-3.5 gpm) to a coil of 1.27 cm (0.5 inch) diameter copper pipe immersed in a cauldron heated by a high-pressure propane burner. The heated water is returned to the well via heavy-duty rubber garden hose. A short segment of pipe attached to the outlet keeps the hose taut in the well. A movable, high capacity hose reel allows for the outlet to be easily raised and lowered in the well, up to depths of more than 150 m (500 ft) bgs (Figures 6-7 and 6-8).

Flow is measured using an Omega piston-type, variable-area inline flowmeter. This device is not ideal for water with high concentrations of suspended solids, which inhibit the motion of the piston. Problems encountered during operation at DN-1440 suggest that the reported heating system flow rates may be underestimates. High flow rates in the well remove more heat from the outlet hose. Therefore, the overall output of the system ranges from approximately 1 to 4 kW. For a pumping rate of 8 l/min (2.1 gpm), this corresponds to a temperature increase of ~2 to 7 °C.

Three single-well tracer tests were conducted in DN-1440. On April 14, 2010, a pilot test was conducted using a conventional wireline temperature tool. The heating system was run at 8.7 l/min (2.3 gpm) for a period of two hours and forty minutes, with the outlet kept stationary at the bottom of the well while the wireline tool was continuously trolled up and down between the bottom of the well and the casing.

An experiment on May 19, 2010 was conducted in a similar manner using DTS. The heating system was run for two hours and forty minutes at ~10 l/min (2.7 gpm), with the outlet briefly at 73 m (240 ft.) bgs for the first 10 minutes and then lowered to just above the bottom of the well (87 m, 285 ft. bgs) for the remainder of the experiment. DTS measurements were collected every minute, at a spatial resolution of 2 m. On May 28, 2009, an additional experiment used the heating system in brief, 10-15 min. pulses with the outlet set at various depths. The migration of the heated water pulses in the well was monitored by DTS at one-minute intervals with a spatial resolution of 2 m. The results of both DTS experiments were calibrated to external reference temperatures collected by Solinst Barologgers, which were co-located with reference coils of cable in known temperature baths.

At IW-512, the DTS system was configured and calibrated in the same manner. The heating system was run mostly continuously from 11:30 to 14:30 at ~13 l/m (3.4 gpm), with the outlet lowered in 12m increments. When the outlet reached ~160m, it was left stationary until 15:50, when it was shut off. The heating system was then pulsed in two 15 min increments at ~130 m bgs and ~95 m bgs, before being permanently shut off.

Results and Discussion

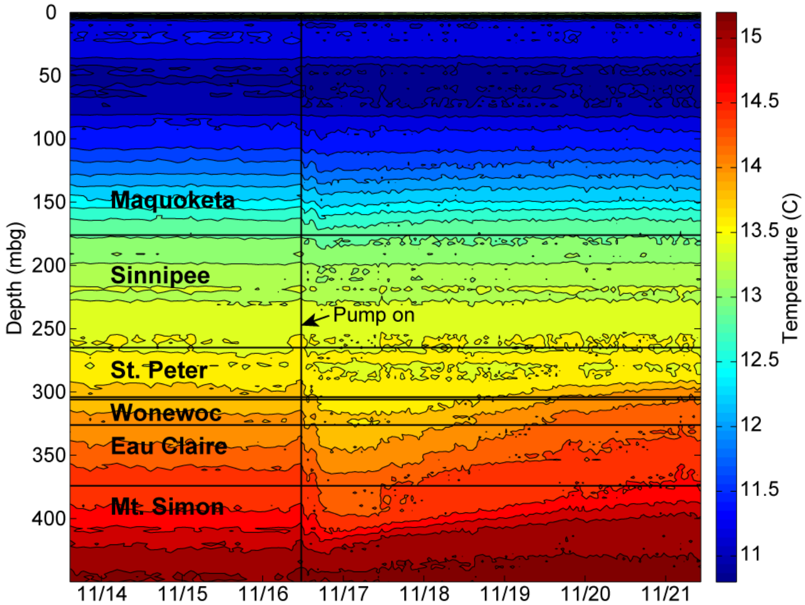

Figure 6: Contour plot of DTS data collected in Well 1 at Oak Creek. Contour interval is 0.2 °C.

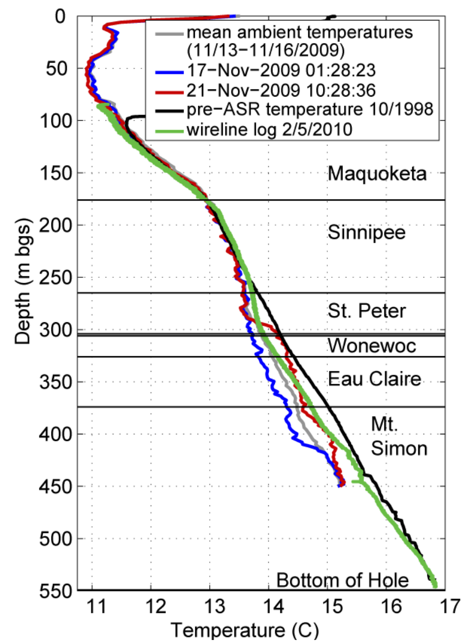

Figure 7: Temperature profiles comparing 2009 DTS data to pre-ASR

The results of the November 2009 DTS experiment at Oak Creek are shown in Figure 6. The temperature changes observed following activation of the pump in Well 3 are primarily caused by vertical borehole flow stimulated in Well 1. The results of the above-mentioned MODFLOW simulation (Leaf 2010) suggest that flow in Well 1 is initially downward, and then reverses after several hours to a steady-state configuration of upward flow from the Mt. Simon into the St Peter. This reversal in borehole flow direction is reflected in initial early-time decreases in temperatures in the Maquoketa and Eau Claire intervals, followed by overall warming at steady-state. The 2-D radial groundwater flow and heat transport modeling results (Leaf 2010) suggest that the ASR cycling produced some residual cooling that remained in 2010, as illustrated by the difference between the black and green curves in Figure . The modeling results also suggest that this cooling did not significantly contribute to the temperature changes observed in the DTS data (Leaf 2010).

Figure 8 shows a series of temperature profiles collected by trolling the wireline temperature tool during the April 14 heating experiment in well DN-1440. The timestamps in the legend indicate the times at which each run was completed. Individual runs (from the casing to the bottom) took between 15 and 25 min, depending on the trolling rate. The temperature/depth profiles therefore provide information that spans this amount of time.

At the beginning of the experiment, there is a relatively uniform rise in temperature along the length of the well caused by heat loss through the outlet hose. This is exemplified by the vertical segment of the black (56 minutes elapsed time) profile in Figure 8, which is warmer than the initial temperature (navy blue profile) by a uniform amount.

Operation of the shallow pump as described in the previous section imposes additional upward flow on the well. This upward flow is evident in the evolving slopes of the measured temperature profiles. Early in the experiment, heated water moving upward in the borehole loses heat to the surrounding rock. This creates a slope in the temperature profile, as seen in the portion of the 56 min. profile below the basal Tunnel City contact. As the rock warms, the rate of heat loss decreases, producing increasingly steeper temperature profiles. A near-vertical profile at 2:35 elapsed time suggests equilibrium has been reached between the flowing heated water and surrounding rock. Deviations from a straight vertical slope would then be expected to indicate the influx of formation water. This could be occurring in the upper Wonewoc.

The large decrease in temperatures between the outlet and the base of the Eau Claire indicates influx of cool water from the Mt. Simon. The linear character of this temperature change suggests that the influx is uniformly distributed (i.e. from porous media flow instead of fractures). Neglecting conduction, a simple mixing calculation (Leaf 2010) suggests that the cumulative flow over this interval is roughly 5.9 to 7.3 l/min (1.5 to 2 gpm). Following the shut-off of the heating system, influx from the Mt. Simon causes a rapid dissipation of heat. Within 15 minutes, temperatures near the bottom of the well are close to those measured prior to the experiment. The subsequent evolution of the temperature profiles following shut-off is similar to that observed at the start of the experiment. The movement of the inflection between the near-vertical and sloping segments of the profiles indicates upward flow velocity, which appears to be approximately 7 l/min, similar to the calculated influx from the Mt. Simon while the heating system was running.

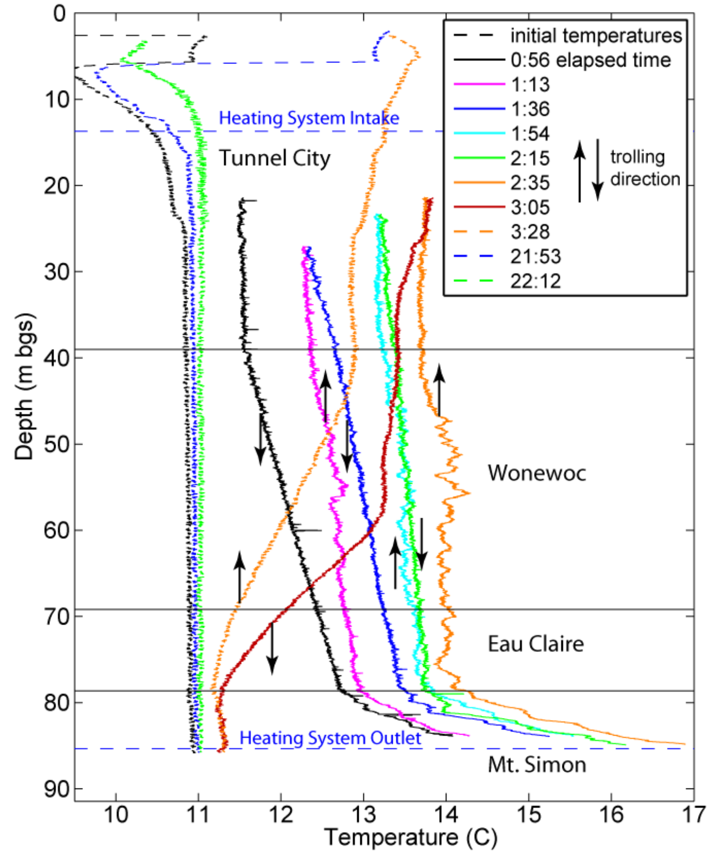

Figure 6: Wireline temperature results from the April 14 experiment in DN-1440.

Figure 9 shows a color-coded image of the results from the May 19 experiment, which used DTS to monitor the continuous operation of the heating system with the outlet fixed at the bottom of the well. Each pixel represents an individual measurement of temperature that is integrated over 2 m of cable and 1 min in time. The initial 50 minutes represent ambient temperatures, which are uniform due to vertical ambient flow. The heating system was activated at 11:55, first at a depth of 73 m and then at 90 m, as shown by the temperature pulse at 73 m bgs and constant temperature at 90 m. The

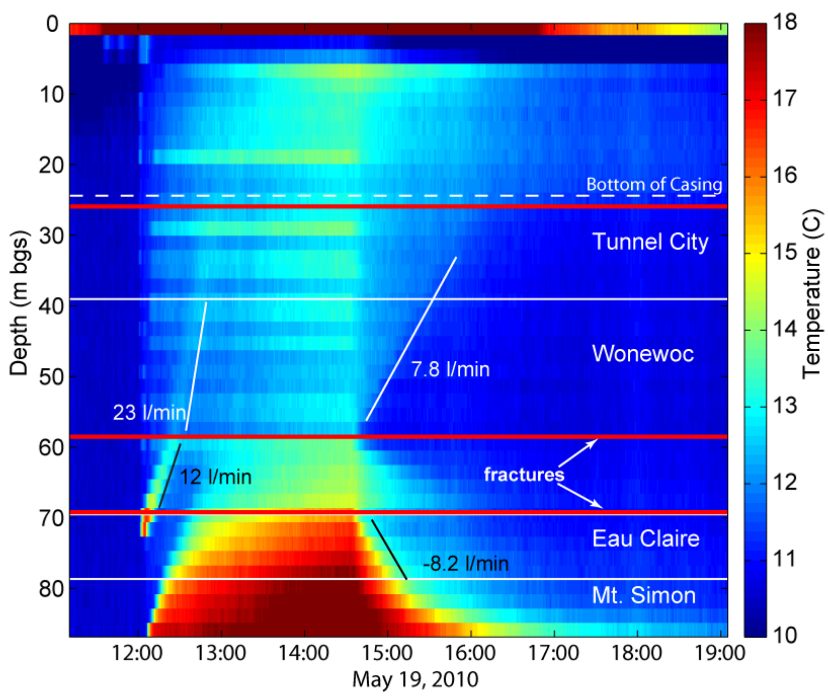

Figure 7: Image plot of DTS results from the May 19 thermal tracer experiment in DN-1440.

upward movement of the temperature disturbance under the influence of the sampling pump is indicated by the distance/time slope of the brighter (warmer) pixels. An abrupt increase in slope, shown by the white lines, above 58 m bgs indicates the influx of water from the above-mentioned fracture cluster. Closer to the outlet, the curved shape of the isotherms in the Mt. Simon and Eau Claire Formations is indicative of the thermal equilibration process between the borehole and the surrounding rock. The abrupt decrease in temperature at the top of the Eau Claire indicates inflow from the other hydraulically active fracture cluster. In the upper part of the profile, leakage of heat from the outlet hose is evident.

The evolution of temperatures following the shut-off of the heating system (at 14:32) provides detailed information on the ambient flow regime in the well. Immediate cooling occurs at the locations of the two important fracture clusters. Interestingly, the flow appears to diverge out of the cluster at 58 m bgs. Above this point, the linear shape of the migrating temperature front suggests uniform flow (i.e., no inputs or outputs). The flow appears to exit the well near the bottom of the casing, where a fracture is indicated in the geophysical logs (Figure 2). Curved isotherms in the bottom of the well reflect re-equilibration of the surrounding rock with the downward flowing cool water. They also suggest the gradual loss flow into the Mt. Simon.

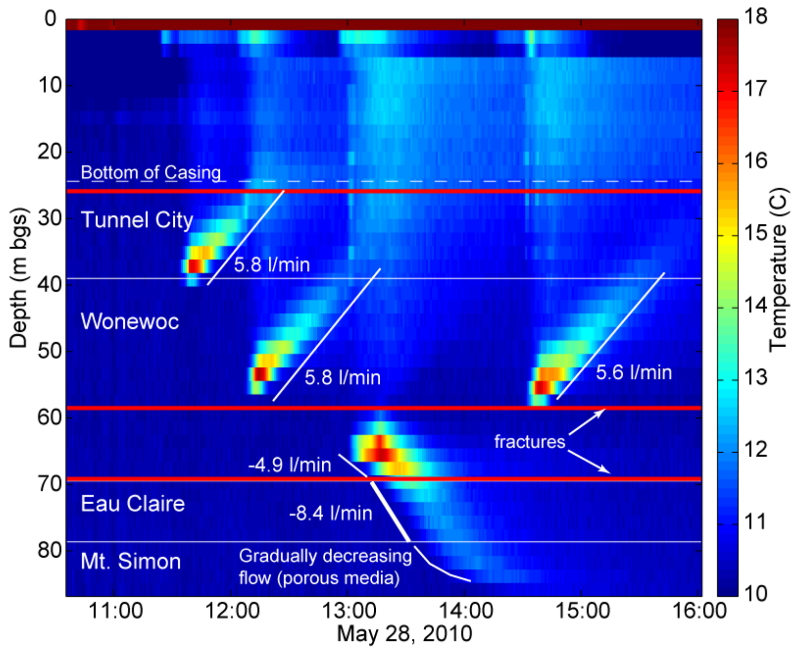

Figure 8: Image plot of DTS results from the May 28 thermal tracer experiment in DN-1440.

The ambient flow conditions observed during the May 28 experiment (Figure10) are similar to those observed on May 19. In the absence of large conduction effects, the curved shape of the temperature disturbance appears to confirm that flow in the Mt. Simon in this well is dominantly intergranular. This is consistent with the geophysical data and a smooth borehole wall texture observed in the downhole video log. In contrast, the linear slopes of the heat pulses migrating above the flow divide (which all agree closely) suggest that flow in the upper aquifer is dominated by fractures.

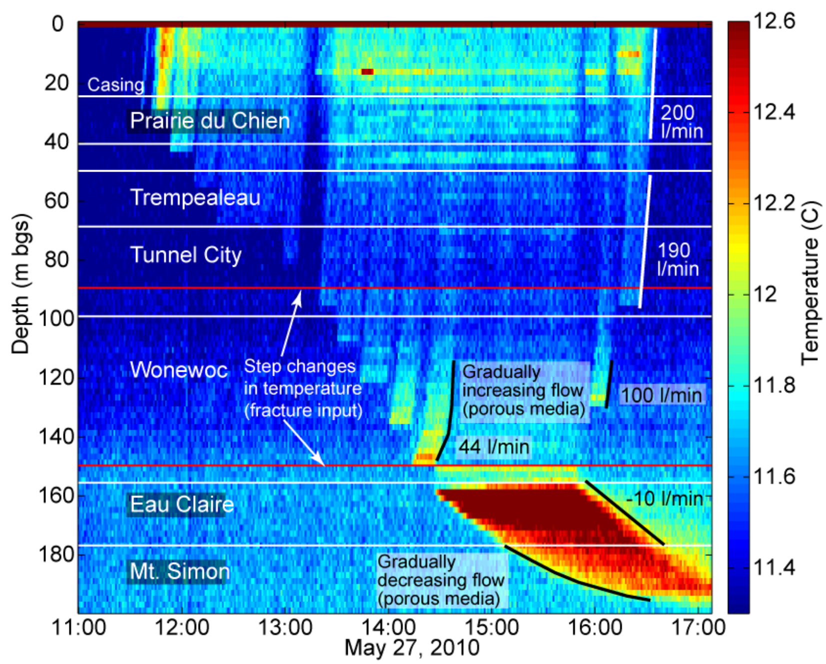

Figure 9: Image plot of DTS results from the May 27 thermal tracer experiment in IW-512.

The results of the IW-512 experiment are shown in Figure 11. High flow rates

(>100 l/min) in the upper part of the well are reflected by the steep distance/time slopes in the temperature changes. The high flow rates limited the effectiveness of the heating system, by removing additional heat from the outlet hose and mixing with the water leaving the outlet. This resulted in a lower temperature contrast. The abrupt changes in temperature at ~90 m and 150 m bgs indicate input from fractures. The latter of these two fractures appears to correspond to the flow divide in the Wonewoc, similar to the fracture cluster in DN-1440. Curved isotherms, indicating a gradual increase in upward flow in the Wonewoc and a gradual loss of flow in the Mt. Simon suggest porous media flow in the lower part of the well.

Conclusions/Recommendations

The DTS data collected at the Oak Creek ASR site helped characterize the evolving borehole flow regime in Well 1 while Well 3 is pumping. In comparison with transient groundwater flow modeling results, they show that samples collected in Well 1 do not discretely represent conditions in the Sandstone Aquifer at the location of the sampling pump. Rather, the samples represent a complex integration of conditions over a large section of the borehole, which is significantly affected by pumping in Well 3.

The DTS monitoring of active thermal tracer experiments elucidated the ambient flow regimes of wells DN-1440 and IW-512 in great detail, confirming previous observations of fracture-dominated flow in the Tunnel City Group and Wonewoc Formation. In the Mt. Simon Formation and other portions of the Wonewoc, they suggest flow to be dominantly intergranular. Diverging vertical flow in both wells appears to emanate from bedding plane fractures in the Wonewoc Formation. Stratigraphically similar positions and high heads in these fractures suggest that they may be regionally important. This finding is significant in light of recent investigations that have characterized the Wonewoc as dominantly intergranular, and warrants further investigation

In addition, the active thermal tracer experiments demonstrate an effective operating range for DTS that exceeds that of conventional heat pulse and spinner flow meter techniques. As a flow measurement tool, DTS effectively integrates measurements over the entire width of the borehole, in contrast to heat pulse and spinner flow techniques, which may be affected by leakage around the diverter or turbulence near the edge of the borehole. As a tool for measuring temperatures, DTS is superior to conventional wireline tools in its response time and its ability to profile temperature synoptically without disturbing the fluid column.

Future work could use DTS methods to characterize aquifer heterogeneity in other wells open to the Sandstone Aquifer system. As shown respectively in the May 19 and May 28 experiments, both constant source and finite-pulse heating techniques can provide useful information. The latter provides the most unambiguous results as a stand-alone technique. An electric resister may provide a superior heat source in comparison to the heat exchanger used in this study.

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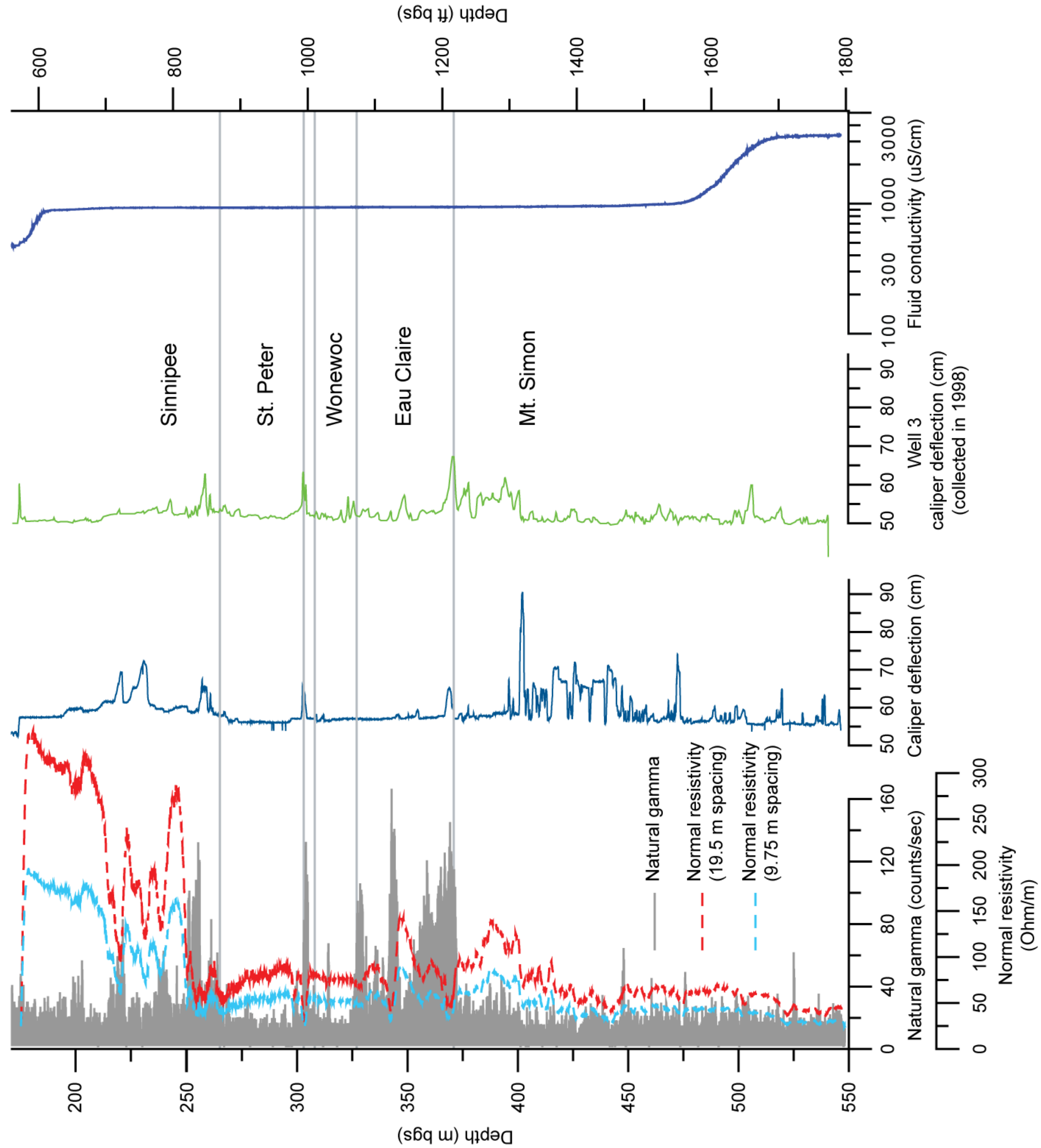
Appendix A: Conference presentations

Leaf, Andrew T., Jean M. Bahr, and David J. Hart 2009. Distributed temperature sensing as a hydrostratigraphic characterization tool. Paper presented at the annual meeting of the Geological Society of America, Portland, OR, October 18-21, 2009.

Leaf, Andrew T., Jean M. Bahr, and David J. Hart 2010. Distributed temperature sensing for characterizing vertical aquifer heterogeneity. Paper presented at the annual meeting of the American Water Resources Association-Wisconsin Section, Middleton, WI, March 4-5, 2010, and at the annual meeting of the Wisconsin Ground Water Association, Waukesha, WI, March 19, 2010.

Leaf, Andrew T., David J. Hart, and Jean M. Bahr 2010. Single-well thermal tracer tests using distributed temperature sensing. Paper presented at the annual meeting of the Geological Society of America, Denver, CO, October 31-November 3, 2010.

Appendix B: Oak Creek Well 1 geophysical logging results



Well 1 heat pulse flow logging results with confidence limits*
(upward flow is positive)

Depth	Stratigraphy	Pulse travel time (s)	Interpreted Flow		-95%	95%
244 m (800 ft.)	Lower Sinnipee Group	10.95 17.97 17.66 19.08	6.20 1.64	l/min gpm	13.64 3.60	-0.32 -0.09
305 m (1000 ft.)	Near the Tunnel City/ St. Peter contact	10.58 13.48 14.09	11.88 3.14	l/min gpm	19.72 5.21	5.01 1.32
366 m (1200 ft.)	Near the Eau Claire/ Mt. Simon contact	19.57 28.66 27.69 26.15	0.27 0.07	l/min gpm	7.29 1.93	-5.88 -1.55

*methods and additional description can be found in Leaf (2010)

Development and Application of a User-Friendly Interface for Predicting Climate Change Induced Changes in Evapotranspiration

Basic Information

Title:	Development and Application of a User-Friendly Interface for Predicting Climate Change Induced Changes in Evapotranspiration
Project Number:	2010WI246B
Start Date:	3/1/2010
End Date:	3/1/2011
Funding Source:	104B
Congressional District:	WI 2nd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Hydrology, Methods
Descriptors:	
Principal Investigators:	Steven Loheide

Publication

1. Jaochim, Douglas R. 2011. Modeling the impacts of future climate change on groundwater recharge and evapotranspiration in Wisconsin. MS Dissertation, Water Resources Engineering, University of Wisconsin, Madison, WI 102p

Development of a User-Friendly Interface for Predicting Climate Change Induced Changes in Evapotranspiration

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

S. P Loheide II
Department of Civil and Environmental Engineering
University of Wisconsin – Madison

D. R. Joachim
Department of Civil and Environmental Engineering
University of Wisconsin - Madison

Project WR10R001

January, 2012

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PROJECT SUMMARY

Title: Development of a User-Friendly Interface for Predicting Climate Change Induced Changes in Evapotranspiration

Project I.D.: WR10R001

Investigators:

Principal Investigator: Steve Loheide, Assistant Professor
Research Assistant: Doug Joachim, M.S.
University of Wisconsin-Madison, Dept. of Civil and Environmental Engineering

Period of Contract: 7/31/10 –2/28/11

Background/Need:

Evapotranspiration (ET) is the second largest component of Wisconsin's (WI) hydrologic budget after precipitation, yet the expected changes to this process due to climate change are not well understood. Changes to ET will impact agriculture, tourism, recreation, and ecosystems.

Objectives:

The objectives of this study were: (1) to develop and calibrate a Penman-Monteith model of ET that predicts daily ET in nine WI regions and for five broad vegetation communities for a range of soil types using downscaled global climate model (GCM) data through 2100, and (2) to package the model into a publically-accessible graphical user interface (GUI) to allow interested parties to evaluate the likely changes to ET in their specific location.

