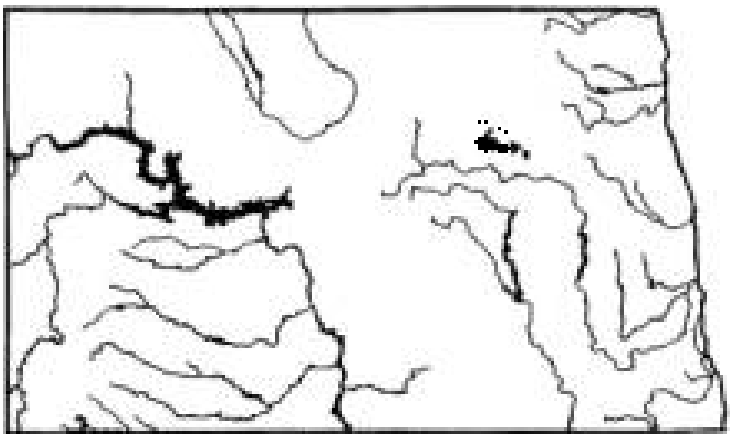

North Dakota
Water Resources Research Institute

North Dakota State University
University of North Dakota

ANNUAL REPORT

For the Period March 2008 to February 2009

Fiscal Year 2008 Report to the U.S. Geological Survey

July 2009

Annual Report

Fiscal Year 2008 Report to the U.S. Geological Survey

Award No. 06-HQ-GR-0104
U.S. Geological Survey

G. Padmanabhan, Director
North Dakota Water Resources Research Institute
North Dakota State University
Fargo, ND 58105

July 2009

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The contents of this publication do not necessarily reflect the views and policies of the Department of Interior, nor does mention of trade names or commercial products constitute their endorsement by the United States Government.

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INTRODUCTION

This report describes the activities of the North Dakota Water Resources Research Institute (NDWRRI) during the period of March 1, 2008 to February 28, 2009.

The ND WRRI is one of the 54 institutes known collectedly as the National Institutes for Water Resources (NIWR). The NDWRRI was founded in 1965, by authority of Congress (Water Resources Research Acts of 1964, 1972, 1984, and 1990), and is administrated through the United States Geological Survey. Section 104 of the Water Resources Research Act requires the NDWRRI to apply its Federal allotment funds to:

1. Plan, conduct or otherwise arrange for competent research that fosters: (A) the entry of new research scientists into the water resources field, (B) training and education of future water resources scientists, engineers, and technicians; (C) the preliminary exploration of new ideas that address water problems or expand understanding of water and water-related phenomena; and (D) the dissemination of research results to water managers and public.

2. Cooperate closely with other college and universities in the state that have demonstrated the capability for research, information dissemination and graduate training, in order to develop a statewide program designed to resolve State and regional water and related land problems.

3. Cooperate closely with other institutes and other organizations in the region to increase the effectiveness of the Institute and for the purpose of promoting regional cooperation.

This year, NDWRRI once again allocated its 104(B) resources to fund the Graduate Fellowship research projects. The institute also continued its efforts to enhance communications between the State and Federal agency personnel and university faculty and students. NDWRRI also worked closely with the Environmental and Conservation Sciences program of North Dakota State University (NDSU), Natural Resources Management program of NDSU, Energy and Environmental Research Center at University of North Dakota (UND), the International Water Institute, Fargo, ND, and the North Dakota Experimental Program to Stimulate Competitive Research (ND EPSCoR) of the National Science Foundation (NSF) on water related research issues and collaboration.

Program Management

The Institute continued the same administrative mechanism with a director managing the institute program with the help of a State Advisory Committee. Dr. G. Padmanabhan, Professor of Civil Engineering, is the director. Linda Charlton, a NDSU employee, has been working part-time for the Institute to assist the director with Institute finances, communications and information transfer. The State Advisory Committee consists of three members representing the three principal water agencies in North Dakota: State Water Commission, State Department of Health, and the USGS North Dakota District. In addition, the Institute also has a Technical Advisory Committee consisting of faculty from the two research universities of the State: North Dakota State University and University of North Dakota.