Methods:

Our modeling approach uses the dual crop coefficient approach to solving the Penman-Monteith ET equation recommended by the Food and Agriculture Organization (Allen et al. 1998; Penman 1948; Monteith 1965) combined with the Jarvis-Stewart model of stomatal conductance (Jarvis 1976; Stewart 1988) to model vegetation-specific ET on a daily timestep. The model was calibrated using eddy flux covariance data from five Ameriflux sites in WI, Minnesota, and Illinois that provide half-hour measurements of climate parameters and actual ET. Surface conductance and growing season parameters were optimized for each of five vegetation types using a Markov Chain Monte Carlo technique (Zobitz et al. *in review*) to best match modeled ET with observed ET at each location. Three GCMs that have been downscaled by the Wisconsin Initiative on Climate Change Impacts provide daily climate data to drive the model during three climate periods: 1981-2000, 2046-2065, and 2081-2100. Nine broad regions coinciding with the National Climate Data Center's climate divisions for the state WI were selected to provide spatial coverage across the state.

The final calibrated model was packaged in a Matlab-based GUI that is freely available to interested users online (http://hydroecology.cee.wisc.edu/research/WisconsinET/index.htm; Joachim & Loheide 2011). Results can be used to better understand the likely changes to future ET in specific regions. Daily ET output can also be used as ET forcing in hydrologic modeling efforts. Default parameters are the values obtained during calibration, but advanced options allow users with additional knowledge of plant phenology to adjust parameters as desired.

Results and Discussion:

Model results differ by GCM, with two relatively wet models predicting an increase in ET between 8-10% by 2100, while a dry model produces a net decrease in ET of 2-5% in southwest WI and a small increase in ET of 1-5% in northeast WI by the end of the century as conditions become increasingly water-limited. Annual ET is expected to be about 100 mm higher in southern WI than northern WI at the end of the century, with annual ET in northern WI in 2100 reaching southern ET levels seen prior to 2000, effectively shifting today's annual ET regime northward.

The impacts of changing ET are important from a water balance perspective. As ET increases, the annual depth of water available after ET is subtracted from precipitation (P – ET) is likely to decrease, unless precipitation increases more quickly that ET. In two of the three GCMs we analyzed, one with marginal precipitation changes and one with large decreases in annual precipitation, P – ET decreased substantially by 2100. Under the wettest GCM, however, P – ET actually increased by the end of the century signifying wetter conditions overall.

Conclusions/Implications/Recommendations:

The implications of this study depend strongly on which GCM most accurately predicts future conditions in WI. While potential ET is expected to increase in every region and for every vegetation type by 2100, regardless of GCM selected, the true impacts of changing actual ET depend largely on how precipitation changes over the same period. Under the wettest GCM we considered, the annual depth of water available for overland flow and groundwater recharge (P – ET) is expected to increase by over 50 mm by 2100. This suggests WI will become wetter, with a decreased need for irrigation, but a higher potential for flood conditions. In contrast, the driest GCM we used leads to a decrease in P – ET of nearly 150 mm. In this scenario, WI will be much drier than in the past, with lower lake levels, increased irrigation demands, and decreased recreational opportunities as possible implications.

To decrease the level of uncertainty in how water availability is likely to change in WI, refined GCM projections of future precipitation would be needed. All models agree that temperatures will increase, with broad agreement on the magnitude of change. Precipitation changes, on the other hand, are less clear with some models predicting more precipitation by 2100 and others predicting substantially less. Until the rainfall changes through 2100 are better understood, considerable uncertainty remains in how WI hydrology will change in the future.

Related Publications:

Joachim, D; Loheide, SP; Desai, AR. Simulated Implications of Future Climate Change on Groundwater Recharge, *in preparation*

Joachim, D (2011). Modeling the Impacts of Future Climate Change on Groundwater Recharge and Evapotranspiration and Wisconsin. *Master's thesis, UW-Madison*

Joachim, D; Loheide, SP (2011). Evaluating the changes to Wisconsin Evapotranspiration under a Future Climate. *AWRA – WI Section*, Annual Meeting.

Key Words: evapotranspiration, climate change, stomatal conductance

Funding: UW Water Resources Institute, USGS 104(b) Research Grant Program

INTRODUCTION

ET is the second largest component of WI's water budget after precipitation, yet the impacts of climate change on this important process are poorly understood. A suite of models of increasing atmospheric carbon-dioxide concentrations under the A1B scenario proposed by the Intergovernmental Panel on Climate Change by 2100 have predicted an increase in average temperature in Wisconsin of ~4°C (IPCC, 2007), which will increase the energy available for ET while increasing growing season lengths across the state. Conversely, changing precipitation and cloud patterns combined with the changing stomatal response of vegetation to environmental factors could serve to counteract these expected increases. A better understanding of how climate change will affect ET across WI will improve the ability of water resources managers and land-use planners to make informed decisions.

The fundamental physics of evapotranspiration as affected by radiation, temperature, wind speed, and relative humidity are well described using a Penman-Monteith approach (Penman 1948, Allen et al, 1998), but vegetation also exerts a strong control on ET, particularly under water-limited conditions. These effects can be quantified by developing relationships between environmental factors and stomatal response (e.g. stomatal conductance). Many studies have shown that increasing atmospheric CO_2 concentrations are likely to increase plant water use efficiency and reduce stomatal conductance in the future (Ainsworth and Rodgers 2007; Field et al. 1995; Karnosky 2003; Medlyn et al. 2001; Saxe et al. 1998; Bunce 2004; Curtis and Wang 1998). Although an increase in atmospheric vapor pressure deficit acts to increase potential ET, it also tends to decrease stomatal conductance which can offset any increases in actual ET (Johnson and Ferrell 1983; Turner et al. 1984; Monteith 1995). It has also been shown that stomatal conductance decreases above or below an optimal air temperature at which conductance is maximized (Stewart 1988), thus increasing temperature could either increase or decrease stomatal conductance. Finally, stomatal conductance tends to increase as solar radiation increases leading to higher stomatal resistance to transpiration on cloudy days (Stewart 1988).

The Ameriflux network of eddy flux covariance towers was established in 1996 to provide continuous observations of CO_2, water, energy and momentum fluxes (Baldocchi et al. 1988; Goulden et al. 1996; Grelle and Lindroth 1996) across North and South America. While the network is largely used to measure CO_2 exchange in ecosystems, the observations also include long term records of vertical water vapor flux (actual ET), radiation, temperature, humidity, wind speed, and precipitation over the same period which make them ideal for comparing observed actual ET and modeled actual ET using climate parameters measured at the same location.

The Wisconsin Initiative on Climate Change Impacts (WICCI) Climate Working Group has statistically downscaled a suite of general circulation models (GCMs) that predict future daily temperature and precipitation with a 0.1° by 0.1° latitude and longitude resolution across WI. The models show an average increase of annual precipitation by 2100, although the differences among models can be large. Changes to temperature, on the other hand, are relatively consistent among models, with a projected increase of ~3.9 °C in average maximum summer temperature by 2100. While the possible changes to precipitation and temperature have been examined in detail, their effects on the partitioning of precipitation into runoff, recharge, and ET remain unclear.

optimum. This process continues until a specified number of iterations are complete and the global optimum, or best possible parameter set has been obtained (Zobitz et al.*in review*).

Three GCMs were chosen for inclusion in the model, one wet (CCCMA), one dry (MIROC) and one intermediate precipitation model (CNRM). The resolution of these three GCMs is the same over the continental United States, which is very coarse at the scale of the state of WI with just six model cells covering the entire state. However, because the National Climate Data Center has designated nine climate divisions in WI which are defined as "areas of the state that have relatively uniform climate characteristics" we adopted these nine regions for predicting future ET. We used WICCI-downscaled maximum and minimum temperature and precipitation at the center of each of the nine climate regions, but we used non-downscaled data for all other climate parameters.

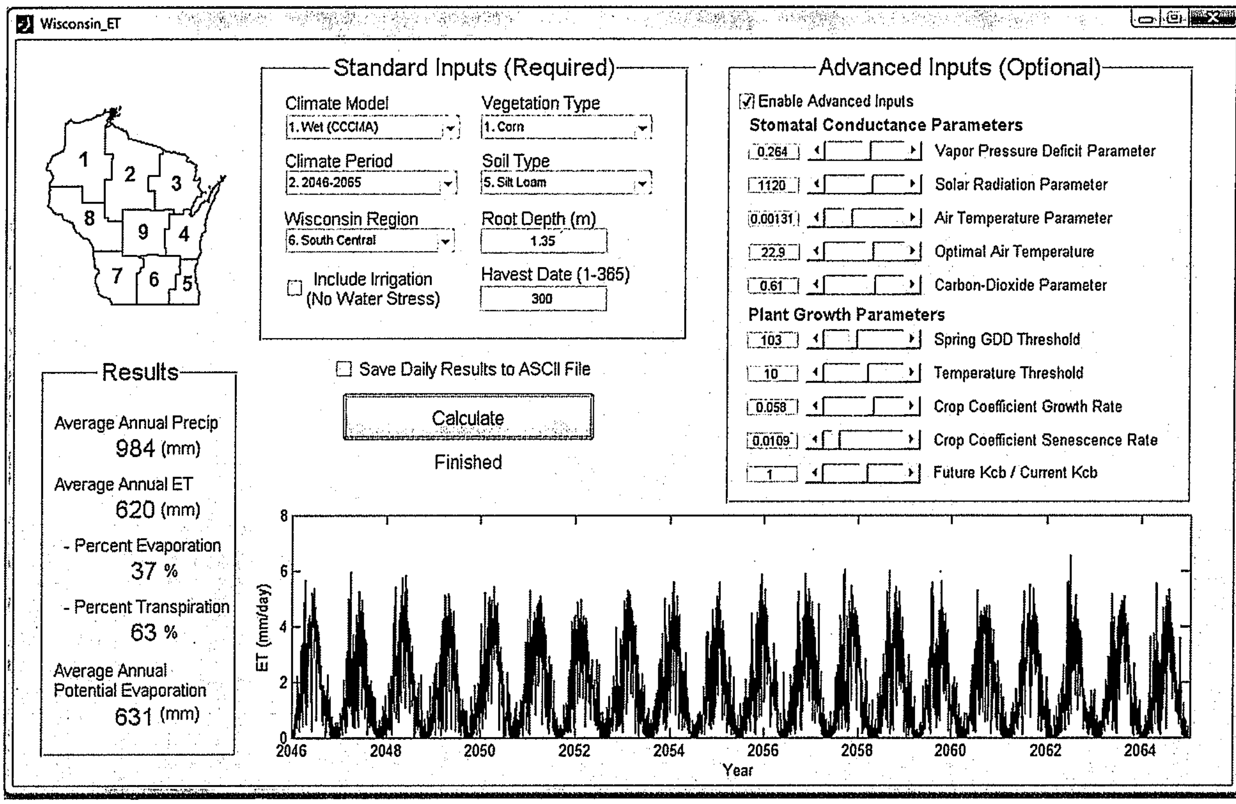

Figure 1. A screen-shot of the graphical user interface developed to allow users to predict future changes to ET. The model is available at http://hydroecology.cee.wisc.edu/research/WisconsinET/index.htm

All three models indicate that average daily temperature will be increasing substantially by 2100. The magnitude of this temperature rise, however, is unclear. MIROC tends to be the warmest of the three and indicates an increase of up to 7 °C can be expected in WI. In contrast, CCCMA and CNRM predict a roughly 4 °C increase on average, more in line with the average of all models submitted to the IPCC.The inter-model variability with regard to precipitation is much larger than that of temperature. In general, CCCMA is the wettest of the models we examined; it predicts an increase in average annual precipitation of over 100 mm by 2100. CNRM predicts an increase of nearly 75 mm by 2046-2065, but a slight decline from 1981-2100 by the end of the century. The MIROC model is the driest of the three and predicts a decrease of about 75 mm in average annual precipitation by 2100. By the end of the 21st century, the inter-model spread in annual precipitation exceeds 150 mm.

After completing the model calibration and parameterization and obtaining future climate predictions for each of the nine WI climate divisions, we created a user-friendly GUI using Matlab (MathWorks, 2011) to allow interested users to predict how ET will change in the future. The GUI, shown in figure 1, allows users to select from three climate models and periods, nine WI regions nine soil types, and five vegetation types to obtain future ET estimates specific to a given location. For users with knowledge of plant phenology and stomatal response, advanced options are available that are used to adjust how plants respond to environmental factors with regard to stomatal conductance and the onset and rate of growth in the spring. The GUI is freely available online (http://hydroecology.cee.wisc.edu/research/WisconsinET/index.htm) and does not require Matlab software to operate (Joachim & Loheide, 2011).

RESULTS AND DISCUSSION

Model results for predicted future ET across the state of WI under the CNRM GCM are plotted in figure 2. The average change in annual ET from 1981-2000 to 2081-2100 is obtained in each region by assuming 20% land cover of each vegetation type is also included in the figure. Similar plots for CCCMA and MIROC are not included here, but the results using these models are described below and are available in Joachim (2011).

Based on model results, ET is likely to increase in the future for all Wisconsin regions and vegetation types by an average of between 8 and 10% under the wet and intermediate models (CCCMA and CNRM) with a maximum relative increase of 13% seen in one region each for both models. Conversely, annual ET is expected to decrease by 2-5% in southwest WI and increase a more moderate 1-5% in northeast WI by the year 2100 under the driest model (MIROC) as water availability decreases and root water uptake becomes more severely limited more often. All models predict an increase in ET for each region and vegetation type through 2065, but these increases are offset by decreases in the later period for CNRM and MIROC, while CCCMA produces another slight increase in ET in the late century.

The model results suggest that differences in ET among vegetation types are important. In CCCMA, for instance, corn is the only vegetation type to see a consistent drop in ET from mid- to late-century, due to the canopy resistance of corn being more affected by increasing atmospheric CO_2 and cloudy conditions than other species. Overall, ET is largest in hardwood forests and shrubs, a result that is consistent under each GCM, time period, climate region, and soil type. The absolute difference in expected annual ET by 2100 between forests and prairies is generally less than 100 mm, or a difference of about 15-18%, which is of similar magnitude to the differences between annual ET in northern and southern WI under a static vegetation community.

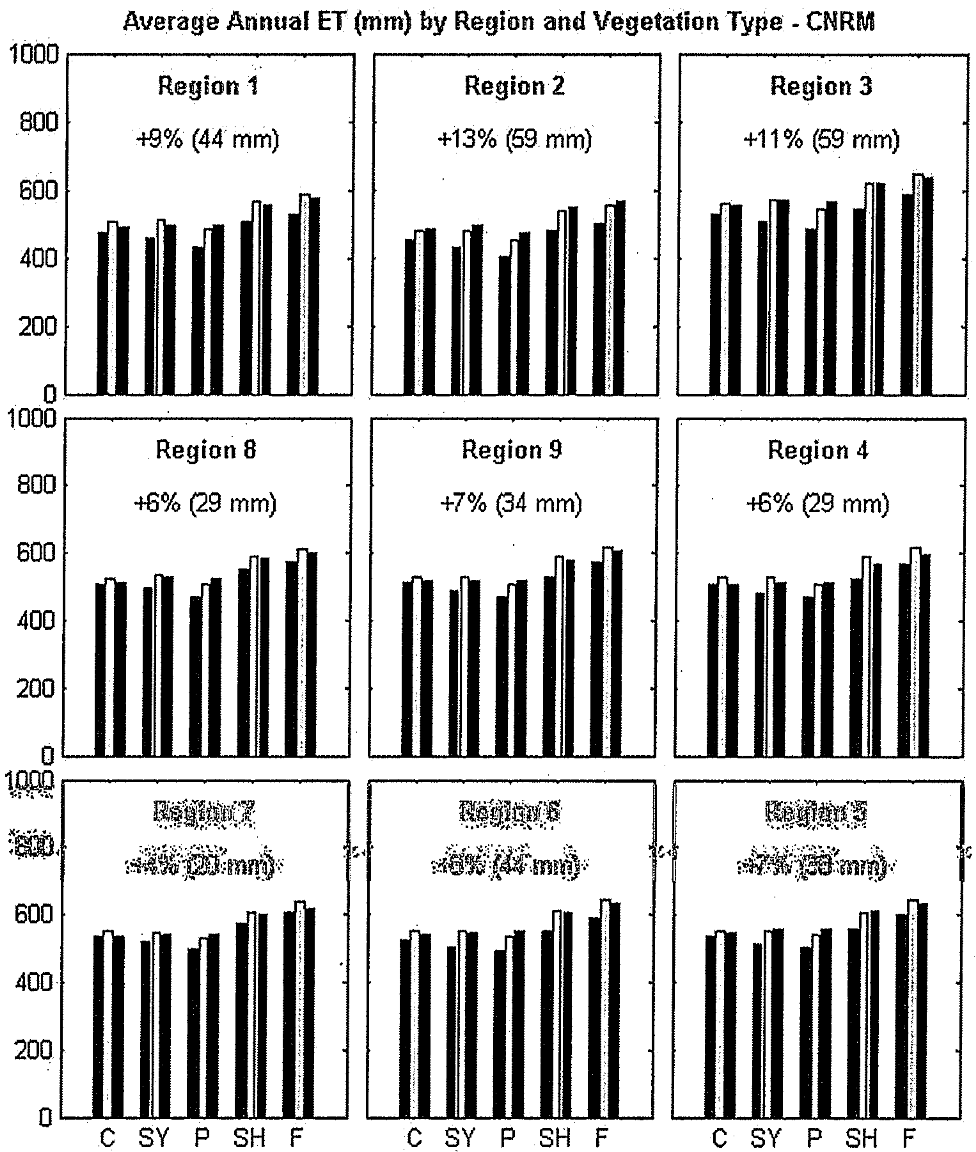

Figure 2. Average annual ET (mm) from a silt loam soil using CNRM. C = Corn, SY = Soybeans, P = Prairie, SH = Shrubs, F = Forest. Blue = 1981-2000, Green = 2046-2065, Red = 2081-2100. Percent change and absolute change from 1981-2000 to 2081-2100 averaged across all species are printed in each panel.

Importance of Soil Texture

The effect of soil texture on future ET is also noteworthy; annual ET is maximum for a silt loam and decreases under both increasing soil coarseness (sand, loamy sand) and decreasing soil coarseness (clay, silt clay) as shown in Fig 3. The differences can be large, particularly in very coarse sandy soils where annual ET can be up to 33% less than seen in silt loam soils. Under these conditions, deep drainage increases and water is more easily able to escape the root zone. Fine grained clay and silt clay soils also see a decrease in annual ET of up to 17% relative to silt loam soils because there is more overland flow.

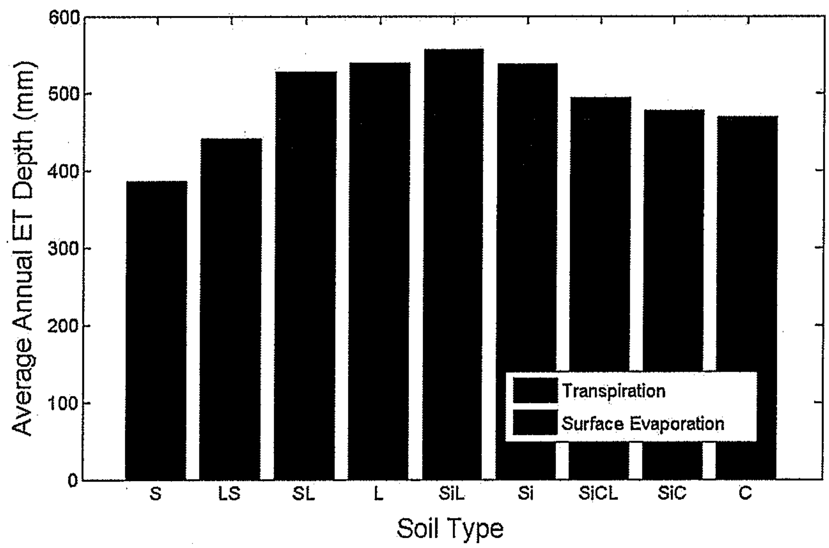

Figure 3. Average annual depths of ET, E and T by soil type under MIROC for WI region 6 and corn. Soils from left to right are sand, loamy sand, sandy loam, loam, silt loam, silt, silt clay loam, silty clay, and clay.

Predicted Changes to the Difference Between Precipitation and ET

The changes to the difference between annual precipitation and ET (P – ET) over time vary greatly among GCMs. Figure 4 shows P – ET changes under CNRM, with changes under other GCMs described below. Under the wettest GCM (CCCMA), P – ET increases substantially by 2046-2065 before decreasing slightly by 2081-2100 resulting in a net increase in annual P – ET of 34% (67 mm) compared to the base case of 1981-2000. In contrast, under the CNRM scenario, P – ET increases slightly by 2046-2065 before dropping to less than that seen in the base case by 2081-2100 with an average decrease of 15% (41 mm) across the state. The driest GCM (MIROC) produces the most pronounced shift in P – ET by 2081-2100, declining an average of 36% (74 mm) which indicates much drier conditions overall.

Spatially, the change in P – ET over time also varies. Under CCCMA, the eastern and central regions of WI see a small increase or decrease in P – ET relative to the large increases in the rest of the state. Northwest WI in particular experiences a very large (> 50%) increase in P – ET. Under the CNRM scenario, P – ET decreases most in the north and southwest (> 15%), with relatively smaller decreases in the rest of the state (< 10%). Under the driest scenario (MIROC) P – ET decreases by about 40% across much of the state, with a somewhat smaller decrease seen in the northeast corner (< 30%).

While the changes to the absolute magnitude of ET expected by 2100 are important, it is the changes in P – ET that will likely have the most direct impact on tourism, agriculture and water resources planning in Wisconsin. P – ET represents the amount of water available for streams, ecosystems, recreation, and many other important functions. An increase in P – ET as seen in CCCMA suggests generally wetter conditions in the future, with an increase in the amount of water supplied to streams by overland flow and baseflow. Depending on the timing and intensity of precipitation, it could also indicate a higher likelihood of flooding events and high lake and groundwater levels. In contrast, a decrease in P-ET as seen in CNRM and MIROC indicates less water is available to be partitioned to streamflow for ecosystem functions and recreation.

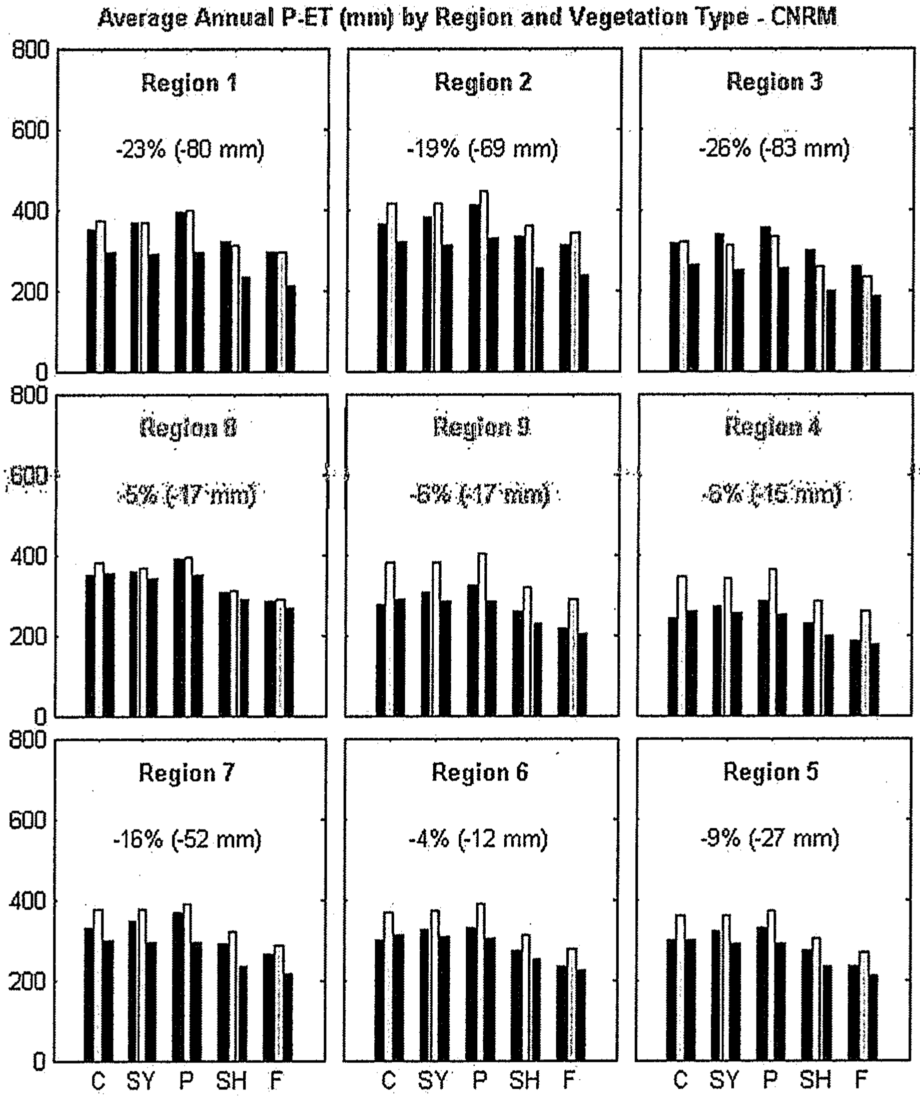

Figure 4.Average annual difference between precipitation and ET (mm) from a silt loam soil using CNRM. C = Corn, SY = Soybeans, P = Prairie, SH = Shrubs, F = Forest. Regional change is the difference between the average ET from all vegetation types in 2081-2100 and average ET under the base case. Blue = 1981-2000, Green = 2046-2065, Red = 2081-2100. Percent change and absolute change from 1981-2000 to 2081-2100 averaged across all species is printed in each panel.

The wide differences among GCMs with regard to future P – ET changes are driven largely by a disagreement in future predicted precipitation patterns. The wettest model (CCCMA) suggests WI will become a wetter state as a result of climate change and that precipitation will increase faster than ET through 2100. Under this scenario, P – ET increases through time. Conversely, the driest model (MIROC) predicts WI will become substantially drier by 2100, with increases in ET combined with decreases in annual precipitation. These results highlight the importance of improving our understanding of future precipitation changes and in using a variety of GCMs when evaluating water resources changes in the future.

CONCLUSIONS AND RECOMMENDATIONS

The methods, program, and GUI developed in this project can be applied to help predict how ET will change in the future. They provide a simple way for users interested in ET to better understand how climate change will impact them. The model provides three different sets of future climate data which allows for a range of possible changes to ET so that the user can assess the implication of uncertainty inherent in the GCMs themselves. The inclusion of three climate periods from 1981-2000, 2046-2065, and 2081-2100 allows for a better understanding of how ET is expected to change through time. The model also divides WI into nine different climate regions, which provides a spatial representation of ET change. The five broad vegetation categories in the model allow users to investigate the importance of land cover in determining any ET changes. Finally, the inclusion of nine separate soil types helps explain the impact of soil characteristics on the hydrologic budget in a future climate.

The results of this study indicate that substantial ET increases will occur across the state as long as precipitation does not decrease substantially over the same period. After applying each GCM to our ET model, we noted 8-10% increases in annual ET from baseline levels under two GCMs, one wet and one intermediate, with some regional increases totaling 15% or more. Under the driest GCM, ET increased by 2046-2065, but decreasing precipitation led to a higher likelihood of water-limited conditions in 2100 and ET decreased slightly in southwest WI (by 2-5%) and increased slightly in northwest WI (by 1-5%) for each vegetation type relative to the base case.

The expected changes to P – ET are less clear, with strong disagreement among GCM scenarios driven by the different precipitation patterns predicted from each model. Under the wettest GCM studied (CCCMA), P – ET increases by the mid-21st century before declining slightly during the latter half of the century, leading to a net gain of 67 mm of P – ET relative to the base case. This may indicate there will be less need to irrigate lawns and crops and could produce greater streamflow on average. This could also lead to a higher likelihood of flood conditions and higher lake levels in the state. In contrast, the GCM with the lowest future precipitation (MIROC) experiences a decrease in P – ET of 150 mm, a decrease of about 35% relative to the P – ET seen in the base case. This change would suggest a large decrease in the amount of precipitation partitioned into streams and lakes, causing stresses to aquatic ecosystems and human recreation that relies on adequate water levels. These results indicate that the impacts of rising ET on WI hydrology depend largely on how precipitation ultimately changes in the coming century.

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Response of Ice Cover, Lake Level and Thermal Structure to Climate Change in Wisconsin Lakes

Basic Information

Title:	Response of Ice Cover, Lake Level and Thermal Structure to Climate Change in Wisconsin Lakes
Project Number:	2010WI248B
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End Date:	3/1/2011
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Congressional District:	WI 2nd
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Models, None
Descriptors:	
Principal Investigators:	Chin H Wu

Publication

1. Hsieh, YF, DM Robertson, RC Lathrop, and CH Wu. 2011. Influences of air temperature, wind, and water clarity on 100-year trends in ice cover and water temperature in a dimictic lake. Limnology and Oceanography (In Press).

Response of Ice Cover, Lake Level, and Thermal Structure to Climate Change in Wisconsin Lakes

Principle Investigator: Chin H. Wu, University of Wisconsin-Madison

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Project Summary

Title: Response of Ice Cover, Water Level, and Thermal Structure to Climate Change in Wisconsin Lakes

Project I.D.: WR10R002

Investigators:

Principal Investigator: Chin Wu, Professor, Department of Civil and Environmental Engineering, University of Wisconsin-Madison

Research Assistant: Yi-Fang Hsieh, Ph.D. Student, Department of Civil and Environmental Engineering, University of Wisconsin-Madison

Research Assistant: Anastasia Gunawan, M.S. Student. Department of Civil and Environmental Engineering, University of Wisconsin-Madison.

Research Assistant: Madeline Magee, M.S. Student. Department of Civil and Environmental Engineering, University of Wisconsin-Madison.

Period of Contract: 3/2/2010-2/28/2011

Background/Need:

Previous research has shown evidence that the climate is changing worldwide, and more specifically, in Wisconsin.

Objectives:

The goal of this project was three-fold. First, taking a specific dimictic lake in southern Wisconsin, we wanted to determine how long-term changes in air temperature and wind speed affect ice cover and thermal structure in during the past century. Second, looking at northern Wisconsin and southern Wisconsin lakes, we wanted to investigate the coherence among lake climate drivers between the two locations as well as coherence of changes in lake physical variables over the period 1989-2010. Finally, using southern Wisconsin lakes, we wanted to investigate what role lake morphometry (i.e. depth and surface area) play in lake response to changing climate.

Methods:

Using the DYRESM-Ice model developed as part of this project, we simulated long-term lake physical variables of ice cover, water temperature, and water temperature to determine how the lakes have responded to the past changing climate.

Results and Discussion:

Overall, our results indicate that there has been a warming trend in air temperature for both northern and southern Wisconsin. Additionally, there has been a trend of decreasing wind speed. During this same period, there has been a decrease in overall ice cover duration and ice thickness during the study period. Additionally, there has been an increase in stratification duration in the study lakes, a decrease in hypolimnetic water temperatures, and an increase in epilimnetic water temperatures. Air temperature and wind speed are both correlated with changes in lake physical variables. There also seems to be a strong coherence between air temperatures among northern and southern lakes and a lower coherence for wind speed. For lake physical variables, there is a strong coherence in freeze dates between the north and south and epilimnetic water temperatures between northern and southern lakes. Other lake variables did not exhibit a strong coherence over the study period.

Conclusion/Implications:

DYRESM-I has demonstrated the capability in accurately predicting ice cover and water temperature over a continuous 100-year period. To our knowledge, this study presents the first attempt to continuously model both ice cover and thermal structure of a dimictic lake over a period of as long as a century. This type of modeling provides a first step toward projecting the impacts of future climate change on lakes, which can help gain better ideas of how the changing climate will affect lakes. To better understand the full effects of climate change, future modeling incorporating physical/chemical/biological interactions would be crucial and essential.

Related Publications:

Hsieh, Y.F., Robertson, D.M., Lathrop, R.C. and Wu, C.H. Influences of air temperature, wind, and water clarity on 100-year trends in ice cover and water temperature in a dimictic lake. *Limnology and Oceanography*. accepted under minor revision

Gunawan, A.A. and Wu, C.H. Coherence pattern of ice cover and thermal regime between Northern and Southern lakes of Wisconsin in response to changing climate. *To be submitted, Limnology and Oceanography*

Magee, M.R. and Wu, C.H. Long-term trends and variability in ice cover and thermal structure in three morphometrically different lakes in response to climate change. *To be submitted, Water Research*

Key Words: Ice cover, hydrodynamics, climate change, lake morphometry, lake response, long-term, coherence

Funding:

Interior, US Geological Survey
NSF-Long Term Ecological Research- North Temperate Lakes

Introduction

Physical lake variables, such as ice thickness and thermal structure, are sensitive to changes in climate. and they may act as indicators of climate change (Adrian, et al., 2009). Understanding how lakes respond to climate drivers is of great interest to the scientific and lake management communities. While many lake variables are sensitive to climate change, physical variables (i.e. ice cover and thermal structure) are generally more coherent with climate than chemical or biological variables (Magnuson et al., 2006). Specifically, evidence shows that lake physical variables are sensitive to air temperature and wind speed (Adrian, et al., 2009; Williams & Stefan, 2006). Increases in air temperature can (a) decrease ice cover duration and ice thickness in lakes (Magnuson et al., 2000; Williams & Stefan, 2006), (b) increase epilimnetic temperatures (Robertson & Ragotzkie, 1990), and (c) increase the length of the summer stratification period (Livingstone, 2003). Wind speed has also been established to be very important in lake mixing (Boehrer & Schultze, 2008) and ice formation (Adams, 1976). Variations of those physical variables due to changes of climate in turn affect lake ecosystems (MacKay et al., 2009). For example, changes in water temperature, lake mixing, timing and duration of stratification, and timing of ice cover affect primary production, growth rates of zooplankton, and nutrient supply (MacKay, et al., 2009). Elevated temperatures during the open water season may cause changes to plankton community compositions (Elliot et al., 2005) and changes in fish populations (Carpenter et al., 1992). To better manage lakes, it is crucial to determine how climate change will affect these physical lake variables.

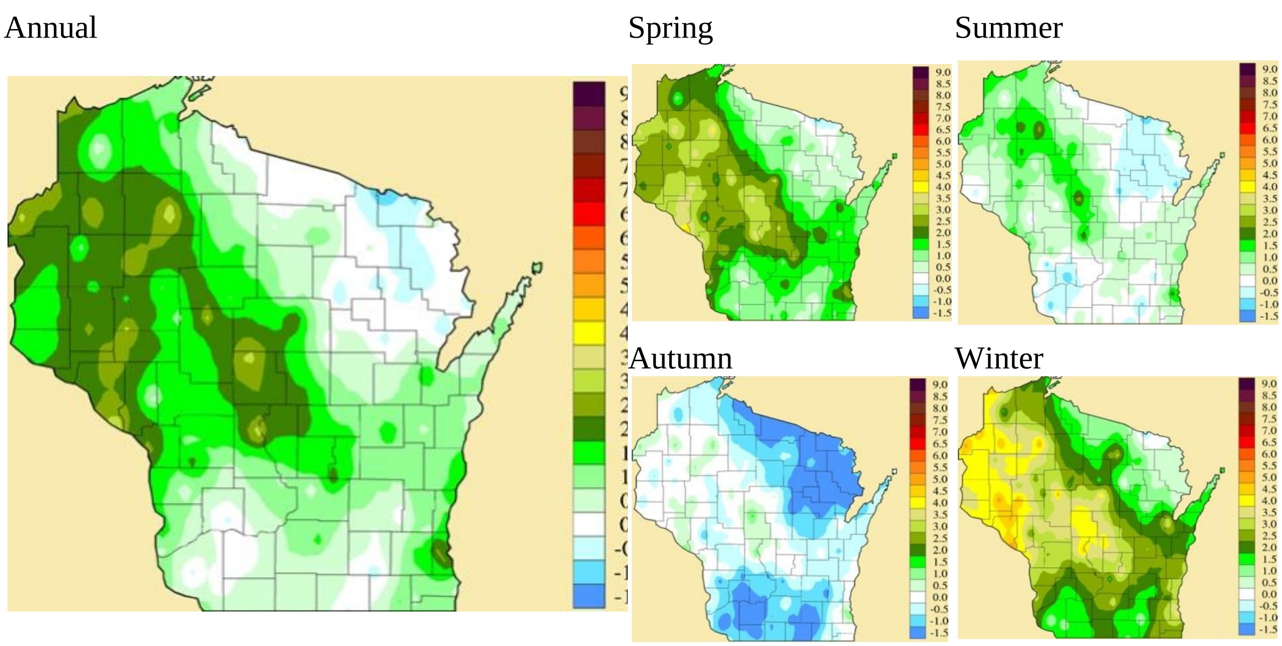

Figure 2 Change in averaged temperature (^{o}F) from 1950 to 2006 from WICCI downscaled data

Evidence shows that over the past 100 years, the global climate has been changing and may continue to change. Global average air temperature has increased by 0.74°C over the last 100 years (IPCC, 2007). Lake-rich regions like the Midwest have seen similar trends in climate change. In Wisconsin, there has been observed a climate warming of 1.1^{o}F averaged across the state. The warming trend shows the greatest warming in the spring (+1.7 ^{o}F across the state) and winter (+2.5 ^{o}F across the state), as shown in Figure 2. Except for northeast Wisconsin, the state appears to be losing the “cold” weather.

Morphometry can impact some of the same physical mechanisms as climate (Adrian et. al. 2009). Previous research has mainly investigated the response of individual lakes and the bulk response of lakes in a geographic region to changing climate (Magnuson et al., 2000). Lake morphometry is known to affect wind fetch, water circulation, and heat storage (Jeffries & Morris, 2007), which can in turn influence ice cover and thermal structure (Brown & Duguay, 2010). Energy for ice growth and decay is determined in part by heat stored in the lake which is mainly affected by the depth, area, and volume of a lake (Williams G. , 1965), and deeper lakes may take longer to freeze as they contain more water that must be cooled (Williams & Stefan, 2006). Larger lake surface area facilitates greater surface heat flux, allowing the lake to adjust to isothermal conditions more quickly (Williams & Stefan, 2006). Lakes with smaller surface areas experience smaller degrees of vertical mixing than those with larger surface area, which may be caused by the significantly large lakes increasing the effects of wind mixing. Differences in vertical mixing caused by surface area may affect the bottom water temperatures especially, as vertical mixing in spring and fall is an important mechanism for transferring heat to the lake bottom. Bathymetric variables, such as lake surface area and mean depth, might account for variability in long term lake responses to climate change. While it is known that morphometry and climate both affect the thermal properties of a lake, previous research has not determined for what variables climate is more dominant than lake morphometry and vice versa.

Additionally, understanding the spatial coherence of climatic drivers (e.g. air temperature and wind) among lake districts is useful in investigating the pattern of lake physical variables (e.g. ice cover and thermal regime) in response to changing climate (Kratz et al. 1998; Benson et al. 2000). Strong coherence pattern in climatic drivers, including the inter-annual and inter-seasonal variation and the long-term trend, may cause a coherent response of lake physical variables that have a profound impact on biological and chemical variables of lake. For example lake ice cover and thermal regime has significance on oxygen distribution, nutrient supply, and biological production (Hondzo and Stefan 1991; King 1997). In addition, lake ice cover can affect lake thermal regime, such as epilimnetic and hypolimnetic temperature, thermocline depth, and duration of stratification during open-water period (Mishra et al. 2011) that has an implication to vertical density variation (Dake and Harleman 1969), oxygen distribution, increase or decrease of the thermal habitat (Magnuson et al. 1990), and fertility and growth rate of fishes (McCauley and Casselman 1981; Coutant 1990). As a result, pattern of lake physical variables influenced by climatic drivers among lake districts is valuable in determining the overall coherent response among different lake districts to the changing climate.

The overall goal of this project consists of three main components. (A) The first is to investigate how long-term changes in three important drivers (air temperature, wind speed, and water clarity) affect ice cover than thermal structure in a dimictic lake during the past century including three selected study periods (1911-1981, 1982-1993, and 1994-2010) as determined by regression analysis to be distinct periods of climate drivers. (B) The second is to investigate the spatial coherence of climate drivers at different time scales: monthly, seasonal, and annual, and determine the temporal coherence of thermal regime and ice cover response between Northern and Southern lakes of Wisconsin for the selected period (1989-2009). In addition, the lake thermal regime and ice cover in response to climate variability (e.g. El Niño and La Niña year) will be investigated. (C)The final component is the investigation of the role of lake morphometry in long-term changes and variability of lake ice cover and thermal structure using the three Southern Wisconsin lakes of Lake Mendota, Fish Lake, and Lake Wingra as our study sites. For all three components of investigation, a newly developed one-dimensional hydrodynamic lake-ice model, DYRESM-I, is validated and employed to run continuously. To determine spatial coherence, the simulations are run continuously from 1989-2010, and for the long-term investigations of climate drivers and lake morphometry, simulations are run from 1910-2010.

Procedures and Methods

Study Lakes

Lakes used in the studies were: Lake Mendota (43°6'N, 89°24'W), Lake Wingra (43°3' N, 89°26' W), Fish Lake (43°17'N, 89°39'W), and Lake Monona (43° 03' N, 89° 21' W) located near Madison, Wisconsin, USA and Trout Lake (46° 01' N, 89° 39' W)located within the Trout Lake Area district in northern Wisconsin. Table 1 summarizes the characteristics of the study lakes.

Table 2 Characteristics of the study lakes.

	Depth (m)		Surface area	Hydrological type[a]		GW[b]	Surface flow		Ice cover duration[1]	Projected ΔT_{air}[d]
	Mean	Max	(ha)	GW[b]	Surface	(%)	Inlet	Outlet	(day)	(°F)
Trout Lake	14.6	35.7	1607.9	GD	DR	35[c]	4	1	135	11.5
Lake Monona	8.2	22.5	1324.0	GD	DR		3	1	105	10.5
Lake Mendota	12.8	25.3	3937.7	GD	DR	~30[d]			119	10.5
Lake Wingra	2.7	6.7	139.6	GFT	DR	35[e]	0	1	120	10.5
Fish Lake	6.6	18.9	87.4	GFT	SE	6[f]	0	0	na	10.5

[a]GD = groundwater discharge; DR = groundwater recharge; GFT = groundwater flowthrough.
[b]GW = percentage groundwater input.
[g]ΔT_{air} = projected change in annual averaged air temperature to the end of century for the A2 scenario from WICCI.
Note: Lake data are from Long Term Ecological Research (LTER) website (http://lter.limnology.wisc.edu/), Webster et al. (1996)[c], Brock et al. (1982)[d], Novitzki and Holmstrom (1979)[e], and Krohelski et al. (2002)[f].

Model Development

An ice model is added to DYRESM-WQ model (Hamilton and Schladow, 1997). The resulting model, DYRESM-I, is validated and employed to simulate vertical distribution of water temperature and ice cover in Lake Mendota. In this model, the lake is represented by a series of Lagrangian horizontal layers with uniform properties that may change in elevation and thickness in response to inflows/outflows and surface mass fluxes (evaporation and precipitation). Layer thickness is updated using an algorithm to give appropriate vertical resolutions at each time step. Mixing in the model is represented by merging the layers that are mixed when the sum of available turbulent kinetic energy (TKE) produced by wind stirring, convective overturn, and shear exceeds the potential energy required to mix the next layer below. Hypolimnetic mixing is modeled with an eddy diffusivity coefficient that is a function of the dissipation of TKE and stratification strength. More detailed descriptions of the simulation of water temperature and mixing can refer to Imberger and Patterson (1981).

In the ice module, heat conduction equations for blue ice, snow ice (white ice) and snow are solved. The ice module is applied when surface water temperature first drops below 0°C, and the initial ice thickness is set to a minimum value of 5 cm. Snow ice is generated in response to flooding, when the mass of snow that can be supported by the ice cover is exceeded. Snow compaction is based on an exponential decay formula, with snow compaction parameters based on air temperature and snowfall/rainfall (Rogers et al. 1995). When ice thickness decreases to less than 5 cm, conduction is discontinued and open water conditions are restored. For brevity, a detailed description of the ice module is not provided here but can refer to Hsieh (2011). Figure 2 illustrates the components in DYRESM-Ice. Heat fluxes between ice or snow and the

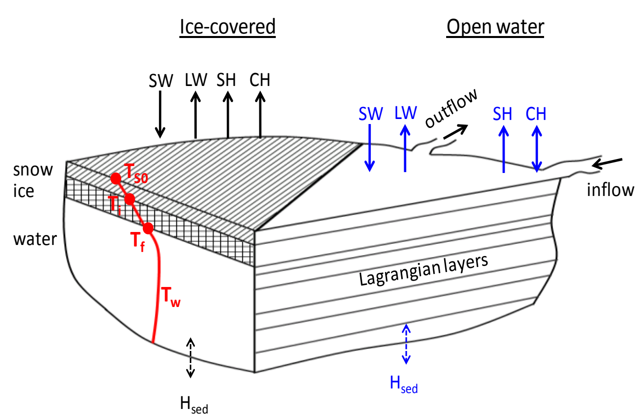

Figure 2: Schematic diagram of the hydrodynamic model. SW: shortwave radiation; LW: longwave radiation; SH: sensible heat flux; CH: conductive heat flux; H_{sed}: sediment heat flux.

atmosphere, ice and water, and bottom sediments and water are calculated to determine water column temperatures beneath the ice and the formation and ablation of ice and snow cover.

Model Calibration

Model validation was conducted by running past climate scenarios in the study lakes. Meteorological data inputs to the model were taken from records at meteorological stations close to the study lakes. Data from Minocqua Dam and Noble F. Lee Municipal Airport at Woodruff represents the climate data for northern lakes. For southern lakes, data from the Dane County Regional Airport are used. These data, taken at various sub-daily intervals, were averaged over the day to provide suitable input for DYRESM-Ice simulations. The data included air temperature, relative humidity, wind speed, total daily shortwave radiation, precipitation, snowfall, and cloud cover. Model performance was evaluated by comparing the simulated results against the measured ice thickness, ice duration, and water temperature values. Figure 3 shows an example of the performance of the model for Lake Mendota.

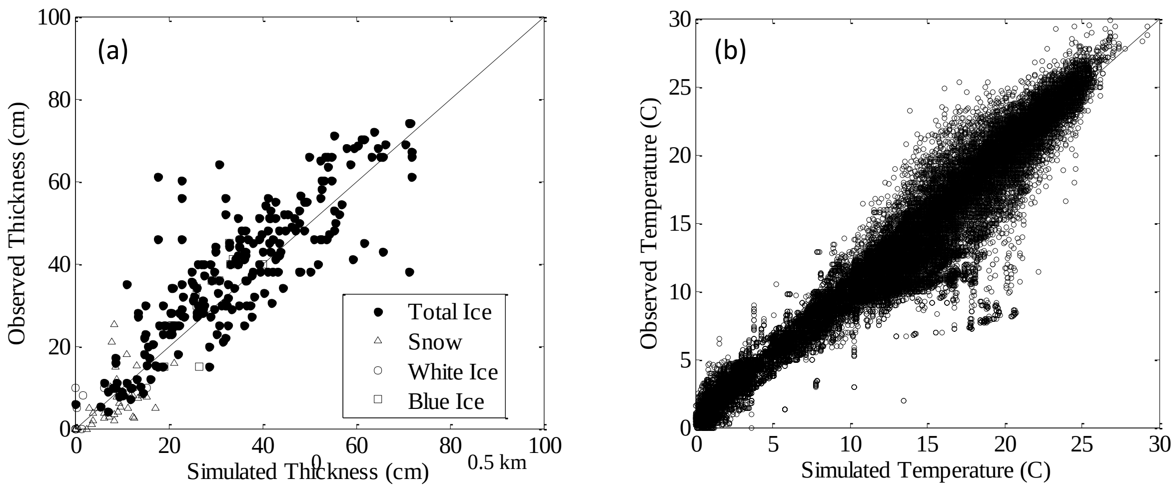

Figure 3: comparison of observed and simulated ice cover and temperature for Lake Mendota

Data Analysis.

For various portions of this project, linear regression is applied to model results and observational data to describe long-term trends and compared to the climate changes. Additionally, Pearson correlation analysis is conducted to investigate how the changes in air temperature and wind speed influence the lake variables. In this analysis, each of the lake drivers is averaged over a fixed period then paired with each of the above-mentioned lake variables from the model results to calculated correlation coefficients. The averaging period for air temperature and wind speed is chosen based on the period that gives the best correlation. Linear regression and Pearson correlation analysis was conducted to determine the coherence between the climate of the northern and southern lake districts and the coherence between the changes in lake variables. Additionally, the Fast Fourier Transform (FFT) procedure was used to determine periodicity or cycles in lake drivers (air temperature and wind speed) and lake variables (ice cover and thermal structure). In this method, the amplitude and the frequency location of the spectral peaks are detected by means of a cubic spline interpolation.

Results and Discussion

Relative importance of lake drivers

Pearson correlation analysis is conducted to investigate how changes in air temperature and wind speed influenced the lake variables (i.e., ice dates, maximum ice thickness, freeze-over water temperature, mid-summer epilimnetic and hypolimnetic temperatures, summer hypolimnetic heating, and dates of stratification onset and fall turnover) and their relative importance for Lake Mendota

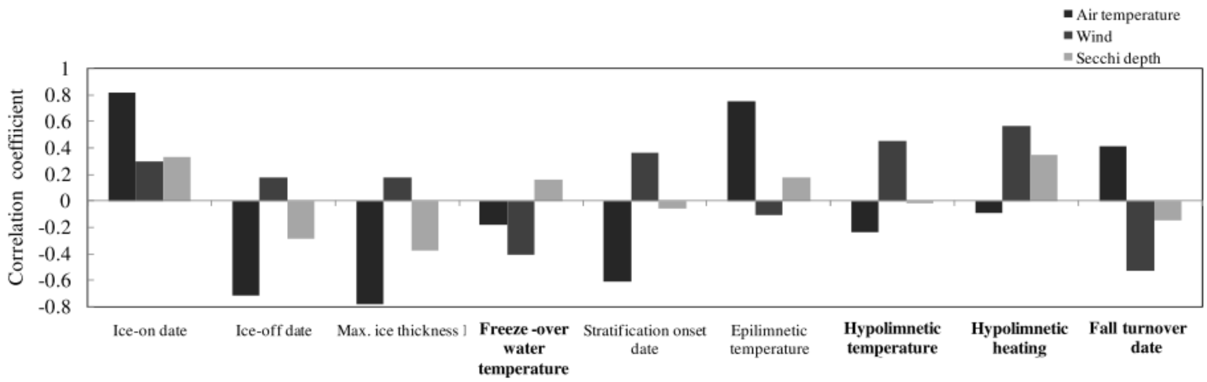

Figure 4: correlation coefficients between lake variables and drivers. Bold font emphasizes variables that are more correlated with wind speed than air temperature. The critical value for significan correlation ($p<0.05$) is 0.194 ($n=99$)

Air temperature, wind speed, and water clarity have been shown to be three important drivers to affect lake ice cover and thermal structure (see Figure 4). Based on the results, air temperature is the most important driver for the ice cover variables (i.e., ice-on and ice-off dates, and maximum ice thickness) and two of the stratification variables (onset of stratification and epilimnetic temperature). Wind speed is the most important driver of freeze-over water temperature, hypolimnetic temperature, hypolimnetic heating, and date of fall turnover. For several of the variables (onset of stratification, hypolimnetic temperature, and fall turnover date), both air temperature and wind speed are dominant drivers. Nevertheless water clarity in this study is found to be a less dominant driver, but can play some role in ice-off date, maximum ice thickness, and hypolimnetic heating.

The date of the onset of stratification is negatively correlated with air temperature and positively correlated with wind speed, indicating that warmer air temperatures and lower wind speeds result in earlier stratification. Austin and Colman (2007) suggested that the declining ice cover combined with higher air temperatures cause the earlier onset of stratification in Lake Superior at a rate of 0.5 day/yr. However, no correlation between ice-off date and the onset of stratification is found for Lake Mendota in this study.

Coherence between northern and southern lakes

(i) Air temperature and wind speed as climatic drivers

Figure 5 shows the coherence of air temperature and wind speed for monthly, seasonal, and inter-annual from 1989 to 2009. A strong spatial coherence ($p<0.05$) of air temperature and different time scales between northern and southern Wisconsin suggests that air temperature is a function of large-scale air masses. In addition, there was also an observed similar pattern of warm and cold years associated with El Niño and La Niña events in northern and southern Wisconsin. The analysis of wind speed coherence indicates that it has a significant coherence at inter-annual level, but has variability of low and strong coherence at monthly and seasonal scale. Depending on the

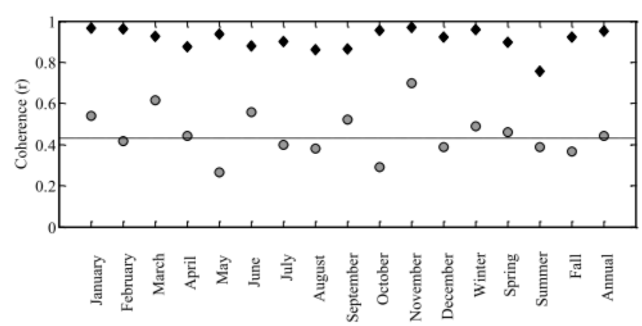

Figure 5: Coherence of annual and seasonal mean air temperature (black filled) and wind speed (gray filled) between lake districts. Dashed line represents the value where strong coherence is defined (0.433 when $p<0.05$).

period of the year where it has low coherence, wind speed acts as a local-scale climate driver that depends on the local topography and varying pressure gradient. In addition, there is a tendency for the coherence of the climatic drivers between northern and southern Wisconsin to be less significant at smaller time-scale (e.g. monthly compared to seasonal) as the variability of the climatic drivers gets larger.

(ii) Spatial coherence of lake physical variables

The computed temporal coherence mean of physical variables of interest from Trout Lake-Lake Monona pair ($\bar{r}$) was 0.43. For ice cover period (freeze date, break-up date, and annual maximum ice thickness) and thermal regime response (epilimnetic temperature, hypolimnetic temperature, onset of stratification date, and fall turnover date), the computed mean of coherence was 0.52 and 0.36, respectively. Figure 6 describes the spatial coherence of seven lake ice cover and thermal regime variables from model simulation result for 21 years. During ice cover period, ice freeze date had a strong coherence (r = 0.75), and ice break-up date had a lower coherence (r = 0.38). Maximum ice thickness annual variation (r = 0.42) had a weaker coherence compared to ice freeze date, but stronger than ice break-up date. For lake thermal regime, coherence was the strongest for epilimnetic temperature (r = 0.80). In the contrary, hypolimnetic temperature was not coherent (r = –0.15). This result was similar to that found by Benson et al. (2000), which the coherence was strong for epilimnetic temperature and it was weak for hypolimnetic temperature between Madison Lake Area and Trout Lake Area. In addition, coherence of water surface temperature was investigated at different temporal scales: monthly, seasonal, and annual. Except for month of January, February, and March and winter season, water surface temperature had a strong coherence (p < 0.05) between Trout Lake and Lake Monona. The grand average of monthly coherence (January – December) was 0.58 and the overall average of seasonal coherence (winter – fall) was 0.62, while the average of annual coherence was 0.69. In addition, the coherence found for onset of stratification date and fall turnover date was low (r = 0.17 and r = 0.29, respectively).