State Appropriation

The State Water Commission continued its support to the 2008 – 2009 federal 104(B) funding for the Graduate Research Fellowship program of NDWRRI. This is fifth year the SWC provided 15% match in support of the Fellowship program.

University Support

North Dakota State University and the University of North Dakota administrations consider the NDWRRI activities important and are supportive of its efforts. NDSU provides approximately 2% cash matching.

Institute Location

The Institute continues to operate from the Administrative Building of the College of Engineering and Architecture of North Dakota State University in Fargo, North Dakota, The director may be reached at:

ND Water Resources Research Institute
North Dakota State University
Department of Civil Engineering
Fargo, ND 58105
Phone: (701) 231-7043
Fax: (701) 231-6185
E-mail: G.Padmanabhan@ndsu.edu

State Advisory Committee

The State Advisory Committee provided guidance on water resources research priorities in the State and region, and participated in the review and evaluation of research proposals and projects. The current committee members are:

> Gregg Wiche, District Chief, U.S. Geological Survey, Water Resources Division, Bismarck, North Dakota
>
> William Schuh, Water Appropriation Division, North Dakota State Water Commission, Bismarck North Dakota
>
> Mike T. Sauer, Environmental Health Section, North Dakota Department of Health, Bismarck, North Dakota

The committee members are senior officials in the three agencies in North Dakota responsible for much of the water resources research done outside of NDSU and UND in North Dakota.

RESEARCH PROGRAM

ANNUAL BASE GRANT (104-B)

In the past several years NDWRRI has offered competitive fellowships to NDSU and UND graduate students for research on water resources topics under a Graduate Research Fellowship (GRF) program effectively using the modest amount of the 104(B) annual base grant. The program meets the requirements of Section 104 of the Water Resources Research Act of 1984. The fellowship program encourages entry of young university faculty and new research scientists into the water resources field; provides training and education to future water resource scientists and engineers; promotes exploration of new ideas that address water problems or expand understanding of water quantity, quality and related phenomena; and engages university faculty in collaborative research programs seeking supports from entities concerned with water problems.

This year, the NDWRRI continued the GRF program and applied bulk of the federal allotment to it. The GRF program is administrated and monitored by the director. Applications are invited from the graduate students and their advisors of the two research universities of the State, NDSU and UND. A rigorous review by the State Advisory Committee and other water professionals in the state determines the awards. Active participation of the academic advisors of the students in meeting matching requirement and seeking co-funding from local, state and other sources is another positive aspect of the program. Periodical review of the progress of the students in meeting the fellowship expectations is ensured by seeking reports from the students and by encouraging them to make presentations in local and regional technical seminars and conferences.

Guidelines for the 2007-2008 Graduate Research Fellowship competition were posted on the Institute website in September 2007, and the competition was announced in the faculty news publications of the two university campuses in last week of October. The following is the request for application that was published on the UND and NDSU campus newsletters, and distributed by e-mail lists:

ND WRRI invites applications for 2008 graduate research fellowships

The North Dakota Water Resources Research Institute (ND WRRI) has announced its 2008 Graduate Research Fellowship program.

NDSU and University of North Dakota graduate students who are conducting or planning research in water resources areas may apply for fellowships varying from three summer months to a full year in duration. Typically in the past fellowship awards for master's degree students have been in the range $800-$1,000 and for doctoral students it has been $1,000-$1,400 per month. The fellowship funds must be applied between March 1, 2008, and Feb. 28, 2009.

Projects proposed for fellowship support should relate to water resources research issues in the state or region. Regional, state or local collaborations or co-funding will strengthen an application. Fellowships have a matching requirement of two non-federal dollars to one federal dollar. Applicants should have a plan of study filed and should have a thesis research topic chosen at the time of applying. Applications need to be prepared in consultation with advisers. Advisers of the applicant should co-sign the applications. Applications from students and advisers who have not met the reporting requirements of their previous fellowship projects will not be considered for funding.

The general criteria used for proposal evaluation include scientific merit, originality of research, research related to state or region, and extent of regional, state or local collaboration and/or co-funding.

Applications are due in the office of the director by 5 p.m., Nov. 16. The proposals will be reviewed by a panel of faculty members and state water resources research professionals. Announcement of awards will be made by early January.

Consult the ND WRRI Web site, www.ndsu.edu/wrri, for background on the program, and guidelines for preparation of applications. Applicants and advisers who are new to the program are urged to contact ND WRRI director, G. Padmanabhan, at 1-7043, or G.Padmanabhan@ndsu.edu.

Send applications to Dr. G. Padmanabhan, Director of North Dakota Water Resources Research Institute, NDSU, CIE 201E, Department of Civil Engineering, P.O. Box 5285, Fargo, ND 58105.

NDWRRI GRADUATE RESEARCH FELLOWSHIPS

Fellowships ranging from $5000 to $15,800 were awarded to graduate students from UND (one) and NDSU (six) conducting research in water resources areas. Selection of student Fellows and the award amounts were based on competitive proposals prepared by the students with the guidance of their advisers. Projects proposed for fellowship support should relate to water resources research issues in the state or region. Regional, state, or local collaboration or co-funding is encouraged. Fellowships have a matching requirement of two non-federal dollars to one federal dollar. A panel of state water resource professionals reviews the proposals and selects the Fellows and award amounts based on the quality of proposals and the priority of the proposed projects for the state and region. The general criteria used for proposal evaluation include: scientific merit, originality of research, research related to state and/or region, and extent of regional, state or local collaboration and/or co-funding.

This year, sixteen applications were received: ten Ph.D. and six MS students. Not all applications could be funded. Highly competitive proposals and limited availability of funds restricted the number and the amount of awards. Seven Fellowships (5 Ph. D. and 2 M.S.) were awarded. Three of the Fellowships were renewals, one M.S. and two Ph.D. The renewals are Yuhui Jin (Ph. D), Sita Krajangpan (Ph. D), and Jay Thompson (M. S.).

The titles of the fellowship projects awarded are given below and details are provided for each project under separate project sections.

2008-09 Fellows and their projects

Graduate Student	Project Title	Advisor
Dimuthu Wijeyaratne, Environmental and Conservation Sciences, NDSU	Chemical Fingerprinting of Sediments and Water of the Souris River for Indentification of Diffuse Pollution Sources	Dr. Marinus Otte , Department head and Professor of Biological Sciences, NDSU
Harjyoti Kalita, Materials and Nanotechnology, NDSU	Iron Imprinted Polymer for Removal and Monitoring of Arsenic	Dr. Achintya Bezbaruah, Assistant Professor, Department of Civil Engineering and Dr. Bret Chisholm, Senior Research Scientist, Center for Nanoscale Science and Engineering, NDSU
Jay M. Thompson, Civil Engineering, NDSU	Selected Pesticide Remediation with Iron Nanoparticles: Modeling and Barrier Applications	Dr. Achintya Bezbaruah, Assistant Professor, Department of Civil Engineering, NDSU
Qigang Chang, Environmental and Conservation Sciences, NDSU	Development of GAC-NZVI Adsorbent for Arsenic Removal	Dr. Wei Lin, Associate Professor, Department of Civil Engineering, NDSU
Rabiya Shabnam, Environmental and Conservation Sciences, NDSU	Interactions between Microorganisms and Metal Nanoparticles: A New Approach for Groundwater Remediation	Dr. Achintya Bezbaruah, Assistant Professor, Department of Civil Engineering, NDSU
Sita Krajangpan, Civil Engineering, NDSU	Modification of Iron Nanoparticles by Amphiphilic Polysiloxane Graft Co-Polymer for Arsenic, TCE, and RDX Remediation	Dr. Achintya Bezbaruah, Assistant Professor, Department of Civil Engineering and Dr. Bret Chisholm, Senior Reserach Scientist, Center for Nanoscale and Engineering, NDSU
Yuhui Jin, Chemistry, UND	Rapid and Sensitive Determination of Bacteria in Water Using Nanoparticles	Dr. Julia Zhao, Assistant Professor, Department of Chemistry, UND

NATIONAL COMPETITIVE PROGRAM (104-G)

No proposal was submitted through the ND Institute. Two projects continued through the period of this report.