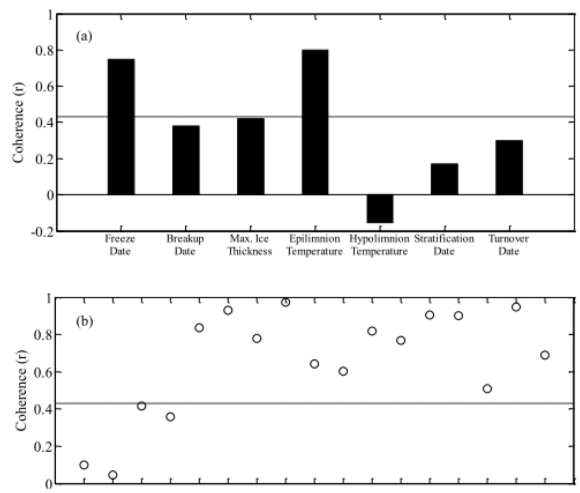

Figure 6: Coherence for seven lake ice cover and thermal regime variables between Trout Lake in northern Wisconsin and Lake Monona in southern Wisconsin (a). Coherence of near surface water temperature for monthly, seasonal, and annual scale (b). Dashed line represents the critical value for significant correlation (p < 0.05)

Effect of lake morphometry on climate change response

(i) Long term trends of variables

Trends for the nine lake variables for each lake during the 100-year study period are given in Table 2. The direction of the trend for each of the three lakes is the same, although the magnitude of the trend can differ greatly among the three lakes. For example, ice on dates in all three lakes have a linear trend of occurring later during the study period; however Lake Mendota and Lake

Wingra have relatively small changes of 7.1 days and 4.4 days, respectively, while Fish Lake has a large change of 20.9 days earlier ice-on per 100 years. Since the early 1900s, the air temperatures near Madison, Wisconsin have increased at a rate of 1.36°C per 100 years, and the wind speeds have decreased at a rate of 0.61 m/s per 100 years. The statistically significant long term trends found in the nine studied lake variables indicate that the changing air temperature and wind speed are influencing these lake variables.

Table 2: trends in lake physical variables for each of the three lakes from 1911-2010

	Lake Mendota	Lake Wingra	Fish Lake
Ice On	7.1 days later	4.4 days later	21.1 days later
Ice Off	9.6 days earlier	15.7 days earlier	14.8 days earlier
Ice Duration	16.7 fewer days	20.1 fewer days	35.9 fewer days
Maximum Ice Thickness	13 cm less	11 cm less	14 cm less
Stratification Onset	11.5 days earlier	N/A	8.1 days earlier
Fall Overturn	11.8 days later	N/A	16.4 days later
Stratification Duration	23.2 more days	N/A	24.5 more days
Summertime Epilimnetic Temperature	0.72°C increase	1.80°C	1.88°C increase
Summertime Hypolimnetic Temperature	0.83°C decrease	N/A	1.20°C decrease

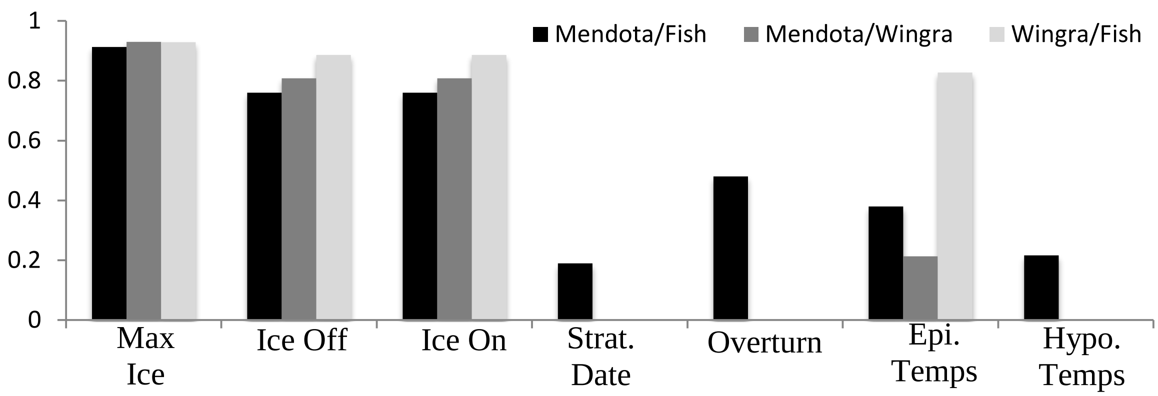

Figure 7: Correlation coefficients for lake groupings. Black is for Lake Mendota and Fish Lake, dark grey is for Lake Mendota and Lake Wingra, and light grey is for Lake Wingra and Fish Lake.

(ii) Variability and coherence among the lakes

While lake variables in all three study lakes have experienced the same direction of change over the past 100 years, the specific value of that change, and variability of the lake changes have differed among the study lakes. Figure 7 shows the correlation coefficient of the lake variables for pairs of study lakes. The pairs are (i) Mendota and Fish Lake, (ii) Lake Mendota and Lake Wingra, and (iii) Lake Wingra and Fish Lake. Ice cover variables (i.e. maximum ice thickness, ice-on date, ice-off date) have high correlation coefficients among the lake variables. Open water season variables (stratification onset, fall overturn, epilimnetic temperatures, and hypolimnetic temperatures) have low correlation coefficients, with the exception of the epilimnetic temperatures of Lake Wingra and Fish Lake. Differences in trends and variability, along with comparisons of correlation coefficients, indicate that differences in lake morphometry may be an important component when determining the response of lake variables to changes in the climate.

(iii) Importance of lake bathymetry under changing climate

The smaller surface area of Fish Lake compared to Lake Mendota likely causes the lake to respond more to changes in climate. Smaller surface lakes tend to gain heat faster in the spring and summer (Boehrer & Schultze, 2008), which likely contributes to the difference in epilimnetic water temperature between the two lakes. Although the main driver to epilimnetic water temperature is air temperature (Boehrer & Schultze, 2008), the larger surface area of Lake Mendota causes a dampening of the heat flux between the epilimnion and the air. Additionally, Fish Lake's smaller surface area allows for the surface of the lake to gain heat faster than for Lake Mendota, causing earlier average stratification onset and less mixing time (Figure 6) for Fish Lake when compared to Lake Mendota, resulting in warmer average hypolimnetic water temperatures in Lake Mendota and cooler average hypolimnetic water temperatures in Fish Lake. Trend in stratification onset dates are larger for Lake Mendota than for Fish Lake. This likely has to do with the effects of decreasing wind speed, which is very important in stratification onset (Hsieh, et al., in press). The larger fetch of Lake Mendota allows the wind to more greatly affect wind mixing in the lake, so a reduction in wind speed likely has a greater effect of stratification onset in the larger Lake Mendota than the smaller Fish Lake. Ice-on dates for Lake Mendota and Fish Lake are very similar, indicating that the differences in surface area do not have as large of an effect on freezing dates.

Comparing Fish Lake and Lake Wingra allows us to investigate the different role that depth plays in a lake's response to the changing climate. A more shallow lake has a smaller amount of heat storage than a deeper lake (Williams, 1965), which allows for shallow lakes to respond more quickly to changes in climate. Lake Wingra does not stratify in the summer months, because it's shallow depth allows wind-induced and heat-transfer-induced mixing throughout the whole depth of the lake. The trend in summer-time epilimnetic water temperatures for both lakes is not statistically different, which may indicate that the depth of the lake is not a major factor in the response of the epilimnion to changes in air temperature. Additionally, Lake Wingra experiences significantly earlier ice-on dates than Fish Lake because the increased depth of Fish Lake results in more heat stored, which takes longer to cool to a freezing temperature.

Conclusion and Recommendations

The one-dimensional hydrodynamic ice model, DYRESM-I, is used to simulate the ice cover and thermal structure of five lakes, Lake Mendota, Lake Wingra, Fish Lake, Lake Monona, and Trout Lake. The model successfully reproduces the variations and trends of ice-cover and thermal structure during this period. Simulated stratification onset dates have occurred earlier, fall overturn has occurred later, and stratification duration has increased for all three study lakes. As a result of earlier stratification dates, summer-time hypolimnion water temperatures have decreased. Additionally, epilimnetic water temperatures have increased due to the trend of increasing air temperatures. Ice-on dates have occurred later, ice-off has been happening earlier, and ice-cover period has decreased for all study lakes during the various study periods. These results agree well with the observed data and previous studies.

Overall, results indicate that of the three lakes, Fish Lake has been more affected by the changing climate over the past 100 years than the other two lakes have. All three study lakes show the same statistically significant trends in lake variables over the past 100 years, corresponding to statistically significant changes in lake drivers over the same period. Analysis of periodicity indicates that the lake drivers and the lake variables generally do not share the same cyclic nature, likely due to how the morphometry and hydrology of the lakes affects the response. Fish Lake, with the smaller surface area, responded more drastically to changes in climate drivers than did Lake Mendota. Additionally, Fish Lake also responded more drastically than did Lake Wingra, which is significantly more shallow. Results indicate that the small, deeper lake is more responsive to changes in the Madison area climate.

Correlation results indicate that air temperatures are the most important drivers of the ice cover variables (ice-on and ice-off dates, and maximum ice thickness) and two stratification variables (date of the onset of stratification and epilimnetic temperatures). Wind speeds are the most important drivers of water temperature when the lake freezes, mid-summer hypolimnetic temperature, summer hypolimnetic heating, and date of fall turnover. Both air temperature and wind speed are dominant drivers of the onset of stratification, hypolimnetic temperature, and fall turnover date. Secchi depth is never the single dominant driver, but in combination with wind speed is important in driving hypolimnetic heating. The wind-dominated variables reveals a regime shift around 1994, which results from the amplified effects of a reduction in wind speed and warming air temperatures.

DYRESM-I has demonstrated the capability in accurately predicting ice cover and water temperature over a continuous 100-year period. To our knowledge, this study presents the first attempt to continuously model both ice cover and thermal structure of a dimictic lake over a period of as long as a century. This type of modeling provides a first step toward projecting the impacts of future climate change on lakes, which can help gain better ideas of how the changing climate will affect lakes. To better understand the full effects of climate change, future modeling incorporating physical/chemical/biological interactions would be crucial and essential (MacKay et al., 2009).

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

Publications:

Hsieh, Y.F., Robertson, D.M., Lathrop, R.C. and Wu, C.H. Influences of air temperature, wind, and water clarity on 100-year trends in ice cover and water temperature in a dimictic lake. *Limnology and Oceanography*. accepted under minor revision

Gunawan, A.A. and Wu, C.H. Coherence pattern of ice cover and thermal regime between Northern and Southern lakes of Wisconsin in response to changing climate. *To be submitted, Limnology and Oceanography*

Magee, M.R. and Wu, C.H. Long-term trends and variability in ice cover and thermal structure in three morphometrically different lakes in response to climate change. *To be submitted, Water Research*

Presentations:

Hsieh, Y.F. and Wu, C.H. Future Scenarios of Water Level and Ice Cover in Two Northern Wisconsin Lakes. Sciences in the Northwoods. Camp Manitowish, Boulder Junction, Wisconsin. 30 September, 2010 *oral presentation*

Magee, M.R. and Wu, C.H. Trends of Ice Cover and Thermal STructure of Three Southern Wisconsin Lakes. National Science Foundation, LTER-NTL Site Review. Trout Lake Station, WI. 8 September, 2011. *poster presentation*

Wu, C.H. and Hsieh, Y.F. Response of Wisconsin Lakes (Ice Cover, Water Level, and Thermal Structure) to Climate Change. WICCI Science Meeting. UW-Sea Grant Institute. 1 September, 2010. *oral presentation.*

Implications of Climate Change and Biofuel Development for Great Lakes Regional Water Quality and Quantity

Basic Information

Title:	Implications of Climate Change and Biofuel Development for Great Lakes Regional Water Quality and Quantity
Project Number:	2010WI253G
Start Date:	9/1/2010
End Date:	8/31/2013
Funding Source:	104G
Congressional District:	WI-002
Research Category:	Climate and Hydrologic Processes
Focus Category:	Models, Water Quality, Water Quantity
Descriptors:	None
Principal Investigators:	Anita Thompson, Bruno Basso, Mike Fienen, David Hyndman, Randall Jackson, K. G. Karthikeyan, Anthony Kendall, Brian J Lepore

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 3/1/2011 - 2/29/2012

Submitted By: Anita Thompson
Submitted: 5/21/2012

Project Title

WR10R008: Implications of Climate Change and Biofuel Development for Great Lakes Regional Water Quality and Quantity

Project Investigators

Anita Thompson, University of Wisconsin-Madison

Progress Statement

Objective 1 - Data Collection and Compilation

Field Data Collection: During Summer and Fall 2011, three additional Equilibrium Tension Lysimeters (ETLs) were installed in the following treatments: hybrid poplar plots (2; within plot duplication) and rotational corn (1). We now have 11 ETLs installed and working. The additional ETL in the rotational corn treatment replicates the ETL previously installed in rotational corn although the two are staggered by one year of rotation. Volumetric soil moisture reflectometers and soil temperature probes were installed at each lysimeter location. Data logger programs for controlling the operation of the ETLs were written and debugged and equipment troubleshooting continued through fall 2011. Lysimeter water samples were collected weekly starting January 1, 2011. Leachate volumes were measured starting January 1, 2011 and leachate samples collected after May 1, 2011 have been analyzed for Nitrate + Nitrite, Ammonia, Total Nitrogen, Total Phosphorus, Dissolved Reactive Phosphorus, pH, EC, and volume. Soil moisture release curves and saturated hydraulic conductivity have been measured for approximately 20 soil cores extracted from a range of depths within the plots. These measurements will be used for the modeling component of the study. Small scale (1m X 1m) surface runoff collection systems were installed during May 2011 in the following treatments: continuous corn (3 replicates), monoculture switch grass (3 replicates), and monoculture Miscanthus (3 replicates). Runoff sample collection started June 1, 2011 and samples were analyzed for Total Nitrogen, Total Phosphorus, Total Dissolved Phosphorus, Dissolved Organic Carbon, Total Sediment, Total Carbon, pH, EC, and volume. All water quality analyses were conducted in the Water Quality Laboratory in the Agricultural Engineering Laboratory Building (Biological Systems Engineering). All sample collection will continue through September, 2013.

GIS Data Collection: We are assembling GIS databases in preparation for building ILHM simulations for Trout River, Black Earth Creek, and Muskegon River watersheds. These include surficial hydrology, subsurface sediment characteristics, basic basemap layers, digital elevation models, SSURGO soil textures, remotely sensed leaf area index (LAI). We have also collected some climate data to drive the models, including NEXRAD hourly precipitation estimates, climate change forecasts (see below), and historical climate reanalyses (also see below). On site weather stations at the Arlington site have been recording local precipitation, temperature, humidity, and solar radiation for more than two years.

Objective 2 - Model Coupling and Development
SALUS Model Development: Construction of Arlington-specific SALUS models has begun, and will be ready in Summer of 2012.

ILHM Model Development: Prior to the start of this project, the research team had an ILHM simulation of the Muskegon River Watershed. We have continued to improve this during the last year, and have incorporated enhancements including: substantial improvement of SSURGO soil hydraulic properties mapping, improved precipitation data inputs, and improved wetlands simulations. These improvements are incorporated in Kendall and Hyndman (in Preparation). Simulations of the Black Earth Creek and Trout River watersheds will be constructed beginning in Fall of 2012.

SALUS-ILHM Coupling: Coupling of SALUS (Systems Approach to Land Use Sustainability) and ILHM (Integrated Landscape Hydrology Model) is following a two-phase approach: 1) initially use SALUS for a representative set of land surface characteristics to derive LAI and root growth values that are input to ILHM (a feed-forward approach), and 2) rewrite the SALUS code from its native Visual Basic to ILHM's language, MATLAB, in a fully-coupled feedback manner. Separating the coupling into two phases was selected in order to provide robust model results more quickly, while the more time-intensive full coupling moves toward completion. Progress on stage 2, the full rewrite coupling, has been steady and is anticipated to be completed during the summer of 2012, with validation and debugging continuing through the Fall of 2012. Stage 1 coupling is also expected to be complete in summer 2012.

Climate Projection Development: During the past year we improved our methods of developing climate forecasts. Improvements include creating continuous daily climate scenarios from 1870-2100 using the 20th Century Version 2 Reanalysis and the 24 models within the CMIP-3 database used by the IPCC AR4. Along with creating continuous scenarios, this gives us the capability to rapidly assess the bias of individual CMIP-3 models relative to the 20thCv2 reanalysis.

Biofuels Land Use Scenario Development: Work done on a related project is yielding insights into a range of adaptive management strategies that may be employed by biofuels agricultural production systems in response to climate changes during the 21st century. These finding will be used along with the originally envisioned regional biofuels production scenarios later in this project.

Objective 3 - Model Validation
Stream Discharge Monitoring: In July of 2011, 3 pressure and temperature transducers were installed in streams in the Yahara River. These are being monitored and downloaded regularly, which stream discharge measurements are collected at regular intervals in order to construct a stage-discharge relationship for each stream gauge station. These will eventually yield over 2 years of detailed stream flow estimates for this watershed.

Groundwater Level Monitoring: In July of 2011, 5 pressure and temperature transducers were installed in wells nearby the Arlington site. The wells are located near a watershed divide

Stream Nutrient Data Collection: Collection of ~100 stream discharge and nutrient samples is anticipated to take place in the Summer of 2012.

Objective 4 - Model Intercomparison
Comparison of SALUS-ILHM and GSFLOW models for the three watersheds is anticipated to begin in Winter of 2012.

Additional
Two project meetings were held during which the P.I.s from the collaborating institutions (University of Wisconsin – Madison, Ball State University, Michigan State University, and the U.S. Geological Survey) discussed project planning, data requirements for the hydrologic models, preliminary field results and data collection, formatting and distribution.

Principal Findings and Significance

Principal Findings and Significance

Description

Significance
The significance of efforts during the past reporting year include: 1) all field equipment required to successfully complete our project was installed, 2) two graduate students were trained in the analytical methods for the required water quality analyses, and 3) one graduate student was trained in the installation and operation of surface monitoring equipment.

Findings
Regional Hydrologic Assessment: Water quantity and quality modeling are currently being performed on watersheds characterized by different hydrological regimes. Differences in the intrinsic physical properties of the study sites imply different groundwater storage and outflow patterns within the watersheds. For instance, the Trout watershed, a groundwater-dominated system has experienced a steady decrease in their annual Q95 streamflow (the natural river flow that is exceeded 95% of the time) values since the mid 80's, with potential impacts on the stream ecology as well as for water management purposes. Such behavior contrasts at the Black Earth watershed, where Q95 values have followed the opposite behavior, even within a longer term perspective. In turn, the concentration and fate of nutrient and pollutants during the driest period of the year may strongly differ according to the observed regime of each watershed.

Furthermore, in order to separate the effects from changes in land use to climate variability and anomaly events (eg. Pacifical Decadal Oscillation, ENSO) that affect the hydrological regime in the Great Lakes region, a set of seven natural watersheds (unaffected by artificial diversions, storage, or other works of man in or on the natural stream channels or in the watershed) located in Michigan and Wisconsin were selected from the Hydro-Climatic Data Network. The beginning of the observations in those watersheds ranges from 1899 to 1967). Additionally, groundwater recharge using the ILHM-SALUS models will be validated with the support of the Active Groundwater Level Network composed of 53 continuous wells in Wisconsin and Michigan. Currently, the data is being pre-processed and converted to the model input format

Soils and Agricultural Water Use: More than any other land use type, agricultural uses were highly sensitive to soil textural variability in a simulation study of the Muskegon River Watershed [Kendall and Hyndman, in Prep.]. Agricultural land uses in finer textured soils allowed less groundwater recharge and had higher evapotranspiration than forest or grassland types, while the reverse was true in coarse sandy textured areas. This finding highlights the need to explicitly simulate plant growth in response to variable soil conditions, and not to rely on fixed functional behavior as is typically done with land surface modeling.

Journal Articles & Other Publications

Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Simulating Spatial and Temporal Variability of Regional Evapotranspiration and Groundwater Recharge: Influences of Land Use, Soils, and Lake-Effect Climate
Author(s)	Kendall and Hyndman
Publication/Publisher	Advances in Water Resources
Year Published	
Volume & Number	
Number of Pages	
Description	In Preparation
Any Additional Citation Information	

Other Project Support

Source	USDA-NIFA Hatch
Dollar Value	$270,983
Description	Linking Cropping System Diversity with Nutrient Loss Dynamics in Alternative Biofuel Production Systems
Start Date	10/1/2009
End Date	9/30/2013

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Source	Wisconsin Groundwater Coordinating Council/UW Water Resources Institute
Dollar Value	$104,695
Description	Groundwater Recharge Characteristics and Subsurface Nutrient Dynamics Under Alternate Biofuel Cropping Systems in Wisconsin
Start Date	7/1/2010
End Date	6/30/2012

Students & Post-Docs Supported

Student Name	Anthony Kendall
Campus	Other

Advisor Name	David Hyndman
Advisor Campus	Other

Degree	Post Doc
Graduation Month	
Graduation Year	
Department	Geological Sciences
Program	
Thesis Title	
Thesis Abstract	

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Student Name	Damodhar Mailapalli
Campus	University of Wisconsin-Madison

Advisor Name	Anita Thompson
Advisor Campus	University of Wisconsin-Madison

Degree	Post Doc
Graduation Month	
Graduation Year	
Department	Biological Systems Engineering
Program	
Thesis Title	
Thesis Abstract	

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Student Name	Michael Polich
Campus	University of Wisconsin-Madison

Advisor Name	Anita Thompson
Advisor Campus	University of Wisconsin-Madison

Degree	Expected Masters
Graduation Month	
Graduation Year	
Department	Biological Systems Engineering
Program	
Thesis Title	
Thesis Abstract	

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Student Name	Ryan Stenjem
Campus	University of Wisconsin-Madison

Advisor Name	Anita Thompson
Advisor Campus	University of Wisconsin-Madison

Degree	Expected Masters
Graduation Month	
Graduation Year	
Department	Biological Systems Engineering
Program	Biological Systems Engineering
Thesis Title	
Thesis Abstract	

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Student Name	Zach Zopp
Campus	University of Wisconsin-Madison

Advisor Name	Anita Thompson
Advisor Campus	University of Wisconsin-Madison

Degree	Other
Graduation Month	
Graduation Year	
Department	Biological Systems Engineering
Program	
Thesis Title	
Thesis Abstract	

Undergraduate Students Supported

New Students: **4**
Continuing Students: **1**

Groundwater Research Characteristics and Subsurface Nutrient Dynamics Under Alternate Biofuel Cropping Systems in Wisconsin

Basic Information

Title:	Groundwater Research Characteristics and Subsurface Nutrient Dynamics Under Alternate Biofuel Cropping Systems in Wisconsin
Project Number:	2010WI282O
Start Date:	7/1/2010
End Date:	6/30/2012
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Nutrients, Agriculture, Groundwater
Descriptors:	
Principal Investigators:	Anita Thompson, Randall Jackson, K. G. Karthikeyan

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 7/1/2010 - 6/30/2011

Submitted By: Anita Thompson
Submitted: 9/29/2011

Project Title

WR10R003: Groundwater Recharge Characteristics and Subsurface Nutrient Dynamics Under Alternate Biofuel Cropping Systems in Wisconsin

Project Investigators

Randall Jackson, University of Wisconsin-Madison
K.G. Karthikeyan, University of Wisconsin-Madison
Anita Thompson, University of Wisconsin-Madison

Progress Statement

This 2 year project was initiated July 1, 2010. The field component of this project is being conducted in Great Lakes Bioenergy Research Center (GLBRC) biofuel cropping system plots located at the Arlington Agricultural Research Station (AARS), Arlington, WI. A randomized complete block design experiment with 8 cropping system treatments planted in 5 replicated blocks was established Spring, 2008. During the first year of the project (July 1, 2010 – June 30, 2011), progress was made in the installation of instrumentation to monitor subsurface water and nutrient dynamics in 4 of the biofuel cropping system treatments in the GLBRC biofuel plots. A detailed topographic survey of the area comprising all 5 treatment blocks was conducted. Instrumentation was purchased and eight subsurface Equilibrium Tension Lysimeters (ETLs) were installed during October and November 2010 in the following treatments: continuous corn (3; between and within plot duplication), corn-soybean-canola rotation (1), monoculture switch grass (3; between and within plot duplication), and monoculture Miscanthus (1). Volumetric soil moisture reflectometers and soil temperature probes were installed at each lysimeter location. Data logger programs for controlling the operation of the ETLs were written and debugged and equipment troubleshooting continued through spring 2011. Lysimeter water samples were collected weekly starting January 1, 2011. Leachate volumes were measured starting January 1, 2011 and leachate samples collected after May 1, 2011 have been analyzed for Nitrate + Nitrite, Ammonia, Total Nitrogen, Total Phosphorus, Dissolved Reactive Phosphorus, pH, EC, and volume. Small scale (1m X 1m) surface runoff collection systems were installed during May 2011 in the following treatments: continuous corn (3 replicates), monoculture switch grass (3 replicates), and monoculture Miscanthus (3 replicates). Runoff sample collection started June 1, 2011 and samples were analyzed for Total Nitrogen, Total Phosphorus, Total Dissolved Phosphorus, Dissolved Organic Carbon, Total Sediment, Total Carbon, pH, EC, and volume. All water quality analyses were conducted in the Water Quality Laboratory in the Agricultural Engineering Laboratory Building (Biological Systems Engineering). All sample collection will continue through June, 2012.

Plant community richness and composition were measured using the point-intercept method in monoculture switchgrass treatments at the GLBRC site. All species present at each point were counted, with each species counted only once per point providing a percent species cover. Six 1.5m x 1.5m quadrats were measured in each treatment plot at the GLBRC site, with three of these quadrats located in a fertilized and three in an unfertilized section of the treatment plot. Three replications of each treatment were measured for a total of 9 quadrats per crop/fertilizer treatment. Measurements were done once in June 2011. Additionally, soil nitrous oxide emissions were measured bi-weekly from May 2011- June 2011 in each quadrat using a closed trace gas flux chamber method. Three soil samples at each of depths 0-20cm, 20-50cm, and 50-80cm were taken from each quadrat every 4-5 weeks from May 2011-June 2011. These samples will be tested for inorganic nitrogen concentrations as well as rates of mineralization.

Data from our study will be used to calibrate and test the APEX and ILHM models. Four meetings (via Skype) were held with the developers (Michigan State University) of ILHM to discuss data requirements for the hydrologic models and data collection, formatting and distribution.

Principal Findings and Significance

Principal Findings and Significance

Description	The significance of efforts during the past reporting year include: 1) the majority of field equipment required to successfully complete our project was installed, trouble-shot and debugged and 2) graduate students were trained in the installation and operation of surface and subsurface water and nutrient dynamics monitoring equipment and in the required laboratory analytical methods.

Other Project Support

Source	USGS-NIWR
Dollar Value	$247,563
Description	Implications of climate change and biofuel development for Great Lakes Regional water quality and quantity
Start Date	9/1/2010
End Date	8/31/2013

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Source	USDA-NIFA Hatch
Dollar Value	$207,656
Description	Sustainability of alternative biofuel production systems
Start Date	10/1/2010
End Date	9/30/2013

Students & Post-Docs Supported

Student Name	Jack Buchanan
Campus	University of Wisconsin-Madison
Advisor Name	Anita Thompson
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month	
Graduation Year	
Department	
Program	Agroecology
Thesis Title	
Thesis Abstract	

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Student Name	Brianna Laube
Campus	University of Wisconsin-Madison
Advisor Name	Chris Kucharik
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month	
Graduation Year	
Department	The Nelson Institute for Environmental Studies

Program	Environment and Resources
Thesis Title	
Thesis Abstract	

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Student Name	Damodhar Mailapalli
Campus	University of Wisconsin-Madison
Advisor Name	Anita Thompson
Advisor Campus	University of Wisconsin-Madison
Degree	Post Doc
Graduation Month	
Graduation Year	
Department	Biological Systems Engineering
Program	
Thesis Title	
Thesis Abstract	

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Student Name	Ryan Stenjem
Campus	University of Wisconsin-Madison
Advisor Name	Anita Thompson
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month	
Graduation Year	
Department	Biological Systems Engineering
Program	
Thesis Title	
Thesis Abstract	

Undergraduate Students Supported

Continuing Students: **2**

Reducing Nitrate in Groundwater with Slow-Release Fertilizer

Basic Information

Title:	Reducing Nitrate in Groundwater with Slow-Release Fertilizer
Project Number:	2010WI283O
Start Date:	7/1/2010
End Date:	6/30/2012
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Agriculture, Nitrate Contamination, Management and Planning
Descriptors:	
Principal Investigators:	, Birl Lowery

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 7/1/2010 - 6/30/2011

Submitted By: Matt Ruark
Submitted: 10/23/2011

Project Title

WR10R004: Reducing Nitrate in Groundwater with Slow-Release Fertilizer

Project Investigators

Meghan Buckley, University of Wisconsin-Stevens Point
Birl Lowery, University of Wisconsin-Madison
Matthew Ruark, University of Wisconsin-Madison

Progress Statement

For the project titled, "Reducing nitrate in groundwater with slow-release fertilizer," substantial progress has been made for the reporting period of 7/1/2010 to 6/30/2010. The field project was successfully established at the Hancock Agricultural Research Station, near Hancock, WI. Potatoes were planted and groundwater monitoring wells were installed. Groundwater samples were collected weekly during the potato growing season and monthly during the fallow season. Samples have been analyzed for nitrate, ammonium, and organic nitrogen concentration and have been appropriately archived. Bromide and chloride were applied to the plots and used a tracers to indicate direction of groundwater flow and potential for plot-to-plot contamination. Results have been reported at two state-level meetings during this period.

Principal Findings and Significance

Principal Findings and Significance

Description

The overall objective of this study was to evaluate nitrate leaching in potato production systems under different nitrogen (N) management practices and to develop a partial N budget for potato production systems with and without use of N fertilizer technologies. An additional objective was to produce updated nutrient management recommendations to the potato industry.

Large field plots (15 x 15 m) were established in potato production. Results from the 2010 growing season suggest that use of controlled-release fertilizer (specifically a polymer coated urea product named Environmentally Smart Nitrogen, or ESN) slightly increased yields and increased N uptake at the same fertilizer rate (280 kg ha-1 of N) as conventional fertilizer (ammonium sulfate and ammonium nitrate, or ASAN). In addition, lower rates of ESN (225 kg ha-1) resulted in similar yields to the higher rates of N sources. This suggests that the one-time application of ESN can maintain or increase yields of potato and increase the nitrogen use efficiency.

Nitrate concentrations in groundwater below each N fertilizer treatment (280 kg ha-1 of ESN, 225 kg ha-1 of ESN, and 280 kg ha-1 of ASAN) indicates that groundwater nitrate trends were different among the treatments. Use of ESN typically resulted in lower average nitrate concentrations, especially later in the growing season, as the ASAN would have been more likely to leached out of the surface horizons. While average nitrate concentrations (an average from three wells per plot and three replications, nine wells in total) were noticeably lower for the ESN treatments compared to the ASAN treatments, these values were not statistically significantly different. There is a large amount of variation around the mean for groundwater concentrations over time, making conclusive statements about treatment differences difficult. A different approach to statistical analysis has been conducted and determined significant differences between the ASAN treatement and the ESN treatments. However, the difference in the average nitrate concentration, when averaged over time, between ASAN and ESN was between 1 and 2 mg L-1.

These results have been presented to the Wisconsin Potato and Vegetable Growers Association. Growers would be willing to adopt ESN as their sole N source, but are asking for multiple years worth of data before taking on the additional costs associated with the ESN product.

Presentations & Public Appearances

Title	Slow-release fertilizer effect on groundwater nitrogen concentration in sandy soils under potato production
Presenter(s)	Nick Bero, Matt Ruark, Birl Lowery
Presentation Type	Seminar
Event Name	American Water Resources Association
Event Location	Green Bay, WI
Event Date	3/4/2011
Target Audience	Scientific audience
Audience Size	50
Description	Presentation to the Annual Wisconsin meeting of the American Water Resources Association. The audience was a mix between scientists and government agency representatives. Results from the 2010 growing season were presented.

Title	Slow-release fertilizer effect on groundwater nitrogen concentration in sandy soils under potato production
Presenter(s)	Nick Bero, Matt Ruark, Birl Lowery
Presentation Type	Seminar
Event Name	2011 Annual Wisconsin Potato Meetings
Event Location	Stevens Point, WI
Event Date	2/1/2011
Target Audience	Regional organization
Audience Size	65
Description	Oral presentation to the Wisconsin Potato and Vegetable Growers Association. The audience was primarily potato growers who would use this information to guide their decision making for fertilizer use. The reception was generally positive and the growers look forward to future research in this area.

Students & Post-Docs Supported

Student Name	Nick Bero
Campus	University of Wisconsin-Madison
Advisor Name	Matt Ruark
Advisor Campus	University of Wisconsin-Madison
Degree	Masters
Graduation Month	May
Graduation Year	2012
Department	Soil Science
Program	Soil Science
Thesis Title	
Thesis Abstract	

Influence of Adsorbed Antibiotics on Water Quality and Soil Microbes

Basic Information

Title:	Influence of Adsorbed Antibiotics on Water Quality and Soil Microbes
Project Number:	2010WI285O
Start Date:	7/1/2010
End Date:	6/30/2012
Funding Source:	Other
Congressional District:	WI 2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Quantity, Geochemical Processes, Sediments
Descriptors:	
Principal Investigators:	Zhaohui Li

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 7/1/2010 - 6/30/2011

Submitted By: Zhaohui Li
Submitted: 9/27/2011

Project Title

WR10R006: Influence of Adsorbed Antibiotics on Water Quality and Soil Microbes

Project Investigators

Zhaohui Li, University of Wisconsin-Parkside
Maria MacWilliams, University of Wisconsin-Parkside

Progress Statement

The goal of this research is to investigate the influence of adsorbed antibiotics on water quality and soil microbes. To achieve this central goal, we conducted the following experiments.
1. Determined the desorption kinetics of tetracycline (TC) and ciprofloxacin (CIP) from external surfaces of nonswelling clays or from the interlayer of swelling clays at different loading levels and their effect on water quality.
2. Determined the desorption of TC and CIP form the clays under different pH conditions.
3. Determined the influence of the presence of different types of cations on the desorption of TC and CIP.
4. Determined the soil microbes develop long term resistance towards clay bound antibiotics? If so what are the genes that contribute to the elevated resistance to clay-bound antibiotics?
5. Determined the antimicrobial activity of TC and CIP bond to external surfaces of kaolinite and in the interlayer spaces of montmorillonite against TC sensitive and TC resistant strains.

Principal Findings and Significance

Principal Findings and Significance

Description

Batch results showed that the higher the charge of the cations, the higher the amount of adsorbed TC and CIP desorbed. Thus, the TC and CIP desorption followed the sequence of $Al^{3+} > Ca^{2+} > Na^{+}$. Also, organic cations such as hexadecyltrimethylammonium (HDTMA), had higher affinity for the clay surfaces, thus, can desorb more adsorbed TC and CIP. Higher solution pH resulted in more TC and CIP desorption. When TC was bound to the external surfaces of kaolinite, slightly loss of it antimicrobial activity was noticed. On the contrary, significant sequestration of TC's antimicrobial activity was noticed when bound to montmorillonite in the interlayer position. On the other hand, TC gradient plate screens did not reveal the clay-exposed cultures to be any more resistant than the unexposed control culture.

Conclusions: The antibiotic activity of TC and CIP decreased slightly in the presence of kaolinite, but significantly in the presence of montmorillonite. The results may suggest that the antibiotics adsorbed on soils may not result in detrimental effect on environmental bacteria population.

Future tests:
1. Continue on microbial activity test for TC and CIP in the presence of real soil.
2. Will start tests on transport of bacteria through TC- and CIP-loaded columns.
3. Comparison of column results with batch results.
4. Continue investigating the likelihood of increased resistance in the presence of adsorbed antibiotics on a longer time frame.

Awards, Honors & Recognition

Title	Removal of tetracycline by kaolinite
Event Year	2010
Recipient	Caren J. Ackley
Presented By	AWRA WI section
Description	Three students Caren J. Ackley, Laura Schulz, and Nancy Fenske received the undergradduate best poster award

Title	Adsorption of tetracycline by kaolinite
Event Year	2010
Recipient	Laura Schulz
Presented By	Geologic Society of American North Central section
Description	

Journal Articles & Other Publications

Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Adsorption and intercalation of ciprofloxacin on montmorillonite
Author(s)	Wu, Q., Li, Z., Hong, H., Yin, K., Tie, L.
Publication/Publisher	Appl. Clay Sci.
Year Published	2010
Volume & Number	50
Number of Pages	204-211
Description	
Any Additional Citation Information	

Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Cation exchange interaction between antibiotic ciprofloxacin and montmorillonite
Author(s)	Wang, C.-J., Li, Z., Jiang, W.-T., Jean, J.-S., Liu, C.-C.
Publication/Publisher	J. Hazard. Mater.
Year Published	2010
Volume & Number	183
Number of Pages	309-314
Description	
Any Additional Citation Information	

Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Mechanism of tetracycline adsorption on kaolinite with pH-dependent surface charges
Author(s)	Li, Z., Schulz, L., Ackley, C., Fenske, N.
Publication/Publisher	J. Colloid Interface Sci.

Year Published	2010
Volume & Number	351
Number of Pages	254-260
Description	
Any Additional Citation Information	

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Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Interaction between tetracycline and smectite in aqueous solution
Author(s)	Li, Z., Chang, P.-H., Jean, J.-S., Jiang, W.-T., Wang, C.-J.
Publication/Publisher	J. Colloid Interface Sci.
Year Published	2010
Volume & Number	341
Number of Pages	311-319
Description	
Any Additional Citation Information	

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Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Sorption and Intercalation of Tetracycline by Swelling Clays
Author(s)	Chang, P.-H., Li, Z., Jiang, W.-T., Jean, J.-S.
Publication/Publisher	Appl. Clay Sci.
Year Published	2009
Volume & Number	47
Number of Pages	27-36
Description	
Any Additional Citation Information	

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Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Sorptive Removal of Tetracycline from Water by Palygorskite
Author(s)	Chang, P.-H., Li, Z., Yu, T.-L., Munkhbayer, S., Kuo, T.-H., Hung, Y.-C., Jean, J.-S., Lin, K-H
Publication/Publisher	J. Hazard. Mater
Year Published	2009
Volume & Number	165
Number of Pages	148-155
Description	
Any Additional Citation Information	

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Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	FTIR and XRD investigations of tetracycline intercalation in smectites
Author(s)	Li, Z., Kolb, V. M., Jiang, W.-T., Hong, H.
Publication/Publisher	Clays Clay Miner.

Year Published	2010
Volume & Number	58
Number of Pages	462-474
Description	
Any Additional Citation Information	

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Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Adsorption of ciprofloxacin on 2:1 dioctahedral clay minerals
Author(s)	Wang, C.-J., Li, Z., Jiang, W.-T.
Publication/Publisher	Appl. Clay. Sci.
Year Published	2010
Volume & Number	53
Number of Pages	723-728
Description	Published in 2011
Any Additional Citation Information	

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Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	A mechanistic study of ciprofloxacin removal by kaolinite
Author(s)	Li, Z., Hong, H., Liao, L., Ackley, C. J., Schulz, L. A., MacDonald, R. A., Mihelich, A. L., Emard, S. M.
Publication/Publisher	Colloids Surf. B.
Year Published	2010
Volume & Number	88
Number of Pages	339-344
Description	Published in 2011.
Any Additional Citation Information	

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Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Mechanism of Tetracycline Sorption on Rectorite
Author(s)	Chang, P.-H., Jean, J.-S., Jiang, W.-T., Li, Z.
Publication/Publisher	Colloids Surf. A: Physicochemical and Engineering Aspects
Year Published	2009
Volume & Number	339
Number of Pages	94-99
Description	
Any Additional Citation Information	

Presentations & Public Appearances

Title	Removal of Tetryclcine using kaolinite
Presenter(s)	Caren Ackley, Laura Schulz, Nancy Fenske, Zhaohui Li
Presentation Type	Poster session

Event Name	ARWA WI annual meeting
Event Location	Middleton, WI
Event Date	3/5/2010
Target Audience	Scientific audience
Audience Size	200
Description	

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Title	Adsorption of tetracycline by kaolinite
Presenter(s)	Laura Schulz, Caren Ackley, Nancy Fenske, Zhaohui Li
Presentation Type	Poster session
Event Name	Geologic SOciety of America North Central annual meeting
Event Location	Branson, MO
Event Date	4/2/2010
Target Audience	Scientific audience
Audience Size	300
Description	

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Title	Removal of ciprofloxacin by kaolinite
Presenter(s)	MacDonald, R. A., Schulz, L. A., Ackley, C. J., Fenske, N., Mihelich, A. L., Emard, S. M. , Li, Z.
Presentation Type	Poster session
Event Name	WI system Undergraduate symposium
Event Location	River falls, WI
Event Date	4/30/2010
Target Audience	University students
Audience Size	300
Description	

Students & Post-Docs Supported

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

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Student Name	Lisa Elliott
Campus	University of Wisconsin-Parkside

Advisor Name	Maria MacWilliams
Advisor Campus	University of Wisconsin-Parkside

Degree	Undergraduate
Graduation Month	May
Graduation Year	2011
Department	Biological Sciences
Program	
Thesis Title	
Thesis Abstract	

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Student Name	Andrea Gleason
Campus	University of Wisconsin-Parkside

Advisor Name	Maria MacWilliams
Advisor Campus	University of Wisconsin-Parkside

Degree	Undergraduate
Graduation Month	December
Graduation Year	2010
Department	Biological Sciences
Program	
Thesis Title	
Thesis Abstract	

.....

Student Name	Renee Hanson
Campus	University of Wisconsin-Parkside

Advisor Name	Zhaohui Li
Advisor Campus	University of Wisconsin-Parkside

Degree	Undergraduate
Graduation Month	May
Graduation Year	2012
Department	Geosciences
Program	Environmental Geosciences
Thesis Title	
Thesis Abstract	

.....

Student Name	Sam Leick
Campus	University of Wisconsin-Parkside

Advisor Name	Zhaohui Li
Advisor Campus	University of Wisconsin-Parkside

Degree	Undergraduate
Graduation Month	May

Graduation Year	2012
Department	Geosciences
Program	Environmental Geosciences
Thesis Title	
Thesis Abstract	

.....

Student Name	Subha Mathew
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Advisor Name	
Advisor Campus	University of Wisconsin-Parkside
Degree	Undergraduate
Graduation Month	
Graduation Year	
Department	
Program	
Thesis Title	
Thesis Abstract	

.....

Student Name	Monica Schmidt
Campus	University of Wisconsin-Parkside
Advisor Name	Maria MacWilliams
Advisor Campus	University of Wisconsin-Parkside
Degree	Undergraduate
Graduation Month	May
Graduation Year	2011
Department	Biological Sciences
Program	with Honor
Thesis Title	
Thesis Abstract	

Undergraduate Students Supported

New Students: **3**

Transport of Manure-Derived, Tetracycline Resistant Escherichia Coli in Unsaturated Soil

Basic Information

Title:	Transport of Manure-Derived, Tetracycline Resistant Escherichia Coli in Unsaturated Soil
Project Number:	2010WI286O
Start Date:	7/1/2010
End Date:	6/30/2012
Funding Source:	Other
Congressional District:	WI 4th
Research Category:	Not Applicable
Focus Category:	Solute Transport, Sediments, Agriculture
Descriptors:	
Principal Investigators:	, Shangping Xu

Publication

1. Walczak JJ, SL Bardy, L Feriancikova, S Xu (In Press) Comparison of the Transport of Tetracycline-Resistant and Tetracycline-Susceptible Escherichia coli Isolated from Lake Michigan. Water, Air and Soil Pollution

Annual Progress Report

Selected Reporting Period: 7/1/2010 - 6/30/2011

Submitted By: Shangping Xu
Submitted: 11/16/2011

Project Title

WR10R007: Transport of Manure-Derived, Tetracycline Resistant Escherichia Coli in Unsaturated Soil

Project Investigators

Shangping Xu, University of Wisconsin-Milwaukee

Progress Statement

As planned, during last year, my group has performed column transport experiments to examine the transport of tetracycline-susceptible and tetracycline-resistant E. coli (manure-derived) within unsaturated soil. Particularly, we have examined the effects of soil moisture and water chemistry on their transport behavior under unsaturated conditions. We found that the mobility of the bacterial cells tends to be lower under low moisture content and high ionic strength conditions.

Principal Findings and Significance

Principal Findings and Significance

Description	Based on our findings to date, we are continuing the investigation on the release of previously immobilized bacterial cells within unsaturated soil zone due to chemical or flow perturbations. The information will provide valuable insight into the transport of antibiotic resistant bacteria within the unsaturated soil zone, a key step in their leaching into the underlying groundwater system. We hope that the improved understanding on the transport of manure-derived antibiotic resistant bacteria within the unsaturated soil will lead to improved manure management practices and the reduction in the risks of public health associated with groundwater microbial contamination.

Journal Articles & Other Publications

Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Comparison of the Transport of Tetracycline-Resistant and Tetracycline-Susceptible Escherichia coli Isolated from Lake Michigan
Author(s)	Jacob J. Walczak, Sonia L. Bardy, Lucia Feriancikova, Shangping Xu
Publication/Publisher	Water, Air and Soil Pollution/Springer
Year Published	In Press
Volume & Number	
Number of Pages	
Description	My group reported that tetracycline could enhance the mobility of manure-derived E. coli within saturated porous media (Walczak et al., 2011). It was also shown, however, that E. coli from various sources could display marked variation in their mobility (Bolster et al., 2009). The focus of this research was to examine if the observed difference in the mobility of manure-derived tetracycline-resistant (tetR) and tetracycline-susceptible (tetS) E. coli strains was source dependent.

Specifically, E. coli were isolated from Lake Michigan and the influence of tetracycline resistance on Lake Michigan-derived E. coli was investigated through column transport experiments. Our experimental results showed that, consistent with previous observations, the deposition rate coefficients of the tetR E. coli strain was ~20%-100% higher than those of the tetS E. coli strain.

Any Additional Citation Information

Students & Post-Docs Supported

Student Name	Lucia Feriancikova
Campus	University of Wisconsin-Milwaukee
Advisor Name	Shangping Xu
Advisor Campus	University of Wisconsin-Milwaukee
Degree	PhD
Graduation Month	
Graduation Year	
Department	Geosciences
Program	Hydrogeology
Thesis Title	N/A
Thesis Abstract	N/A

Groundwater Nitrate Processing in Deep Stream Sediments

Basic Information

Title:	Groundwater Nitrate Processing in Deep Stream Sediments
Project Number:	2010WI287O
Start Date:	7/1/2010
End Date:	6/30/2012
Funding Source:	Other
Congressional District:	WI 6th
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Nitrate Contamination, Sediments
Descriptors:	
Principal Investigators:	Robert Scott Stelzer

Publication

1. Stelzer RS, and LA Bartsch. 2012. Nitrate removal in deep sediments of a nitrogen-rich river network: a test of a conceptual model. Journal of Geophysical Research- Biogeosciences, In Press.

WR10R005: Groundwater nitrate processing in deep stream sediments

11 October 2011

Principal Investigator- **Dr. Robert S. Stelzer**, Associate Professor, Department of Biology and Microbiology, University of Wisconsin Oshkosh

Co-Principal Investigator- **Mr. Lynn Bartsch**, Research Fishery Biologist United States Geological Survey, Upper Midwest Environmental Sciences Center

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PROJECT SUMMARY

Title: Groundwater nitrate processing in deep stream sediments
Project I.D. WR10R005
Investigators: Principal Investigator- **Dr. Robert S. Stelzer**, Associate Professor, Department of Biology and Microbiology, University of Wisconsin Oshkosh, Oshkosh, WI
Co-Principal Investigator-**Mr. Lynn Bartsch,** Research Fishery Biologist United States Geological Survey, Upper Midwest Environmental Sciences Center La Crosse, WI 54603

Period of Contract: 7/1/2010 - 6/30/2011

Background/need: Elevated nitrate concentration in ground water is a pressing environmental problem in many regions of the world, including Wisconsin (Browne et al. 2008, Rupert 2008, Saad 2008). The nitrate concentration of ground water in many areas of the Central Sand Ridges Ecoregion of Wisconsin exceeds the recommended limit for drinking water (10 mg NO_3-N L^{-1}) set by the Environmental Protection Agency. Current federal policy mandating the use of biofuels (e.g. ethanol produced from corn) and world demands for food may lead to further increases in nitrate concentrations and loads in groundwater. Identification of hot spots of nitrogen processing will improve the ability of scientists to predict nitrogen retention and loss from watersheds and will aid land and water managers who need to make decisions that balance nitrogen removal with needs of other stakeholders. The proposed project addresses the following priorities of the University of Wisconsin System: Interactions of groundwater and surface water including chemical transformations in the hyporheic zone.

Objectives: The main objectives of the proposed project were: 1) To determine if nitrogen processing in groundwater associated with deep stream sediments is widespread throughout a river network, 2) To determine if high nitrate concentration in groundwater saturates denitrification in stream sediments.

Methods: We identified eight study sites on streams and rivers in the Waupaca River Network in Central Wisconsin. Sites were chosen that spanned a large range in groundwater nitrate concentration (<0.01 to 9 mg NO_3-N/L on average), were located in upwelling reaches, and had fine sediments present. We measured denitrification on sections at 5 cm intervals from four to five sediment cores (to a depth of 20 to 30 cm) collected from each stream to determine how denitrification rates vary by depth, among cores, and among streams. The organic matter content of the sediment cores, as well as the nutrient and dissolved oxygen concentrations of the groundwater used in the denitrification incubations, will be used to develop regression models for predicting denitrification rates in stream sediments. Three peeper samplers and piezometer nests were deployed in each stream to determine fine-scale vertical profiles of nitrate and chloride concentration in the groundwater to a sediment depth of 90 cm. Our combined approach (denitrification measurements and nitrate profiles) has resulted in some of the most high-resolution estimates of groundwater nitrate processing in stream sediments.

Results and Discussion: Mean denitrification rates were higher in shallow sediments than deeper sediments. However, core sections deeper than 5 cm accounted for about 70%, on average, of the total denitrification (integrated throughout the entire core). The magnitude of denitrification rate differed strongly among sites. At many sites denitrification rates were higher in shallower sediments, while other locations showed similar denitrification rates at various sediment depths or higher denitrification rate in deeper sections. Denitrification rate increased linearly with groundwater nitrate concentration at low concentrations (< 2 mg NO_3-N/L) but denitrification varied considerably at high groundwater nitrate concentrations (> 5 mg NO_3-N/L), a pattern that suggests nitrate saturation.

For most of the study sites nitrate concentration was higher in deep groundwater than in shallower groundwater. At most sites including the Tomorrow River Site I, Bear Cr., Emmons Cr. and the Crystal River nitrate concentration tended to decline to very low concentrations as groundwater moved from deeper to shallower sediments, while chloride concentration changed much less. Two piezometer nest locations showed that groundwater nitrate remained high as water moved from deeper to shallower sediments. At two nest locations at Tomorrow River Site II chloride and nitrate concentrations were both higher in the deep groundwater than in the shallow groundwater. Finally, all piezometer nest locations at Hartman Cr. and the Waupaca R. revealed nitrate concentrations at or below the detection limit for both deep and shallow groundwater. The ratio of NO_3-N:Cl^- was lower in shallow groundwater than in deep groundwater at 14 of 18 of the locations in which the nitrate concentration in the deep groundwater was above the detection limit. This result suggests that nitrate was removed in most cases as groundwater upwelled from deep to shallower sediments.

Conclusions/Implications/Recommendations: The denitrification results and nitrate profile results both suggest that nitrate removal from groundwater is widespread in deep sediments of streams and rivers in the Waupaca River Network. Our results suggest that estimates of nitrogen processing based exclusively on shallow sediment cores or on whole-stream injections of nitrate may underestimate stream ecosystem N-removal by not capturing nitrogen processing that occurs in deep sediments. We think that processes in deep sediments will need to be considered when modeling nitrate removal at the network and watershed scales. Failing to account for nitrate removal in deep sediments could lead to errors when closing nitrogen budgets at these scales. Our results also emphasize the importance of healthy intact sediments for groundwater nitrate removal in nitrate-contaminated stream ecosystems.

Related Publications: none currently (a manuscript is in preparation)

Key words: nitrate, groundwater, denitrification, sediments, streams, sand plains, biogeochemistry, river network, scale

Sources of funding: University of Wisconsin Water Resources Institute; University of Wisconsin Oshkosh Faculty Development Program

PROJECT COMPLETION REPORT for WR10R005: Groundwater nitrate processing in deep stream sediments

Introduction-

Humans have dramatically altered the nitrogen cycle during the past several decades, doubling the amount of fixed nitrogen worldwide (Galloway et al. 2008, Schlesinger 2009). Global increases in fertilizer production and application and increases in nitrogen oxide generated by burning fossil fuels are major causes for increases in the amount of available nitrogen in ecosystems. These changes have resulted in increases in the concentration and fluxes of available nitrogen in rivers (Howarth et al. 1996, Donner et al. 2002) and increases in the concentrations of available nitrogen in groundwater in many parts of the world, including Wisconsin (Browne et al. 2008, Rupert 2008, Saad 2008). Elevated nitrate in groundwater has implications for human health (Kross et al. 1992) and contributes to nitrogen loading in river and lakes where groundwater discharges to surface water. When available nitrate reaches high levels, the ability for ecosystems to process this nitrogen can become saturated (Aber et al. 1997, O'Brien et al. 2007). For example, Mulholland et al. (2008) showed that stream water nitrate concentration saturated denitrification in streams at the continental scale. It is less clear if elevated nitrate concentration in groundwater saturates nitrate retention and removal mechanisms in stream sediments.

Because the supplies of available nitrogen to ecosystems have been increasing and are projected to continue to increase, there is growing interest in processes that can retain or remove available nitrogen in streams and rivers (Alexander et al. 2000, Mulholland et al. 2008). Processes contributing to nitrate retention in streams include assimilatory uptake by autotrophs and by heterotrophic microbes (e.g. Stelzer et al. 2003) and dissimilatory uptake, including denitrification, by microbes (Burgin and Hamilton 2007). Denitrification has been shown to be influenced by nitrate concentration, carbon supply, and oxygen status (Arango et al. 2007, Groffman et al. 2009). It is well known that processes in riparian zones (e.g. Hedin et al. 1998), in hyporheic zones (where groundwater and surface water mix) (Hill and Lymburner 1998) and in the surface water of streams and rivers (Mulholland et al. 2008) can retain and remove substantial amounts of available nitrogen. Much less is known about the role of deep sediments beneath the stream channel (below the hyporheic zone) in nitrogen processing. Many studies of nitrogen processing in streams do not include deep sediments. For example, most studies of denitrification in streams only include denitrification measurements from surficial sediments (cores less than 5 cm deep) (e.g. Arango et al. 2007, Herrman et al. 2008). In groundwater-fed streams groundwater typically passes through substantial quantities of sediment before discharging to the stream. Previous studies have suggested that available nitrogen is retained along upwelling flow paths in deep sediments (Duff et al. 2008, Puckett et al. 2008, Stelzer et al. 2011). However, most previous studies have not included process-oriented measurements in deep sediments (but see Fischer et al. 2005, Inwood et al. 2007) or have not included the fine-scale vertical profiles of available nitrogen necessary to infer where nitrogen retention occurs in deep sediments. We have reported fine scale changes in nitrate and chloride concentration from a single stream in the Waupaca River Network (in the Central Sand Ridges Ecoregion of Wisconsin) that suggests nitrate processing can be substantial in deep sediments associated with streams (Stelzer et al. 2011). In the current study, we determined the applicability of these findings to a network (the Waupaca River Network) of streams and rivers spanning a 100-fold range in groundwater nitrate concentration. We addressed the following questions:

1. Is nitrogen processing in groundwater associated with deep stream sediments widespread throughout a river network?
2. Does high nitrate concentration in groundwater saturate denitrification in stream sediments?