INFORMATION DISSEMINATION

Information dissemination is done through an annual newsletter initiated in 1992, a website initiated in 1999, and presentations and publications by grant and fellowship recipients. The institute's website address is http://www.ndsu.edu/wrri. The newsletter is usually issued in the month of December of each year. Past newsletters can be accessed through the institute web site. Technical reports of Fellowship projects authored by the Fellows and advisers are also placed on the institute web site.

The North Dakota Water Resources Research Institute sponsored a day of seminars by WRRI Research Fellows and advisors at the North Dakota Heritage Center, Bismarck, on April 15th, 2008.

The presentations can be viewed online or downloaded from the link:

http://www.swc.state.nd.us/4dlink9/4dcgi/GetSubCategoryRecord/News%20and%20Information/WRRI%20Sponsors%20Seminars

The advisory committee of the Institute consisting of Bill Schuh of North Dakota State Water Commission, Gregg Wiche of US Geological Survey, and Mike Sauer of North Dakota Department of Health has been instrumental to host the event in Bismarck. There were twelve presentations attended by more than sixty water professionals.

Standing (left to right): Mike Sauer (WRRI Advisoyr committee member), Sita Krajangpan (Fellow), William Schuh (WRRI ACM), Thunyalux Ratpakdi (F), Achintya Bezbaruah (Faculty Adviser), Eakalak Khan (FA), Jay Thompson (F), Edward Dekeyser(FA), Breanna Paradeis (F), Mary Schuh (F), Donald Kirby (FA), Harjyoti Kalita (F)

Sitting (left to right): Marinus Otte (FA), Dimuthu Wijeyaratne (F), Ryan klapperich (F), Scott Korom (FA), Rubiya Shabnam (F), Julia Zhao (FA), G. Padmanabhan (WRRI Director)

Phil Gerla (FA), Yuhui Jin (F), Damion Knudsen (F), and Gregg Wiche (WRRI ACM) could not join the group and missed the photo opportunity.

Presentation Schedule

8:45 Introduction - Bill Schuh, ND State Water Commission

8:50 The North Dakota Water Resource Research Institute- Dr. G. Padmanabhan, Director

9:00 Morning Session - Moderator Gregg Wiche, USGS, Bismarck

9:05 Yuhui Jin and Julia Zhao: *Simultaneous determination of multiple-bacteria using fluorescent nanoparticles*

9:30 Damion Knudsen and Bernhardt Saini-Eidukat: *High resolution site characterization for ground water monitoring.*

9: 55 Breanna Paradeis and Donald Kirby: *Community composition and function of wetlands located in restored prairie*

10:20 Break

10:45 Ryan Klapperich and Scott Korom: *Electron donor potential of eastern North Dakota shale formations*

11:10 Harjyoti Kalita, Achintya Bezbaruah, Bret Chisholm**:***Ion-imprinted polymers: A new approach to remove arsenic from drinking water*

11: 35 Phil Gerla, Corey Askin, Bill Lenarz, and Andy Bongard: *Hydrological balance and water quality of springs and seeps at Pigeon Point Preserve, Ransom County, North Dakota*

12:00 Lunch

1:00 Afternoon Session - Moderator Mike Sauer, ND State Health Department

1: 05 Rabiya Shabnam, Achintya Bezbaruah: *Groundwater decontamination with metal nanoparticles and microorganisms encapsulated in biopolymer microreactors*

1:30 Sita Krajangpan, Achintya Bezbaruah, Bret Chisholm: *Efficacy of novel polymer coated iron nanoparticles in trichloroethylene (TCE) degradation*