Procedures and Methods-

We identified eight study sites on streams and rivers in the Waupaca River Network (Fig. 1). Sites spanned a large range (100-fold) in groundwater nitrate concentration, were in upwelling reaches, and had fine sediments (silt, sand) present. The study took place during late spring through early fall of 2010. We addressed our research questions by completing the following tasks: 1) We measured denitrification rates on sectioned sediment cores to determine if denitrification rate varied with sediment depth, 2) We determined if denitrification rates saturates at high groundwater nitrate concentrations, and 3) We measured fine-scale variation in groundwater nitrate and chloride concentrations using both peepers and piezometer nests.

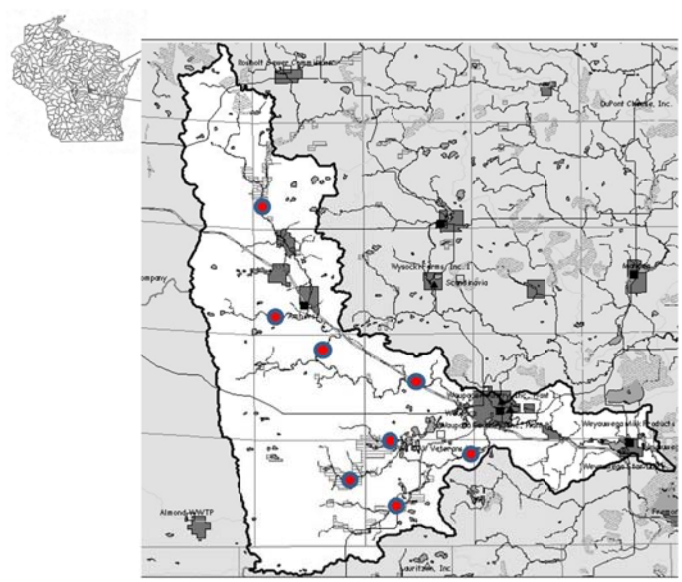

Fig. 1. Map of Waupaca River Watershed with sampling sites indicated (modified from map by the Wisconsin Department of Natural Resources)

Denitrification rate measurements- Four to five sediment cores (7.6 cm diameter, 20 to 30 cm length) were collected in upwelling locations (as determined by measurements of vertical hydraulic gradient) at each site. Each core was divided into 5-cm sections and placed in Whirl-Pak bags for transport to the Aquatic Ecology Laboratory at UW Oshkosh. Within 24 to 48 hrs denitrification rates were measured using the chloramphenicol-amended (1 mg ml^{-1}) acetylene block method (Richardson et al. 2004, Groffman et al. 2006) in the laboratory. Incubations (and core storage prior to incubation) were carried out in a Fisher Isotemp Model 307C incubator set to the ambient temperature of groundwater at the time of sediment core collection. Groundwater was pumped from piezometers adjacent to the location of each sediment core (see below) and was added to the sediments prior to the incubations. Denitrification rates were calculated as the rate of nitrous oxide (N_2O) production during 90 minute incubations. Subsamples of sediments from each core section will be analyzed for organic matter content and bulk density using standard methods. Samples from groundwater used in the incubations were analyzed for nitrate and dissolved organic carbon. Sediment and groundwater parameters will be used in multiple regression models to determine the drivers of denitrification in deep stream sediments in the Waupaca River Network. Nested ANOVA was used to compare denitrification rates among sites and among core sections (core section was nested within site in the models).

Groundwater Nitrate Profiles- Piezometers in groups of six (nests) were installed at three upwelling locations at each site. Piezometers were constructed of CPVC (1.2 cm inner diameter) with the terminal 4.5 cm screened (3 mm holes covered with 100 µm Nitex mesh). Modified Pore Water Hesslein Samplers (peepers) were deployed within each piezometer nest. The piezometers were installed at different depths within each nest so that the nitrate and chloride concentrations in relatively deep groundwater (35 to 90 cm) could be characterized while the peepers provided nutrient concentrations at 1.3 cm vertical intervals in the 1 to 25 cm range. Together, water samples collected from the piezometers and peepers provided a high-resolution profile of nitrate and chloride in the sediments to about 70-90 cm. Groundwater nitrate and chloride concentrations were used to calculate NO_3-N:Cl^- ratios. Unpaired t-tests were used to compare the NO_3-N:Cl^- ratios of deep groundwater (from the 6 piezometers) to those in shallower groundwater (from the 6 deepest peeper samples) for each piezometer nest-peeper complex. We predicted that the NO_3-N:Cl^- ratio would be higher in deep groundwater than in shallow groundwater if nitrate removal was occurring in the deep sediments.

Results and Discussion-

Mean denitrification rates were higher in shallow sediments than in deeper sediments (Table 1, ANOVA P <0.01). However, core sections deeper than 5 cm accounted for about 70%, on average, of the total denitrification (integrated throughout the entire core). The magnitude of denitrification rate differed strongly among sites (ANOVA P <0.01, Fig. 2). At many sites (Fig. 2a, b, e, f) denitrification rate was higher in shallower sediments, while other locations showed similar denitrification rates at various sediment depths (Fig. 2c) or higher denitrification rate in deeper sections (Fig. 2d, g). Denitrification rates tended to be much higher on average at locations with high concentrations of groundwater nitrate such as Bear Cr., Tomorrow River Site II, and Radley Creek (Fig. 2). Denitrification rate increased linearly with groundwater nitrate concentration at low concentrations (< 2 mg NO_3-N/L) but denitrification varied considerably at high groundwater nitrate concentrations (> 5 mg NO_3-N/L), a pattern that suggests nitrate saturation (Fig. 3).

Table 1. Denitrification rates (mean, SD, N) by core section for the sites in the Waupaca River Network.

Core Section (cm)	Mean (ug N2O-N/cm2/h)	SD	N
0-5	2.04	2.78	33
5-10	1.98	3.68	33
10-15	0.94	1.81	33
15-20	0.68	1.39	33
20-25	0.71	2.08	30
25-30	0.80	1.97	17

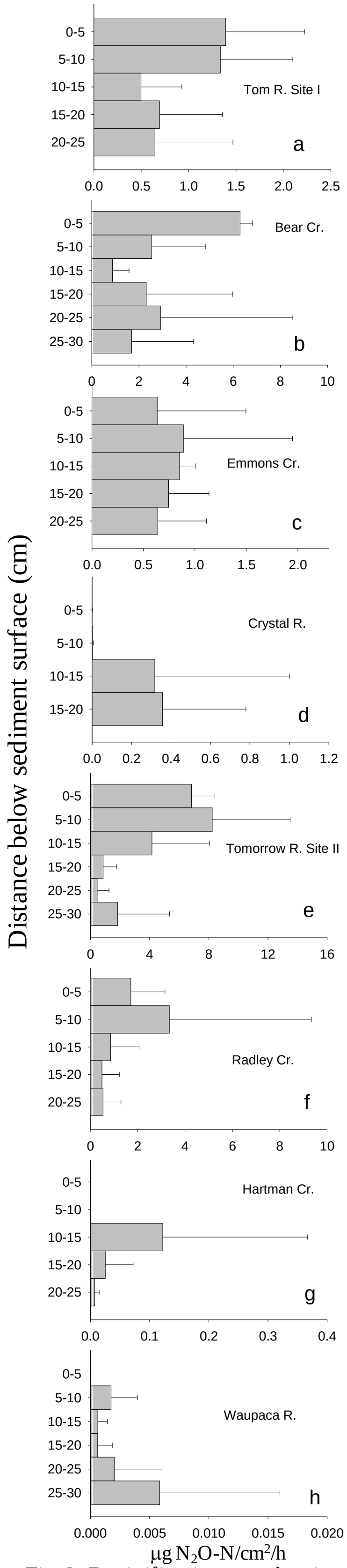

Fig. 2. Denitrification rates by site and by core section in the Waupaca River Network

For most of the study sites nitrate concentration was higher in deep groundwater (sampled with the piezometers) than in shallower groundwater (sampled with the peepers) (Fig. 4). At most sites including the Tomorrow River Site I, Bear Cr., Emmons Cr. and the Crystal River nitrate concentration tended to decline to very low concentrations (at or below the detection limit) as groundwater moved from deeper to shallower sediments, while chloride concentration changed much less (e.g. Fig 4a,c,e,g,l). Two piezometer nest locations showed that groundwater nitrate remained high as water moved from deeper to shallower sediments (Emmons Cr.-Fig. 4h, Radley Cr.-Fig. 4r). At two nest locations at Tomorrow River Site II (Fig. 4m,n) chloride and nitrate concentrations were both higher in the deep groundwater than in the shallow groundwater. This may reflect that different groundwater flow paths were sampled by the peepers and piezometers at these locations or that chloride did not behave conservatively. Finally, all piezometer nest locations at Hartman Cr. and the Waupaca R. revealed nitrate concentrations at or below the detection limit for both deep and shallow groundwater. The ratio of NO_3-N:Cl^- was lower in shallow groundwater than in deep groundwater at 14 of 18 of the locations in which the nitrate concentration in the deep groundwater was above the detection limit (one-tailed t-tests, $P<0.05$). This result suggests that nitrate was removed in most cases as groundwater upwelled from deep to shallower sediments.

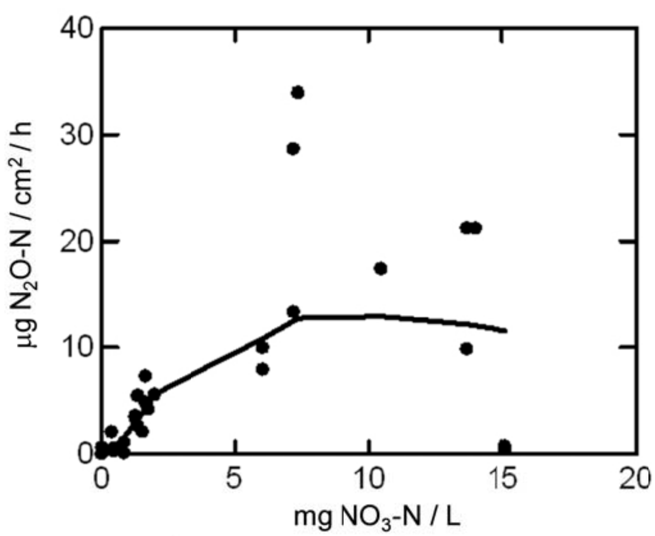

Fig. 3. Denitrification rates (integrated across core sections) plotted against groundwater nitrate concentrations associated with each core for sites in the Waupaca River Watershed.

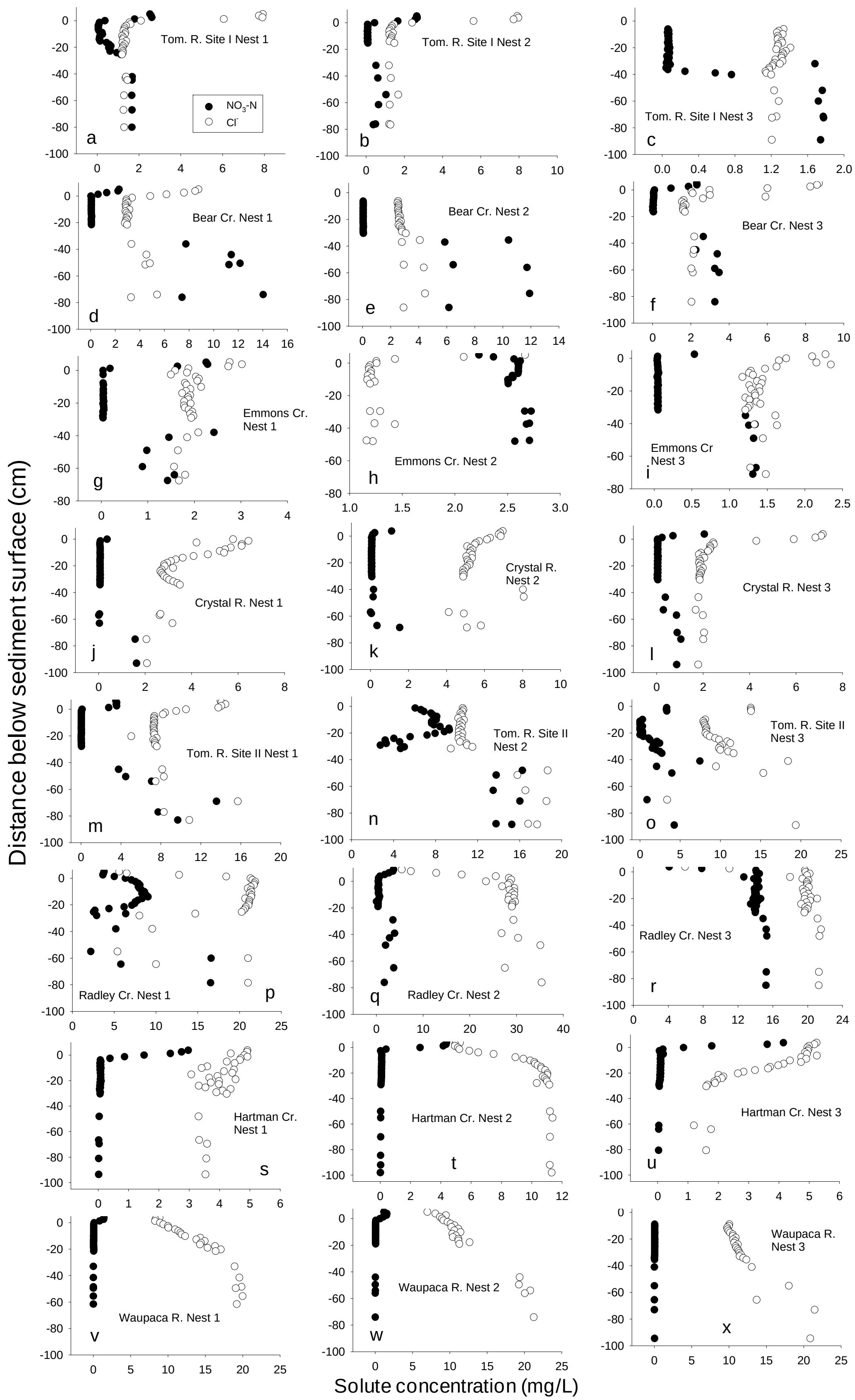

Fig. 4. Nitrate and chloride depth profiles for each piezometer nest at the 8 sites.

Conclusions and Recommendations-

The denitrification results and nitrate profile results both suggest that nitrate removal from groundwater is widespread in deep sediments of streams and rivers in the Waupaca River Network. Our results suggest that estimates of nitrogen processing based exclusively on shallow sediment cores or on whole-stream injections of nitrate may underestimate stream ecosystem N-removal by not capturing nitrogen processing that occurs in deep sediments. We think that processes in deep sediments will need to be considered when modeling nitrate removal at the network and watershed scales. Failing to account for nitrate removal in deep sediments could lead to errors when closing nitrogen budgets at these scales. Our results emphasize the importance of healthy intact sediments for groundwater nitrate removal in nitrate-contaminated stream ecosystems. If stream sediments become degraded because of toxin exposure or physical removal (e.g. dredging) ecosystem services they provide, such as nitrate removal, may be compromised.

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Stelzer, R.S., J.B. Heffernan, and G.E. Likens. 2003. The influence of dissolved nutrients and particulate organic matter quality on microbial respiration and biomass in a forest stream. Freshwater Biology 48:1925-1937.

Stelzer, R.S., L.A. Bartsch, W.B. Richardson, and E.A. Strauss. 2011. The dark side of the hyporheic zone: depth profiles of nitrogen and its processing in stream sediments. Freshwater Biology, 56: 2021-2033, DOI: 10.1111/j.1365-2427.2011.02632.x

APPENDIX A:

Presentations at state and national conferences

Stelzer, R.S., L.A. Bartsch. 2011. Nitrate processing in deep sediments of a Central Wisconsin river network. Abstract of an oral presentation at North American Benthological Society Annual Meeting, Providence, RI.

Stelzer, R.S., L.A. Bartsch. 2011. Denitrification of groundwater nitrate in a Central Wisconsin river network. Abstract of an oral presentation at American Water Resources Association (Wisconsin Section) Annual Meeting, Appleton, WI.

Simulating Lake Responses to Climate Change with a Mechanistic Water Quality Model

Basic Information

Title:	Simulating Lake Responses to Climate Change with a Mechanistic Water Quality Model
Project Number:	2011WI266B
Start Date:	3/1/2011
End Date:	2/29/2012
Funding Source:	104B
Congressional District:	WI-2
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Water Quality, Models
Descriptors:	None
Principal Investigators:	Trina McMahon

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 3/1/2011 - 2/29/2012

Submitted By: Katherine McMahon
Submitted: 5/23/2012

Project Title

WR11R001: Simulating Lake Responses to Climate Change with a Mechanistic Water Quality Model

Project Investigators

Katherine McMahon, University of Wisconsin-Madison

Progress Statement

We continue to work on calibrating and validating our coupled hydrodynamic-ecosystem process water quality model based on driver data and observations during the ice-free seasons. We have expanded this calibration and validation process beyond the 2008 data set to include years 2009 and 2010. Statistical analyses are being done to quantify the closeness of fit between the modeled output and observed data. These analyses are part of the parameter sensitivity analysis to determine the multi-year parameter values to use in the climate change simulations. We are also identifying periods of observation data in the 2001-2010, ten year data set that match the conditions of our climate change scenarios. This actual observation data will then be merged with other driver data to simulate the entire ice-off period of the climate change scenario. We continue to collaborate with Dr. Paul Hanson in the Center for Limnology and members of the Global Lake Ecological Observatory Network. The modeling effort will be used as a template for further modeling projects within GLEON. We are planning a workshop for October 2012 to disseminate our findings to interested GLEON members, and to initiate a similar modeling project for Lake Erken in Sweden. This demonstrates an international level of impact of our work.

Principal Findings and Significance

Principal Findings and Significance

Description

We report a significant change in knowledge: Graduate students Emily Kara and Josiah Hawley continue to advance their knowledge on how to perform water quality modeling, including model calibration and validation. A deeper understanding of the impact of key parameters on the model output has been gained by expanding the simulations to include the 2009 and 2010 data sets. Calibrating and validating the models for multiple years is helping us to better constrain the range of reasonable parameter values for Lake Mendota and their effect on key water quality components. This increased understanding of the model parameters should improve the accuracy of the climate change scenario outputs.

Description

Participant training and collaborations. Ms. Emily Kara, PhD candidate in Environmental Engineering. Emily is calibrated and validated the water quality model that is the foundation for the project. She is also conducting analyses of bacterial community composition data and relating it to the project. Mr. Josiah Hawley, MS candidate in Environmental Engineering. Josiah is further calibrating and validating the water quality model that is the foundation for the project. Collaborators include: Dr. Paul Hanson, Scientist in the Center for Limnology. Dr. Hanson is working closely with Emily to calibrate and validate the model. He is also performing spectral analysis on the model output to determine how well it captures variability at different temporal scales. Training and Professional Development: The project is providing training and professional development opportunities to Ms. Kara, Mr. Hawley and three undergraduate students majoring in Civil and Environmental Engineering (Douglas Chalmers, sophomore; Aaron Besaw, junior; and Craig Snortheim, junior).

Committees, Memberships & Panels

Group Name	Dane County Lakes and Watershed Commission
Description	PI McMahon is a citizen representative sitting on the Dane County Lakes and Watershed Commission. The findings for this project will be communicated to the commission and factored into policy-level decisions for management of the Yahara watershed in Dane County.
Start Date	7/1/2009
End Date	6/30/2015

Students & Post-Docs Supported

Student Name	Josiah (Jay) Hawley
Campus	University of Wisconsin-Madison

Advisor Name	Katherine McMahon
Advisor Campus	University of Wisconsin-Madison

Degree	Expected Masters
Graduation Month	December
Graduation Year	2012
Department	Civil and Environmental Engineering
Program	Civil and Environmental Engineering
Thesis Title	TBD
Thesis Abstract	TBD

Student Name	Emily Kara
Campus	University of Wisconsin-Madison

Advisor Name	Katherine McMahon
Advisor Campus	University of Wisconsin-Madison

Degree	Expected PhD
Graduation Month	July
Graduation Year	2012
Department	Civil and Environmental Engineering
Program	Civil and Environmental Engineering
Thesis Title	TBD
Thesis Abstract	TBD

Undergraduate Students Supported

New Students: **2**
Continuing Students: **1**

Climate Change Impacts on Stream Temperature and Flow: Consequences for Great Lakes Fish Migrations

Basic Information

Title:	Climate Change Impacts on Stream Temperature and Flow: Consequences for Great Lakes Fish Migrations
Project Number:	2011WI267B
Start Date:	3/1/2011
End Date:	2/29/2012
Funding Source:	104B
Congressional District:	WI-2
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Ecology, None
Descriptors:	None
Principal Investigators:	Peter Biek McIntyre

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 3/1/2011 - 2/29/2012

Submitted By: Peter McIntyre
Submitted: 5/21/2012

Project Title

WR11R002: Climate Change Impacts on Stream Temperature and Flow: Consequences for Great Lakes Fish Migrations

Project Investigators

Peter McIntyre, University of Wisconsin-Madison

Progress Statement

Objective 1: Quantifying the historical timing of Great Lakes fish migrations in Wisconsin tributaries.

Large historical data sets are rare for fish migrations and long term analysis of migration phenology has not yet been conducted for the Great Lakes. The US Fish and Wildlife Service collected a unique data set as part of their lamprey control program that includes data for multiple migratory species over a period of 25 years with a few sites continuing to the present. Our goals were to determine historic migration timing, determine whether phenology changed during the sampling period, and compare historic timing with data from the present day.

Historical fish migration data were obtained from the USFWS. Data have been distilled into summary values for migration phenology for alewife, steelhead, white and longnose suckers, and sea lamprey. Migration timing for all species is correlated with latitude. Initial analysis using a multiple regression predicting day of arrival from latitude and year revealed a significant positive relationships with both latitude and year, seemingly indicating that migrations times are becoming later. We believe that this puzzling temporal pattern is a result of artifacts in the data set due to the sampling regime. For example, a later start to the sampling season over the years could skew arrival and median migration dates and result in the observed pattern. We are in communication with the USFWS to obtain detailed information on the sampling period. Additionally, we are looking into alternative metrics that are robust to variability in the details of the sampling period. The most promising metric is peak migration date, which should be consistent as long sampling began prior to the peak. Each stream/year needs to be evaluated individually to ensure that sampling captured the peak in the migration, and that is a laborious task that is currently underway.

Additionally, there are approximately 10 streams represented in the USFWS database for which we have collected phenology data in the past few years. We are in the process of conducting a separate analysis of these specific locations to evaluate whether phenology has shifted.

Objective 2: Monitoring the current migration timing along a latitudinal gradient of Wisconsin tributaries to identify temperature and flow levels that trigger the onset of migrations.

Citizen science is an effective way to engage citizens and educate them about the local impacts of climate change. Additionally, it provides a mechanism for collecting data simultaneously across a broad geographic range. Our goal was to establish a volunteer monitoring network to observe the sucker migration along the Wisconsin shore of Lake Michigan to determine the current migration phenology and evaluate migration cues. Suckers were chosen because they are ubiquitous, abundant, and easily identifiable.

We collaborated with the WDNR and UW Extension volunteer monitoring program to identify and contact potential volunteers. The USGS provided stream gauges that were installed in each stream along with a temperature logger. Each volunteer was trained in fish identification, and an observation site was chosen to maximize visibility and convenience. In 2011, 20 volunteers monitored sucker arrival, temperature, and flow levels in 15 tributaries spanning over 200 miles of Lake Michigan shoreline.

Arrival was closely linked with temperature but showed no clear pattern relative to flow. Mean temperature on the day of the first pulse of fish was 7.6° C (SD = 0.6) (e.g., Fig. 1). Despite the variability among sites in the start date of the migration, water temperatures at the start of the migration were highly consistent. In contrast, fish arrival was not associated with any particular hydrograph component. In some streams, fish arrived during high flows, but in others they arrived after long periods of declining flows (Fig. 2). This indicates that migration timing depends primarily on water temperature.

In 2012, volunteers were again prepared to monitor, but unfortunately the fish arrived two months prior to the 2011 arrival date. Thus, our citizen monitoring had not yet been initiated when most migrations began, and we were unable replicate the 2011 results. Nonetheless, data on phenology were collected opportunistically at a few northern Wisconsin streams where the migration had not yet begun, and in Green Bay through another project in my lab group. We plan to continue the volunteer monitoring effort in 2013 to bolster the data set and engage a larger set of volunteers.

Objective 3: Predicting how the timing of migrations is likely to shift with future climate change, and evaluate the implications at the species, community, and ecosystem levels.

Understanding how climate change will influence particular aquatic species is essential for public education and to guide management responses. Our goal is to combine the latest modeling efforts for climate change effects on temperature and flow regimes with our analysis of migration phenology and cues to determine the ecological consequences for fish migrations.
We are collaborating with John Walker and Randy Hunt at the USGS Wisconsin Water Science Center to adapt their ongoing work to predict future stream flow and temperature of Great Lakes tributaries. Following several meetings to outline needs for the collaboration, their team is currently working on models specific to locations with data on sucker phenology. We expect these results later in 2012. Using the temperature cue identified through the results of our volunteer network, we expect to be able to predict how migrations are likely to shift in the future. These predictions will contribute to the evaluation of specific impacts on the ecology of Great Lakes migratory fishes.

We are also monitoring community and ecosystem roles of these fish migrations. Based on our previous work in Michigan, we believe that nutrient concentrations and stream productivity change when migratory fishes arrive. In April-May 2012, we have monitored nutrients and productivity in a series of Wisconsin tributaries on the Door Peninsula, where background nutrient loads are relatively modest. Our analyses are currently underway, and will be completed by August 2012. To connect the timing of fish migrations to the ecology of resident sport fishes, we have been assessing consumption of sucker eggs and larvae by brook trout in these same streams. We find the trout diets consist almost entirely of sucker eggs during the height of the migration, indicating strong linkages between these species. As a result, shifts in the timing of sucker migrations could affect both the fundamental productivity of Wisconsin tributaries, and the health of valuable sport fish populations.

Principal Findings and Significance

Principal Findings and Significance

Description

Outreach activities:

A daily program educating the public about fish migrations, sucker life history, and the impacts of climate change was developed and implemented at the Crossroads at Big Creek Nature Center in 2011 and 2012 during the sucker migration. We prepared a brief lecture for the staff to present to visitors, after which visitors would observe sucker spawning in a local creek. Brief lectures were given to two volunteer groups about fish migration ecology and climate change. This project has been featured in newsletters for multiple citizen groups, as well as on the WRI Press Room website in August 2011 (http://wri.wisc.edu/pressroom/Details.aspx?PostID=1138).

Two unanticipated outreach opportunities have also arisen from this project. First, I am exploring the possibility of working with the Aldo Leopold Nature Center (Madison, WI) to create an educational display about how climate change is impacting the timing Great Lakes fish migrations. This would provide an ideal venue for sharing our research with children. Second, this project has led to a collaborative agreement with the Shedd Aquarium (Chicago, IL) to support a post-doctoral researcher studying Great Lakes fish migrations starting in August 2012. The position will be based in Chicago but involve close collaboration with my lab group at UW-Madison, thereby expanding the scope and impact of this WRI project enormously. As a result, we anticipate jointly designing a display in the Shedd Aquarium to highlight Great Lakes migratory fishes, and how climate change could impact them.

Results of this research project will be presented by Evan Childress at the American Fisheries Society annula meeting in Minneapolis in September 2012. We are currently working on developing a project webpage, and discussing how to package the initial results for publication.

Supporting students

Doctoral student Evan Childress has received a stipend for Spring and Summer 2012. To conserve WRI funds, I was able to support Evan's work on the project using other sources during Spring 2011. As a result, I plan to request a no-cost extension of the project to enable support of Evan for an additional semester.

Journal Articles & Other Publications

Publication Type	Newsletter/Periodical (Not Peer-Reviewed)
Title	Sucker Migration, Harbinger of Climate Change
Author(s)	Carolyn Rumery Betz
Publication/Publisher	Aquatic Sciences Chronicle
Year Published	2010
Volume & Number	4
Number of Pages	
Description	
Any Additional Citation Information	

Students & Post-Docs Supported

Student Name	Evan Childress
Campus	University of Wisconsin-Madison

Advisor Name	Peter McIntyre
Advisor Campus	University of Wisconsin-Madison

Degree	PhD
Graduation Month	May
Graduation Year	2015
Department	Zoology
Program	Limnology & Marine Science
Thesis Title	
Thesis Abstract	

Undergraduate Students Supported

Continuing Students: **1**

Uncertainty and Variability of Wisconsin Lakes in Response to Climate Change

Basic Information

Title:	Uncertainty and Variability of Wisconsin Lakes in Response to Climate Change
Project Number:	2011WI268B
Start Date:	3/1/2011
End Date:	2/29/2012
Funding Source:	104B
Congressional District:	WI-2
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Water Quality, Geochemical Processes
Descriptors:	None
Principal Investigators:	Chin H Wu

Publications

1. Magee M, and CH Wu (In Review) Long-term trends and variability in ice cover and thermal structure in three morphometrically different lakes in response to climate change. Limnology and Oceanography
2. Magee M, and CH Wu (In Review) Hanging climate on three lakes with differing morphometry. Water Research

Annual Progress Report

Selected Reporting Period: 3/1/2011 - 2/29/2012

Submitted By: Chin Wu
Submitted: 5/5/2012

Project Title

WR11R003: Uncertainty and Variability of Wisconsin Lakes in Response to Climate Change

Project Investigators

Chin Wu, University of Wisconsin-Madison

Progress Statement

We are investigating the physical responses of ice cover and water temperature in Wisconsin lakes to climate change. During the project period, we have been looking at lakes in southern Wisconsin (Madison area) and lakes in northern Wisconsin (Vilas County) to analyze the response to physical lake variables to climate. Specific lakes researched were Lake Mendota, Lake Wingra, and Fish Lake in Dane County, and Trout Lake, Crystal Lake, and Allequash Lake in Vilas County. During the course of the year, we (i) improved the one-dimensional lake-ice model, DYRESM-I to simulate ice cover and water temperature at sub-hourly time intervals, (ii) developed a 3D lake ice/snow/hydrodynamic model that can simulate spatial distribution in ice cover and lake thermal structure, (iii) investigated the importance of climate drivers to lake physical variables, and (iv) conducted sensitivity studies to address uncertainty of lake variables response to climate change.

Model Development:
A one dimensional lake-ice model, called DYRESM-I, was developed to simulate vertical distribution of water temperature and ice cover in the study lakes. This model can continuously simulate lake hydrodynamics during open water and ice cover using thermodynamic principals. Addition of the ice component and calculations of sediment heat flux in the model are improvements over previous hydrodynamic lake models. Improvements to the DYRESM-I module also include the ability to simulate ice and water temperature at sub-hourly time intervals. The final model was calibrated to each of the study lakes to thoroughly investigate the response of thermal structure and ice cover. In addition, the one-dimensional model was used to project lake ice cover, lake level, and water temperature for use through the Interactive Nowcast/Forecast Operation System for Yahara Waters (INFOS) website. This website allows users to see real-time information on water temperature, ice cover, and water level of the Yahara Lakes (Madison, Monona, Waubesa, Kegonsa).

The ice module from DYRESM-I was extended and coupled with the existing three-dimensional hydrodynamic (3DHD) model, and this new model is capable of simulating spatial distribution of ice/snow cover and under-ice water temperature. The model was used to run a scenario of winter 2009-2010 in Lake Mendota. Additionally, the model was used to run a scenario of winter 2011-2012 in Fish Lake and well as specific spring mixing and large wind events in Fish Lake.

Importance of Climate Drivers to Lake Variables:
Using past historical climate data, and the DYRESM-I lake model, we were able to determine the correlation between climate drivers of air temperature, wind speed, and precipitation on the ice cover and open water lake variables. For maximum ice thickness, the January through March air temperature is the most highly correlated lake variable regardless of lake morphometry. Wind speed and precipitation were not significantly correlated with maximum ice thickness. For ice cover duration, air temperature is the most highly correlated lake variable, with deep lakes having a higher correlation than more shallow lakes. Wind speed is significantly correlated as well, with the correlation increasing as lake surface area increases. Precipitation was not significantly correlated with ice cover duration. We found that air temperature works to decrease the ice cover duration, while the decreasing wind speeds in the Madison Area work to increase the ice cover duration. Thus, the decreasing wind speed slightly mitigates the effect of increasing air temperature

For stratification onset and fall overturn dates, wind speed was the most correlated of the climate variables, with decreasing wind speeds in the Madison Area leading to earlier stratification onset dates and later fall overturn dates regardless of lake morphometry. The wind correlation increases with the surface area of the lake. Air temperature was also significantly correlated, with increasing air temperature leading to earlier stratification onset dates and later fall overturn dates. Overall, the decreasing wind speed and increasing air temperature work together to cause earlier stratification onset dates and later fall overturn dates. This increase in total stratification duration increases the likelihood that bottom waters of the lake will become oxygen deficient during the stratified period, resulting in oxygen stress on cold water fish populations.

Sensitivity of climate variables to changes in air temperature and wind speed
Experiments were conducted to look at the effects of changing the air temperature by increases of 1°C to 10°C and changing the wind speed by changes of ±2%, ±5%, ±8%, and ±8%. Results show that, as expected, increasing air temperature results in decreasing ice cover duration and decreasing maximum ice thickness. Looking only at increases in air temperature, it is apparent that deeper lakes are more prone to experience ice-free conditions, while more shallow lakes may still have ice-cover conditions for short periods (<10 days) even with increase in air temperature of 10°C. Looking at changes in wind speed, in general, lower wind speed results in earlier ice formation and larger ice thicknesses, although there is significant variability due to the timing of air temperatures, which are the main climate driver for ice cover. For instances when air temperature was cold enough for ice cover conditions, ice only was able to form when wind speed was low. If, however, wind speed was low enough for ice cover condition, but air temperature was too warm for ice formation, wind speed did not affect ice cover onset.

Evaporation of lakes with varying morphometries response to climate change
As temperatures increase from climate change it is clear that lake evaporation will increase, however the responses of lakes with varying morphometry is not fully understood. A one-dimensional hydrodynamic lake model (DYRESM-I) is used to simulate lake evaporation and compare how three lakes of varying morphometry respond to idealized temperature-increase climate scenarios. The model simulates the one-hundred year period from 1911 to 2010 for Lake Mendota, Lake Wingra, and Fish Lake in Dane County WI. Four mass-transfer evaporation equations (Marciano-Harbeck 1954, Horton 1917, Harbeck 1958, & Ryan-Harleman 1995) are compared see a range in results. Probability density functions are employed to show how each lake evaporation increases from the increase in temperature as well as the increase in days without ice-cover. Initial results show that evaporation on the most shallow lake, Lake Wingra, is the least sensitive to a temperature increase. Finally, seasonal evaporation responses to climate change is assessed by lake. Since lakes with more depth and volume store more heat, they evaporate less in the spring and more in the fall than shallow lakes; this report seeks to identify how those trends are affected as evaporation is increased.

Principal Findings and Significance

Principal Findings and Significance

Description

The most direct benefit of the project is the development of the DYRESM-I lake-ice model and the 3DHD lake-ice model for use in investigation of past and future changes in climate. Use of the DYRESM-I model allows researchers and lake manager to quickly and accurately simulate lake temperature and ice cover response under specific climate conditions. The 3DHD model allows researchers to more accurately simulate the effect of specific climate situations on the full-lake scale. This allows for increased preparedness to climate changes. Use of the DYRESM-I model within the INFOS system has direct, positive benefits to the Madison, Wisconsin area, as it provides easily accessible lake information to the public.

Results of the investigation of the impact of changing climate to Wisconsin lakes provides quality information to lake managers and other researchers. Understanding the change of water temperature may allow regulatory agencies to determine which lakes may become at risk for invasive species. This allows agencies to direct their manpower to a few specific lakes to prevent species spread rather than having to monitor a variety of lakes, some of which may not be at risk to invasive species. Additionally, as water temperature greatly affects fish species within the lakes, understanding which lakes may be at risk for fish kills due to increasing stratified period or increasing water temperatures may allow for mitigation efforts to protect important fish populations

Committees, Memberships & Panels

Group Name WICCI Water Resources and Coastal Community Working Group

Description The Wisconsin Initiative on Climate Change Impacts (WICCI) assesses and anticipates climate change impacts on specific Wisconsin natural resources, ecosystems and regions; evaluates potential effects on industry, agriculture, tourism and other human activities; and develops and recommends adaptation strategies that can be implemented by businesses, farmers, public health officials, municipalities, resource managers and other stakeholders.

Start Date 8/1/2010

End Date 4/16/2012

Journal Articles & Other Publications

Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	Long-term trends and variability in ice cover and thermal structure in three morphometrically different lakes in response to climate change
Author(s)	Magee, M. and Wu, C.H.
Publication/Publisher	Limnology and Oceanography
Year Published	In Review
Volume & Number	
Number of Pages	
Description	Climate trends and variability act as external drivers of lake dynamics, but individual lakes express the signals differently based on a variety of factors including lake morphometry (i.e. lake depth and lake surface area). A one-dimensional hydrodynamic lake model (DYRESM-I) is employed to simulate ice cover and water temperatures in Lake Mendota, Lake Wingra, and Fish Lake located in Madison, WI, USA over the period 1911-2010. The model is used to study the effect of lake thermal variables (water temperature, stratification, ice dates, and ice cover) to changes two important lake drivers, air temperature and wind speed for the three lakes, which have different morphometry. During the last century, epilimnetic temperatures have increased, hypolimnetic temperatures have decreased, and the length of the stratified season has increased for the study lakes. Additionally, the ice cover period has decreased due to earlier ice-on dates and later ice-off dates and the maximum ice cover thickness has decreased for the three lakes. Results indicate that the open water lake variables are more sensitive to differences in lake morphometry (i.e. lake depth and surface area) than are changes in the ice-cover lake variables.
Any Additional Citation Information	

Publication Type	Journal Article/Book Chapter (Peer-Reviewed)
Title	hanging climate on three lakes with differing morphometry
Author(s)	Magee, M. and Wu, C.H.
Publication/Publisher	Water Research
Year Published	In Review
Volume & Number	
Number of Pages	
Description	Previous research has indicated that climate is an important driver of lake ice cover, such as maximum ice thickness, ice cover duration, and ice growth. Three such climate drivers are (i) air temperature, (ii) wind speed, and (iii) precipitation. In addition, lake morphometry may impact the expression of these climate signals. A one-dimensional hydrodynamic lake model (DYRESM-I) is employed to simulate ice cover in Lake Mendota, Lake Wingra, and Fish Lake located in Madison, WI over the period 1911-2010. The model is used to study the effect of the three climate drivers on the study lakes which have differing morphometries. Using model results and climate data from the last century, it was determined that December to March air temperature is the climate driver most closely correlated with ice cover characteristics, with wind speed being the second most closely correlated, and precipitation having little correlation with maximum ice thickness or ice cover duration. Increasing air temperature is the primary driver for decreasing ice cover durations in the study lakes; however, decreasing wind speed acts to increase ice cover duration, which slightly mitigates the effect of increasing air temperature. An additional investigation of the effects of air temperature perturbations was also performed. It was determined from this that air temperature increases as small as 3°C may cause no ice cover on some lakes. Lake Wingra, the shallow study lake, was determined to be the most resilient lake as temperature increases as high as 10°C did
Any Additional Citation Information	

Other Project Support

Source	NSF Long Term Ecology Research
Dollar Value	$48,500
Description	Research Assistant for supporting a graduate student
Start Date	1/1/2012
End Date	12/31/2012

Presentations & Public Appearances

Title	Response of Wisconsin Lakes (Ice Cover, Water level, and Thermal Structure) to Climate Change
Presenter(s)	Chin Wu
Presentation Type	Seminar
Event Name	WICCI Science Meeting
Event Location	WDNR
Event Date	12/9/2011
Target Audience	Scientific audience
Audience Size	30
Description	The response of lake ice cover, water level, and thermal structure to the WICCI's future climate projections in Wisconsin will be obtained. Specifically we examine how the ice characteristics will change and how the change will affect the water level and lake thermal structure due to the changing climate. For this talk I focus on the following questions: (i) whether/how and to what degrees are the thermal structures of Wisconsin lakes in response to the climate condition? What would be the difference between the northern and southern lakes associated with changing climate variables (e.g. air temperature, snowfall, and snow depth) (ii) How would lakes with three different morphometry respond to the changing climate in Wisconsin?

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Title	Impact of Climate Change on Ice Cover and Thermal Structure in Three Southern Wisconsin Lakes with Differing Morphometry
Presenter(s)	Madeline Magee and Chin Wu
Presentation Type	Professional meeting
Event Name	Wisconsin American Water Resources Association
Event Location	Wisconsin Dells, Wisconsin
Event Date	3/1/2012
Target Audience	
Audience Size	50
Description	Climate variability and change are very important external drivers of lake dynamics, but individual lakes may express the signals differently based on a variety of factors including lake morphometry (i.e. lake depth and surface area). This study employs a one-dimensional hydrodynamic lake-ice model (DYRESM-WQ-I) to simulate ice cover and water temperature in Lake Mendota, Lake Wingra, and Fish Lake located in Madison, WI, USA, which have three different morphometry characteristics. The model studied (a) the effect of lake thermal variables (water temperature, stratification, ice dates, and ice cover) to changes in air temperature and wind speed over the period 1911-2010 and (b) under the condition of temperature and wind speed perturbations to analyze sensitivity to changes in lake drivers. This allows for the investigation of the effects of lake morphometry on response to the experienced changing climate and for investigation into how morphometry impacts the sensitivity of the response to future climates. Several findings were revealed. During the last century, epilimnetic temperatures have increased, hypolimnetic temperatures have decreased, and the length of the stratified season has increased for the study lakes. Additionally, the ice cover period has decreased due to earlier ice-on dates and later ice-off dates and the maximum ice cover thickness has decreased for the three lakes. The open water lake variables are more sensitive to differences in lake morphometry over the past 100 years than are changes in the ice-cover lake variables. Response to temperature perturbations for all lake variables also appears to be impacted by morphometry.

Students & Post-Docs Supported

Student Name	Madeline Magee
Campus	University of Wisconsin-Madison

Advisor Name	Chin Wu
Advisor Campus	University of Wisconsin-Madison

Degree	Masters
Graduation Month	
Graduation Year	
Department	Civil and Environmental Engineering
Program	Environmental Fluid Mechanics and Water Resources Engineering
Thesis Title	Effect of Lake Morphometry on Response to Climate Change
Thesis Abstract	Lakes may have dampened or heightened response to changing climate based on differences in lake morphometry. To investigate this aspect of lake response, we looked at Lake Mendota, Lake Wingra, and Fish Lake in Dane County, as the three lakes have experienced the same climate over the past 100 years, but have differing surface area and depths. Trends, variability, and periodic cycles for the three lakes were compared to each other and to air temperature and wind speed data. Results show that there are the same statistically significant increasing and decreasing trends for ice cover and water temperature variables in all three lakes, but the inter-annual variability and significant periodic cycles differ. For all three lakes there have been decreasing ice cover duration and ice thickness over the past 100 years in addition to increasing stratification duration, increasing epilimnetic temperature, and decreasing hypolimnetic temperature. The fact that each lake is experiencing the same trend of increasing or decreasing lake variables indicates that the climate has been causing significant changes in the lake's physical structure. Differences in magnitude of trend, variability, and periodic cycle indicate that morphometric differences among the lakes also plays a significant role in determining the exact physical response of lakes to changing clim

Undergraduate Students Supported

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

USGS Award no. G11AP20226 GLMRIS Water Quality Modeling (Marquette U.)

Basic Information

Title:	USGS Award no. G11AP20226 GLMRIS Water Quality Modeling (Marquette U.)
Project Number:	2011WI288S
Start Date:	9/12/2011
End Date:	9/11/2012
Funding Source:	Supplemental
Congressional District:	
Research Category:	Water Quality
Focus Category:	Surface Water, Water Quality, Management and Planning
Descriptors:	aquatic invasive species, separating watersheds
Principal Investigators:	Anders W. Andren, Charles Steven Melching

Publications

There are no publications.

Annual Progress Report

Selected Reporting Period: 3/1/2011 - 2/29/2012

Submitted By: Charles Melching
Submitted: 5/23/2012

Project Title

WR11R008: GLMRIS Water Quality Modeling

Project Investigators

Charles Melching, Marquette University

Progress Statement

Background

The GLMRIS feasibility study is being undertaken by the U.S. Army Corps of Engineers (Corps) to develop a long-term solution to prevent aquatic invasive species from traveling between the Great Lakes and Mississippi River watersheds. One primary goal of the study is to assess the feasibility of hydrologically separating the two watersheds, which are currently connected via the manmade Chicago Sanitary & Ship Canal and Cal-Sag Channel. These waterways were constructed in the early 20th Century, which allowed the Chicago River and other area waterways to flow to the Illinois River, instead of to Lake Michigan. Re-separating the watersheds will radically alter the existing flow patterns in the system, and is expected to cause significant water quality changes. Modeling and analysis of water quality impacts to both the CAWS and Lake Michigan are needed to ensure any selected alternative will be in compliance with Illinois water quality standards and with the Clean Water Act.

Objective

The existing DUFLOW model (developed by Marquette University for the Metropolitan Water Reclamation District of Greater Chicago, MWRDGC) will be utilized to provide supporting data to quantify water quality impacts to area waterways resulting from hydrologic separation alternatives.

Tasks and Progress

The existing DUFLOW model shall be updated and recalibrated to model water quality in the Chicago Area Waterways System (CAWS). Waterways within the scope of this project include:

• North Shore Channel (NSC)
• North Branch Chicago River (NBCR) downstream of confluence with NSC
• Chicago River Main Stem
• South Branch Chicago River (SBCR)
• South Fork of South Branch Chicago River (SFSBCR) or Bubbly Creek
• Chicago Sanitary & Ship Canal (CSSC)
• Cal-Sag Channel
• Little Calumet River (LCR) from Cal-Sag Channel to junction with Calumet and Grand Calumet Rivers
• Little Calumet River from Cal-Sag Channel to South Holland
• Calumet River

The capability of modeling the stretch of the Calumet River from the lakefront to O'Brien Lock and Dam shall be added to the DUFLOW model.

Progress: During the first six months of this project (i.e. through 2/29/12) the channel geometry and layout data for the Calumet River have been added to the DUFLOW model, appropriate boundary conditions for this reach have been determined, and preliminary hydraulic runs for the Calumet River have been made.

Modeling Scenarios

Five distinct hydrologic scenarios shall be modeled. Additional scenarios may be identified as the GLMRIS study progresses, in which case these scenarios may be added to the modeling scope of work as options to the contract.

Progress: During the first six months of this project all effort has been directed to updating and recalibrating the model, and no work has been done on scenario analysis except an initial trial run of separation of the watersheds with a barrier near Loomis Street on the South Branch Chicago River as part of the training of Dr. Liang on the use of the DUFLOW model. This trial revealed some interesting results on the potential pollutant loads to Lake Michigan and the decline in water quality conditions in some portions of the CAWS, particularly for the SBCR.

Flow Conditions

Water quality for each hydrologic scenario shall be modeled for wet (2008), dry (2003), and average (2001) year flow conditions in the waterways. Additionally, the system shall be modeled both with and without all MWRDGC TARP reservoirs (currently under construction) in operation. Expected flow data necessary for modeling reservoirs in operation shall be provided by the Corps.

Progress: The project team obtained flow and stage data from the U.S. Geological Survey for Water Year (WY) 2008 at all their gages in 2011. They also received most flow and stage data from the MWRDGC for the treatment plants, waterway locations, and combined sewer overflow (CSO) pumping stations. However, some questions regarding possibly erroneous data had not been resolved as of 2/29/12. The Corps completed simulations of gravity CSOs to the CAWS in WY 2008 for actual operations in February or early March 2012. These computed flows were provided to Marquette University in mid-March 2012. The Corps has not yet completed simulations for WYs 2001, 2003, or 2008 for conditions representing post-TARP reservoir completion.

Water Quality Parameters

The following water quality parameters are required for modeling. If the DUFLOW model did not originally model a parameter it is indicated with a * below, the capability of modeling the parameter was added during the first six months of the project with details given in the subsequent “Progress” sections.

- DO
- Ammonia
- Nitrate/Nitrite
- BOD
- TSS
- Total Phosphorus
- Fecal Coliform*
- Temperature*
- pH*
- Chloride*

A version of the DUFLOW model that simulates fecal coliform concentrations did exist at the start of this project, but it needed to be updated to consider the extension of the downstream boundary from Romeoville to the Lockport Controlling Works, the increase in representative combined sewer overflow (CSO) locations from 28 to 43, and any new fecal coliform data collected by the MWRDGC since 2005 (when the original fecal coliform model was developed).

In the original DUFLOW model of the CAWS, temperature is not simulated, rather hourly temperatures measured at the MWRDGC continuous measurement sondes are used in the model. Experience filling in missing temperature data has indicated that temperatures at all sonde locations in the CAWS can be reasonably estimated from the temperatures measured at nearby sondes. Thus, the changes in temperature along the waterways may be reliably estimated via statistical models. Such statistical models will be developed for each sonde location and mass balance model principles will be applied at each proposed separation point to consider the reduction in cooler Lake Michigan water (daily Lake Michigan temperature data are available from the Chicago Department of Water Management) reaching various reaches of the CAWS after separation. After the change in water temperature in the vicinity of the point of separation is determined by mass balance, the temperature changes will propagate downstream through the CAWS using the statistical relations between points.

Modeling of chloride in the CAWS will be difficult for the following reasons.

1) Chloride is measured only once per 7 days at the outfalls of the Stickney and North Side Water Reclamation Plants (WRPs) and no chloride data are available for the outfall of the Calumet WRP.
2) Chloride concentration data for the CSOs is sparse, i.e. single samples during a CSO event are available for the three CSO pumping stations as opposed to event mean concentrations.

Progress:

Fecal Coliform Modeling

The necessary revisions to the domain of the model and the number of CSO input points were made and fecal coliform concentrations were simulated for WYs 2001 and 2003. Generally good agreement between simulated and measured fecal coliform concentrations was obtained at all measurement locations for both years.

Chloride Modeling

Researchers have found a strong correlation typically exists between total dissolved solids (TDS) and chloride in water. Thus, a linear regression relation was derived between chloride and TDS for the Stickney WRP effluent and this relation was used to estimate the chloride concentration in the Calumet WRP effluent. Similarly, a limited amount of data on chloride concentrations and conductivity values were available for storm sewers in Evanston and Crestwood, IL. From these data, linear regression relations between chloride and conductivity were developed that were used to estimate chloride concentrations in CSO flows on the basis of available conductivity data for CSOs in snow and non-snow periods throughout the year.

Using the foregoing estimates for the chloride concentrations for the Calumet WRP and the CSOs, chloride concentrations throughout the CAWS were simulated for WYs 2001 and 2003. Generally good agreement between simulated and measured chloride concentrations was obtained at all measurement locations for both years.

pH

Available pH data on CSOs and flows in the TARP drop shafts were used to estimate typical pH values for the northern (to the NSC and NBCR), central (to the Chicago River Main Stem, SBCR, and CSSC), and southern (to the LCR and Cal-Sag Channel) CSOs. Preliminary pH simulations were made and reasonable agreement between measured and simulated pH values was obtained for many locations and different times of the year. However, it was obvious that having detailed information on the pH of Lake Michigan throughout the year could have an important influence on the quality of the pH simulation at many locations. The Corps has requested daily pH data for Lake Michigan from the Chicago Department of Water Management. Once these data are received the pH model can be finalized.

Temperature

In the early 1990s, the University of Iowa developed the CHARIMA Model to simulate temperature for 55 miles of waterway from Roosevelt Road on the SBCR to Dresden Island Dam on the Illinois River in a project done for Commonwealth Edison. Short segments of Bubbly Creek, Cal-Sag Channel, Des Plaines River, Hickory Creek, DuPage River, and Kankakee River are included in the model where they flow into the waterway. The CHARIMA model computed the flows using the de Saint Venant Equations (also used in DUFLOW) solved on a one-mile spatial grid at a 30 min time step and computed temperature using an Advection-Diffusion-Source equation for unsteady transport of a fully mixed, dissolved constituent. A key part of the temperature model was the Source/Sink Term for Heat Exchange Between Water and the Atmosphere, which comprised detailed expressions for the physical processes of water heating due to incoming short-wave and long-wave radiation and condensation, water cooling due to outgoing long-wave radiation and evaporation, and water heating due to conduction. Also, time-dependent discharges and water temperatures were specified at the primary model inflow point and all tributary inflows, including the Stickney WRP. The 6 generating stations were modeled as links that withdraw the condenser flow rate from the main channel, heat it by an amount proportional to the temperature rise at full load using the specified time-dependent generation schedule, and return it to the channel. This complex, physics-based model yielded results typically with errors on the order of ±1°F (0.556°C). Thus, it was hoped that the statistical model could yield predictions with similar standard errors (i.e. ≤0.556°C).

By 2/29/12, statistical relations to estimate daily temperature at 20 of the 31 monitoring locations internal to the CAWS had been developed. For 14 of these 20 locations the standard error of the predicted temperature was less than 0.556°C, indicating that the simple statistical temperature model could yield similar results to the much more complex, physics-based CHARIMA model. These results indicate that the statistical models are adequate for the purposes of the GLMRIS study.

Summary

It is hoped that all model upgrades and recalibration will be completed by July 2012, so that scenario simulations can begin in late summer.

Principal Findings and Significance

Principal Findings and Significance

Description

During the first six months of this project (9/12/11 to 2/29/12) the research activity has focused on updating and upgrading the DUFLOW computer model for the Chicago Area Waterways System as proposed and as detailed in the Annual Progress

Report. Thus, there are no major applications, impacts, or benefits from the first six months of the project to describe.

Students & Post-Docs Supported

Student Name	Jin Liang
Campus	Marquette University
Advisor Name	Charles Melching
Advisor Campus	Marquette University
Degree	PhD
Graduation Month	December
Graduation Year	2010
Department	Civil and Environmental Engineering
Program	Civil and Environmental Engineering
Thesis Title	Evaluation of Runoff Response to Moving Rainstorms
Thesis Abstract	

Establishing Paleoclimate Records from Spring Tufa Deposits in the Driftless Area of Wisconsin

Basic Information

Title:	Establishing Paleoclimate Records from Spring Tufa Deposits in the Driftless Area of Wisconsin
Project Number:	2011WI295O
Start Date:	7/1/2011
End Date:	6/30/2012
Funding Source:	Other
Congressional District:	6th
Research Category:	Climate and Hydrologic Processes
Focus Category:	Groundwater, Hydrology, Water Quantity
Descriptors:	
Principal Investigators:	Maureen Muldoon, Susan Swanson

Publications

There are no publications.

WRI: FY 2012 State of Wisconsin Groundwater Research and Monitoring Proposals

Proposal Number:
12-HDG-02

Title:
Establishing Paleoclimate Records from Spring Tufa Deposits in the Driftless Area of Wisconsin

Abstract:
Wisconsin's Driftless Area is home to thousands of springs that help support the region's world-class trout streams. The relationship of these springs to the groundwater flow system is not well understood. Some springs appear to be supplied by a laterally-extensive perched flow system while other springs appear to be sourced by deeper flow systems. A previous project provided preliminary evidence that two tufa-depositing springs may be supplied by a perched aquifer within the Sinnipee Group. These tufa-depositing springs provide an excellent opportunity to develop a paleoclimatic record for the Driftless Area.
The objectives of the project are to gain an understanding of how Sinnipee Group stratigraphy affects flow patterns in the vicinity of the tufa-depositing springs and to use the tufa-depositing springs to understand changes in Holocene climate and the effects that climate change had on groundwater flow.
Correlation of detailed outcrop stratigraphy with borehole geophysical and flow logs will provide a better understanding of the flow system that is supplying the tufa-depositing springs. We will assess seasonal variations in tufa deposition by collecting monthly water samples. Continuous records of water levels in the spring pools and of fluid temperature and conductivity will be used to assess seasonal variability in spring discharge. Three existing tufa cores will be used to develop a paleoclimatic record that includes variations in stable isotopes and major and trace element molar ratios. U/Th methods will be used to date the cores.
Project results will be of interest to water resources managers trying to assess how climate change might impact the springs of the Driftless Area. Better understanding of past climate variations could help inform groundwater models trying to predict future impacts to the laterally extensive perched flow system in southwestern Wisconsin. The resulting paleoclimatic record will be of interest to climate researchers.

Location of Research:
Grant County, WI

Investigator(s):
Maureen Muldoon, UW-Oshkosh (Principal Investigator)
Susan Swanson, Beloit College (Associate Investigator)

Preferential flow paths in heterogeneous glacially-deposited aquitards

Basic Information

Title:	Preferential flow paths in heterogeneous glacially-deposited aquitards
Project Number:	2011WI296O
Start Date:	7/1/2011
End Date:	6/30/2012
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Hydrology, Water Quantity, Models
Descriptors:	
Principal Investigators:	David J. John Hart

Publications

There are no publications.

WRI: FY 2012 State of Wisconsin Groundwater Research and Monitoring Proposals

Proposal Number:
12-HDG-03

Title:
Preferential flow paths in heterogeneous glacially-deposited aquitards

Abstract:
Preferential flow paths allow for faster movement of fluids than the surrounding matrix due to their hydraulic properties and connectivity. These paths are important to both groundwater flow and contaminant transport, but are difficult to detect and quantify. The main contribution of this research will be to determine the nature of preferential flow paths in heterogeneous glacially-deposited aquitards and how they affect groundwater flow and transport. This is significant as previous studies in glacially-deposited aquitards have focused on flow through the aquitard, but not considered flow within the aquitard.

Flow paths will be delineated using multiple-point geostatistics. This geostatistical method uses a training image, instead of a variogram, to represent the general features of the subsurface. A training image maintains geologic structure and connectivity, features not easily captured by the traditional variogram method. A combination of well log data, geophysics, drilling, and measurements of hydraulic conductivity will be used to create and compare a variogram model and numerous three-dimensional hydrostratigraphic models of a representative site using multiple-point geostatistics. These models will be imported into groundwater flow and transport models to quantify and assess the connectivity of preferred paths in the flow system. The representative site is located in Outagamie County, Wisconsin, where a bedrock valley has been filled with a thick sequence of low conductivity sediment that occasionally contains sand lenses of unknown extent and continuity. These sand lenses provide water for many private wells and may provide recharge to bedrock aquifers used by municipalities.

An additional research objective is to demonstrate the use of multipoint geostatistics, to determine whether or not our flow and transport models can benefit from this technique. A secondary and applied goal is to better understand the flow system in Outagamie County, which will be useful to both the municipal and private well owners.

Location of Research:
Outagamie County, Wisconsin

Investigator(s):
David Hart, UW-Extension (Principal Investigator)

The Effects of Particulate Organic Carbon Quantity and Quality on Denitrification of Groundwater Nitrate

Basic Information

Title:	The Effects of Particulate Organic Carbon Quantity and Quality on Denitrification of Groundwater Nitrate
Project Number:	2011WI297O
Start Date:	7/1/2011
End Date:	6/30/2013
Funding Source:	Other
Congressional District:	6th
Research Category:	Ground-water Flow and Transport
Focus Category:	Hydrogeochemistry, Sediments, Water Quality
Descriptors:	
Principal Investigators:	, Robert Scott Stelzer

Publications

There are no publications.

WRI: FY 2012 State of Wisconsin Groundwater Research and Monitoring Proposals

Proposal Number:
12-GCP-01

Title:
The effects of particulate organic carbon quantity and quality on denitrification of groundwater nitrate

Abstract:
Groundwater nitrate concentrations are elevated and rising in many aquifers throughout the world, including those in Wisconsin. High nitrate concentration in groundwater can lead to human health problems and can contribute to eutrophication in ecosystems. Many comparative studies have shown that denitrification rates are positively related to organic carbon quantity. However, there have been few manipulative studies in field settings that have addressed how carbon quantity affects groundwater nitrate removal. Even less is known about how carbon quality, especially particulate organic carbon (POC) quality, regulates denitrification of groundwater nitrate. The overall objective of the proposed research project is to determine how POC quantity and quality influence groundwater nitrate removal and retention in stream sediments. We propose to use field experiments to test the following hypotheses: 1) POC supply (quantity) limits denitrification rate and nitrate retention in stream sediments with high concentrations of groundwater nitrate; 2) Denitrification rate and nitrate retention in stream sediments will increase with POC quality. POC quantity and quality will be manipulated in Emmons Creek, a high-nitrate groundwater-fed stream in the Central Sand Ridges Ecoregion of Wisconsin. In Year 1, POC of different quantities will be buried in sandy sediments within open-ended mesocosms deployed in Emmons Creek. In Year 2, POC of varying quality, at identical quantities, will be buried in sandy sediments in the mesocosms. Response variables in both years will include denitrification rate (based on acetylene block assays using sediment slurries and measurements of in situ N_2 concentrations in the field), net nitrate and ammonium retention along groundwater flow paths, and groundwater dissolved oxygen profiles. The project will be one of the first studies to use manipulative experiments to test how organic carbon quantity and quality affect removal of groundwater nitrate.

Location of Research:
Field: Emmons Creek in Portage County, WI Lab: University of Wisconsin Oshkosh, Upper Midwest Environmental Sciences Center (La Crosse, WI), University of Arkansas

Investigator(s):
Robert Stelzer, UW-Oshkosh (Principal Investigator)
Thad Scott, Other (Associate Investigator)
Lynn Bartsch, Other (Associate Investigator)

Silage Leachate: Waste Quality Assessment and Treatment

Basic Information

Title:	Silage Leachate: Waste Quality Assessment and Treatment
Project Number:	2011WI298O
Start Date:	7/1/2011
End Date:	6/30/2013
Funding Source:	Other
Congressional District:	2nd
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Solute Transport, Nitrate Contamination
Descriptors:	
Principal Investigators:	, Rebecca A Larson

Publications

There are no publications.

WRI: FY 2012 State of Wisconsin Groundwater Research and Monitoring Proposals

Proposal Number:
12-CTP-01

Title:
Silage Leachate: Waste Quality Assessment and Treatment

Abstract:
Silage leachate is a high strength waste which contributes to groundwater contamination of various pollutants, including arsenic and nitrates, by direct leaching through concrete storage structures and infiltration of runoff. Feed storage is required for the majority of livestock operations in the state and country, leading to widespread contamination. Limited data on silage leachate quality and treatment has made management and regulation based solely on observation. The proposed project will assess the water quality characteristics of silage leachate from various feed sources and surrounding environmental factors. Surface and subsurface sample collection from feed storage structures will be analyzed for a number of parameters to assess water quality. Data analysis will have direct implications to current management and treatment of silage leachate, and control of parameters that have a direct effect on production and movement to waterways. Hydrologic data in combination with pollutant concentrations will provide the data needed to develop models for predictive tools which aid in management and treatment design. Direct management applications include determination of first flush volumes required for separation of waste streams to ease management in terms of operation and cost, reduce loading to treatment systems, and reducing the overall environmental impact. Finally, current filter strip treatment designs result in leaching of nitrates (lack of denitrifying or anaerobic zone) and metals (anaerobic soil conditions) as determined from recent research, indicating a need for a multi-step treatment system. An innovative proof of concept deign is to be evaluated with a multiple cell design to increase depth of treatment, and decrease nitrate and metal leaching. Assessment of surface and subsurface performance of the modified agricultural filter strip treatment system will provide additional information for future designs, and have the potential to apply a cost effective solution directly to current treatment practices. This would have a direct impact of groundwater and surface water contamination. In addition, the research proposed falls in line with continuing research for all land applied waste, having a larger impact on ground and surface water contamination through increased application.

Location of Research:
Wisconsin Dairy Farm

Investigator(s):
Rebecca Larson, UW-Madison (Principal Investigator)
John Panuska, UW-Madison (Associate Investigator)

Information Transfer Program Introduction

The University of Wisconsin Water Resources Institute (WRI) facilitates research, training and information transfer on state, regional and national water resource problems. It is the focal point for water resources research, education and outreach within the University of Wisconsin System, fostering strong collaborative scientific exploration that links researchers with state water managers and users statewide.

The new knowledge and technology born of WRI-funded work is shared with varied audiences and is within the scope of work of the information transfer program. Depending on the receiving audiences, the non-advocating, science-based information then leads to certain activities and results. For WRI's research audience, it is inspiration for further work, or validation of prior work. For WRI's policy maker/decision maker audience, it leads to science-based policies and decisions. For WRI's student audience, it encourages a career in the water resources field, and fosters the skills needed for success. For WRI's general public audience, it builds science literacy, which in turn, leads to understanding and stewardship of water resources.

The information transfer program adopts both strategic and tactical methods to disseminate WRI results and techniques. Information is pushed out through the program's websites, outreach activities, social media channels, earned media efforts and publications of various types. This ensures the latest water-related research findings and processes reach those who will convert it to further results. Faculty, staff and students; public officials; administrators; and industry representatives rely on WRI as a source of objective, scientifically sound information.

University of Wisconsin Water Resources Institute - 5 Year Information Transfer Program

Basic Information

Title:	University of Wisconsin Water Resources Institute - 5 Year Information Transfer Program
Project Number:	2011WI265B
Start Date:	3/1/2011
End Date:	2/28/2015
Funding Source:	104B
Congressional District:	WI-2
Research Category:	Not Applicable
Focus Category:	Education, Climatological Processes, Groundwater
Descriptors:	
Principal Investigators:	Moira Harrington

Publications

1. White, Elizabeth; Carolyn Rumery Betz; Aaron Conklin; Moira Harrington; Ann Moser. 2011, Volume 1 Aquatic Sciences Chronicle 8 pages
2. White, Elizabeth; Carolyn Rumery Betz; Aaron Conklin; Moira Harrington; Ann Moser. 2011, Volume 2 Aquatic Sciences Chronicle 8 pages
3. White, Elizabeth; Carolyn Rumery Betz; Aaron Conklin; Moira Harrington; Ann Moser. 2011, Volume 3 Aquatic Sciences Chronicle 10 pages
4. White, Elizabeth; Carolyn Rumery Betz; Aaron Conklin; Moira Harrington; John Karl; Ann Moser. 2011, Volume 4 Aquatic Sciences Chronicle 12 pages
5. Karl, John Streams Neutralize Nitrates in Groundwater 2011 5:51-minute video
6. Harrington, Moira; Aaron Conklin. wri.wisc.edu program website
7. Moser, Anne; Sarah Leeman. aqua.wisc.edu/waterlibrary program website
8. Conklin, Aaron; Carolyn Rumery Betz; Moira Harrington. facebook.com/UWiscSeaGrant Facebook page for University of Wisconsin Water Resources Institute and University of Wisconsin Sea Grant Institute
9. Conklin, Aaron; Carolyn Rumery Betz, Moira Harrington. @UWiscSeaGrant Twitter address for both University of Wisconsin Water Resources Institute and University of Wisconsin Sea Grant Institute
10. Rumery Betz, Carolyn; et al. 2011,35th Annual Meeting Program and Abstracts Wisconsin's Role in Great Lakes Restoration, American Water Resources Association, Wisconsin Section. 76 pages
11. Babiarz, Christopher; James P. Hurley; David P. Krabbenhoft; James G. Wiener July, 19, 2011, Wisconsin Leads the World in Mercury Research opinion-page column, 2 pages
12. Rumery Betz, Carolyn; Kevin Masarik.March 7, 2011 Spring is a Good Time to Test Well Water news release, 2 pages
13. Rumery Betz, Carolyn; Kevin Masarik.March 2, 2011 Celebrate Groundwater Awareness Week by Properly Filling and Sealing Unused Wells news release 2 pages
14. Rumery Betz, Carolyn; Kevin Masarik March 1, 2011 Dispelling Groundwater Myths news release 2 pages

The University of Wisconsin Water Resources Institute (WRI) Information Transfer Program is multi-platform and targeted to researchers, professionals and resource managers, along with members of the general public to build science literacy. It is an ongoing project.

In this reporting period, the program presented on Wisconsin's changing climate to significant national audiences, as well as K-12 instructors in Wisconsin; distributed fact sheets, news releases, publications, a quarterly newsletter, an opinion-page column, messages through social media outlets and a new video; fostered good media relations through meetings with newspaper editorial boards; maintained two websites; co-sponsored and planned a major statewide conference on water resources; and maintained and expanded a library on water resources that also conducts outreach through presentations.

Information Transfer and Outreach Activities

WRI information transfer activities reach professionals in water resources research and management to: expand the scientific body of knowledge, ensure translation of the research into sustainable practices and produce highly qualified professionals. Information transfer also reaches members of the general public to build a better-informed citizenry. The knowledge transfer happens through outreach, such as to the national American Water Resources Association meeting that in 2011 featured two presentations on Wisconsin's changing climate by a WRI staff member. That staff member was also invited to share the presentation with the U.S. EPA's Office on Water in Washington, D.C. Finally, the climate change presentation was modified and delivered to Wisconsin K-12 educators to encourage that group to adopt more climate change lessons into curriculum.

In this reporting period, the information transfer project also distributed six news releases, met with the editorial board at two Wisconsin daily newspapers and distributed an opinion-page column regarding mercury in aquatic environments.

Social media offers the means to speak directly, and interactively, with engaged audiences interested in water resources. WRI reached an estimated 48,000 people a week through Facebook, Twitter, Flickr, YouTube and Tumblr.

The WRI website, wri.wisc.edu, orients visitors to the Wisconsin program and includes a variety of information for those interested in water-related issues. One of the site's main audiences is researchers. To that end, the site provides a clear navigational path to the WRI project listing, project reports, groundwater research database, funding opportunities and conference information sections. The areas are updated on a regular basis to ensure currency of information transfer. The WRI site had 26,500 visitors in this reporting period. The topics of funding opportunities and previously funded projects drew the most visitors.

Wisconsin Water Resources Institute Publications, Videos and Audio Podcasts

An online publication store, aqua.wisc.edu/publications, serves as a one-stop location to download no-cost WRI material, or to access material to purchase at a nominal fee. The three most popular publications in this reporting period were all no-cost and included a fact sheet on groundwater drawdown, with the PDF being accessed 1,582 times; “Design Guidelines for Stormwater Bioretention Facilities,” with 1,279 downloads; and a booklet, “Climate Change in the Great Lakes Region,” appealing to 457 people who downloaded it.

The program’s YouTube channel, youtube.com/asc, was revamped during this reporting period to better categorize and display its videos. In this reporting period, a new video was produced and added to the channel. It details the work of researchers looking into the role streams may play in neutralizing nitrates in groundwater. One of the most popular videos on the channel is “Testing Well Water for Microorganisms.” It has more than 3,200 views, a large number for such a scientific topic. The video garnered a national communications award, an APEX, in 2011.

WRI is also reaching audiences through an informative and entertaining seven-part audio podcast about mercury in aquatic environments. The series is offered through the WRI site, as well as through the University of Wisconsin-Madison iTunes University site.

Water Resources Research Highlighted in Newsletter

The Aquatic Sciences Chronicle is published quarterly and distributed to more than 2,700 subscribers. Chronicle readers include local and state water management agencies; faculty, staff and students; water-related non-governmental organizations; peer WRI personnel; and members of the news media. During this reporting period, Chronicle news stories have included details on the use of fiber optic cable in groundwater research, stream sediments and nitrates, the impact of biofuel cultivation on groundwater and announcements about water-related meetings.

AWRA 2011 Annual Conference

The Wisconsin Section of the American Water Resources Association conducts an annual meeting. WRI assists with meeting planning and provides material support, as a co-sponsor, for the gathering. In 2011, nearly 200 people attended. WRI contributed two presentations and one poster as well. The plenary session focused on Wisconsin’s role in Great Lakes Restoration. Other conference sponsors were the University of Wisconsin-Stevens Point Center for Watershed Science and Education, Wisconsin

Department of Natural Resources, Wisconsin Geological and Natural History Survey and the U.S. Geological Survey's Wisconsin Water Science Center.

Wisconsin's Water Library Outreach Activities

Wisconsin's Water Library disseminates objective, science-based information to government agencies, the research community, the private sector and the public. It reaches out with a water research guide (researchguides.library.wisc.edu/waterresearchguide), presentations in the community and through social media. The library has prepared recommended reading lists on topics such as climate change, groundwater, water conservation and water supply. Library personnel respond to specific water-related queries.

Library staff regularly assesses literature in the field and acquires appropriate material to maintain the collection's relevancy. There are now more than 30,000 volumes, with a particular focus on groundwater and the Great Lakes. About 1,400 library publications annually are loaned to state and local water resources agencies, state and federal legislators, UW-Extension and other university outreach staff, K-12 teachers and students, and environmental organizations, as well as the interested public. In 2003, Wisconsin's Water Library became the first academic library in the state to make its collection available to the general public.

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.

Library staff members have forged a science-literacy-building relationship with the Ho-Chunk Nation of Wisconsin. Staff have conducted monthly story hours with the nation's youngest members. Staff also participate in a similar program in Madison, Wis., in a neighborhood with high numbers of economically disadvantaged youth.

Library Website and Online Tools

The library maintains several information transfer tools to reach library patrons and the most frequently accessed is the library's website (aqua.wisc.edu/waterlibrary), which had 85,607 visitors during this reporting period.

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

The library employs Web 2.0 tools to reach new library patrons and raise visibility. A blog, aqualog2.blogspot.com, reports on news, publications, and resources about water and the Great Lakes. The blog has seen increased usage over the time it has been active. The library also reaches audiences through Facebook and Twitter.

Student Supported

Name: Sarah Leeman

Campus: University of Wisconsin-Madison

Advisor: Anne Moser

Advisor Campus: University of Wisconsin-Madison

Degree/Training: Master of Library Science

Graduation: May 2012

Department: Library and Information Studies

Program of Degree: Library and Information Studies

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	5	1	0	0	6
Masters	2	2	2	1	7
Ph.D.	2	0	1	1	4
Post-Doc.	0	2	0	1	3
Total	9	5	3	3	20

Notable Awards and Achievements

Professor Craig Benson was elected to the National Academy of Engineering in January 2012, with a citation to his work related to long-term containment of low-level radioactive wastes.

"Testing Well Water for Microorganisms," a video in the collection of the University of Wisconsin Water Resources Institute (WRI) won a 2011 national Apex Award of Excellence. The video focuses on the WRI-funded work of University of Wisconsin-Madison post-doctoral research associate Sam Sibley, who is using a filtration system to detect the sources of bacterial contamination in rural wells near Fond du Lac, Wis.

Three students of Professor Zhaohui Li (Caren J. Ackley, Laura Schulz, and Nancy Fenske) received the 2010 undergradduate best poster award from the American Water Resources Association Wisconsin Section for their presentation on “Removal of tetracycline by kaolinite”

A WRI staff member was invited to make a special presentation of Wisconsin climate change data to the U.S. EPA's Office on Water in Washington, D.C

Publications from Prior Years

1. 2006WI136B ("Assessing the Ecological Status and Vulnerability of Springs in Wisconsin") - Dissertations - Bartkowiak, B. 2007. Geochemical and flow characteristics of two contact springs in Iowa County, Wisconsin. B.S. Thesis, Department of Geology, Beloit College, Beloit Wisconsin.
2. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Articles in Refereed Scientific Journals - Benson, C, A Sawangsuriya, B Trzebiatowski, and W. Albright. (2007), Post-Construction Changes in the Hydraulic Properties of Water Balance Cover Soils, J. Geotech. and Geoenvironmental Eng., 133(4), 349-359.
3. 2007WI204O ("Monitoring Septic Effluent Transport and Attenuation using Geophysical Methods") - Dissertations - Summitt, A. 2009. Geophysical Mapping of Septic Effluent and the Evaluation of Performance of Mounded Septic Leach Fields. MS Thesis, Geological Engineering, University of Wisconsin-Madison
4. 2005WI005O ("Climate Signals in Groundwater and Surface Water System: Spectral Analysis of Hydrologic Processes") - Articles in Refereed Scientific Journals - Namdar GR, HR Bravo, JJ Magnuson, WG Hyzer, BJ Benson 2009. Coherence between Lake Ice Cover, Local Climate, and Teleconnections (Lake Mendota, Wisconsin) Journal of Hydrology, 374(3-4):282-293 DOI:10.1016/j.jhydrol.2009.06.024
5. 2005WI005O ("Climate Signals in Groundwater and Surface Water System: Spectral Analysis of Hydrologic Processes") - Articles in Refereed Scientific Journals - Namdar GR, HR Bravo. 2009. Trend and Oscillations in the Ice Cover Duration of Lake Mendota, Wisconsin, Hydrological Sciences Journal. 54(3): 497-512 DOI: 10.1623/hysj.54.3.497
6. 2006WI136B ("Assessing the Ecological Status and Vulnerability of Springs in Wisconsin") - Articles in Refereed Scientific Journals - Swanson SK, KR Bradbury, and DJ Hart. 2009. Assessing the vulnerability of spring systems to groundwater withdrawals in southern Wisconsin, Geoscience Wisconsin 20 (1).
7. 2007WI199S ("Grant No. 08HQGR0001 Alternative Cover Guidance Document") - Other Publications - Albright W, C Benson, and W Waugh. 2010. Water Balance Covers for Waste Containment: Principles and Practice, ASCE Press, Reston, VA, 158 p.
8. 2007WI203O ("Influence of Wetland Hydrodynamics on Subsurface Microbial Redox Transformations of Nitrate and Iron.") - Articles in Refereed Scientific Journals - Craig L, J Bahr and E Roden. 2010. Localized zones of denitrification in a floodplain aquifer in southern Wisconsin, Hydrogeology Journal, 18(8): 1867-1879
9. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Book Chapters - Benson C and J Scalia (2010), Chapter 10: Hydrologic Performance of Final Covers Containing GCLs, in Geosynthetic Clay Liners for Waste Containment Facilities, A. Bouazza and J. Bowders, eds., CRC Press, Boca Raton, FL, 203-211.
10. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Conference Proceedings - Benson C and J Scalia. (2010), Hydraulic Conductivity of Exhumed Geosynthetic Clay Liners from Composite Barriers, Proc. 3rd International Symposium on Geosynthetic Clay Liners, SKZ ConSem GmbH, Wurzburg, Germany, 73-82.
11. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Articles in Refereed Scientific Journals - Benson C, I Kucukkirca, and J Scalia. (2010), Properties of Geosynthetics Exhumed from the Final Cover at a Solid Waste Landfill, J. Geotextiles and Geomembranes, 28, 536-546, doi:10.1016/j.geotexmem.2010.03.001.
12. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Articles in Refereed Scientific Journals - Scalia J and C Benson. (2010), Preferential Flow in Geosynthetic Clay Liners Exhumed from Final Covers with Composite Barriers, Canadian Geotechnical J., 47, 1101-1111.
13. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Articles in Refereed Scientific Journals - Scalia J and C Benson. (2010), Effect of Permeant Water on the Hydraulic

Conductivity of Exhumed Geosynthetic Clay Liners, Geotechnical Testing J., 33(3), 1-11.

14. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Other Publications - Schlicht P, C Benson, J Tinjum, and W Albright. (2010), In-Service Hydraulic Properties of Two Landfill Final Covers in Northern California, GeoFlorida 2010, Advances in Analysis, Modeling, and Design, Geotechnical Special Publication No. 199, D. Fratta, A. Puppula, and B. Muhunthan, eds., ASCE, Reston, VA, 2867-2877
15. 2006WI179S ("Grant No. 07HQGR0025 Effectiveness of Engineered Covers: From Modeling to Performance Monitoring") - Other Publications - Benson C, W Albright, D Fratta, J Tinjum, E Kucukkirca, S Lee, J Scalia, P Schlicht, X Wang. 2011. Engineered Covers for Waste Containment: Changes in Engineering Properties & Implications for Long-Term Performance Assessment, NUREG/CR-7028, Office of Research, U.S. Nuclear Regulatory Commission, Washington.
16. 2005WI005O ("Climate Signals in Groundwater and Surface Water System: Spectral Analysis of Hydrologic Processes") - Articles in Refereed Scientific Journals - Namdar G. R., and H.R. Bravo. 2011. Evaluation of Correlations between Precipitation, Groundwater Fluctuations, and Lake Level Fluctuations Using Spectral Methods (Wisconsin, USA), Hydrogeology Journal, 19(4):801-810. DOI:10.1007/s10040-011-0718-1
17. 2005WI005O ("Climate Signals in Groundwater and Surface Water System: Spectral Analysis of Hydrologic Processes") - Articles in Refereed Scientific Journals - Namdar GR, and HR Bravo. 2011. Coherence among Climate Signals, Precipitation, and Groundwater, Ground Water Journal. 49(4):455-615. DOI:10.1111/j.1745-6584.2010.00772.x
18. 2009WI217B ("The Lethal and Sublethal Effects of Elevated Groundwater Nitrate Concentrations on Infaunal Invertebrates in the Central Sand Plains") - Articles in Refereed Scientific Journals - Stelzer RS, LA Bartsch, WB Richardson, and EA Strauss. 2011. The dark side of the hyporheic: nitrogen processing and profiles in deep stream sediments. Freshwater Biology, 56:2021-2033. DOI: 10.1111/j.1365-2427.2011.02632.x
19. 2007WI204O ("Monitoring Septic Effluent Transport and Attenuation using Geophysical Methods") - Articles in Refereed Scientific Journals - Summitt A, DJ Hart, K Masarik, and D Fratta. 2011. Evaluation of Septic Tank Effluent Fate using Geophysical Imaging Techniques. Journal of Environmental Quality (In Prep).
20. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Articles in Refereed Scientific Journals - Scalia J and C Benson. (2011), Hydraulic Conductivity of Geosynthetic Clay Liners Exhumed from Landfill Final Covers with Composite Barriers, J. Geotech. and Geoenvironmental Eng., 137(1), 1-13.
21. 2005WI154O ("Validation of transport of VOCs from Composite Liners") - Articles in Refereed Scientific Journals - Park MG, CH Benson and TB Edil, 2012, Comparison of Batch and Double Compartment Tests for Measuring Geomembrane-VOC Transport Parameters, Geotextiles and Geomembranes, 31:15-30.
22. 2005WI154O ("Validation of transport of VOCs from Composite Liners") - Articles in Refereed Scientific Journals - Park MG, TB Edil and CH Benson, 2012, Modeling Volatile Organic Compound Transport in Composite Liners, Journal of Geotechnical and Geoenvironmental Engineering, American Society of Civil Engineers, 138(6).
23. 2007WI210O ("Multi-Parameter, Remote Groundwater Monitoring with Referencing Using Crossed Optical Fiber Fluorescent Sensor Arrays.") - Articles in Refereed Scientific Journals - Henning PE, MV Rigo, and P Geissinger. 2012. Fabrication of a Porous Fiber Cladding Material Using Microsphere Templating for Improved Response Time with Fiber Optic Sensor Arrays. The Scientific World Journal Analytical Chemistry. 876106 (7 pp)
24. 2007WI200S ("Grant No. 07HQGR0170 ACAP Test Section Exhumation") - Articles in Refereed Scientific Journals - Albright W, C Benson, and P Apiwantragoon. (2012), Field Hydrology of Landfill Final Covers with Composite Barrier Layers, J. Geotech. and Geoenvironmental Eng., In Press