1:55 Dimuthu Wijeyaratne and Marinus Otte: *Chemical fingerprinting of sediments and water of the Souris River for identification of diffuse pollution sources*

2:20 Break

2:35 Thunyalux Ratpukdi and Eakalak Khan: *Fractionation of natural organic matter in water from the Red River and the Moorhead water treatment plant, Minnesota using a novel solid phase extraction technique*

3:00 Mary Schuh and Francis Casey :*Farm-scale reconnaissance of estrogens in subsurface waters*

3:25 Jay Thompson, Achintya Bezbaruah: *Pesticide remediation and treatment using nanoscale zero-valent iron*

3:50 Adjourn

Research results of NDWRRI Graduate Research Fellows were published and presented in various other conferences also.

PUBLICATIONS AND PRESENTATIONS FROM INSTITUTE FUNDED PROJECTS

Publications

Bezbaruah, A.N., **Krajangpan, S**., Chisholm, B.J., Khan, E., Bermudez, J.J.E., (2009). Entrapment of Iron Nanoparticles in Calcium Alginate Beads for Groundwater Remediation Applications, Journal of Hazardous Materials, 166, 1339-1343.

Hearne, R. and **C. Kritsky**. In Press. Characteristics of Active Local Water Management Districts In the Red River Basin. *Water Policy*.

Hill, C. and Khan, E. (2008) A Comparative Study of Immobilized Nitrifying and Co-immobilized Nitrifying and Denitrifying Bacteria for Ammonia Removal from Sludge Digester Supernatant. Water, Air, and Soil Pollution, April 2008.

Jin, Y., Lohstreter, S., Pierce, D.T., Parisien, J., Wu, M., Hall, C. III, Zhao, J. X., "Silica Nanoparticles with Continuously Tunable Sizes: Synthesis and Size Effects on Cellular Imaging," *Chem. Mater.*, **2008**, 20 (13), 4411-4419.

Krajangpan, S., Chisholm, B.J., **Kalita, H**., and Bezbaruah, A.N. Challenges in Groundwater Remediation with Iron Nanoparticles: Enhancement Colloidal Stability (Chapter 8) in Nanotechnologies for Water Environment Applications (Eds: Tian C. Zhang, , Rao Y. Surampalli, Keith C. K. Lai, Zhiqiang Hu, R. D. Tyagi, and Irene M. C. Lo), American Society for Civil Engineers/EWRI, pp. 191-212, 2009. ISBN: 978-0-7844-1030-1

Krajangpan, S., Jarabek, L., Jepperson, J., Chisholm, B., Bezbaruah, A. (2008). Polymer modified iron nanoparticles for environmental remediation. Polymer Preprint, 49, 921.

McEwen, D.C. and Butler, M.G. 2008. Impacts from Water-Level Regulation on Benthic Community Structure in Namakan Reservoir and Rainy Lake, Voyageurs National Park. Natural Resource Technical Report NPS/NRPC/WRD/NRTR-2008/129.

Ratpukdi, T., Bezbaruah, A., Rice, J., Chilom, G., and Khan, E. Rapid Natural Organic Matter Fractionation Using a Novel Solid Phase Extraction Technique. Accepted for Publication in Water Environment Research.

Torpen D. and R. Hearne. (2008) "Stakeholder Preferences for Water Management Alternatives in the Red River Basin." Agribusiness and Applied Economics Report N0. 639. Department of Agribusiness and Applied Economics, North Dakota State University. April, 2008.

Presentations

Butler, M.G. and **D.C. McEwen.** 2008. Predicting aquatic insect growth rates and voltinism as a function of temperature and body mass. Presentation given at the 93rd Annual Conference of Ecological Society of America Meeting, Milwaukee, WI, 3-8 August 2008.

Clark, W.H., **McEwen, D.C.**, and M. Clark. 2008. Land-use effects on white sucker (*Catostomus commersoni*) life history and diet in portions of North Dakota and Minnesota. Presentation given at the 93rd Annual Conference of Ecological Socieity of America Meeting, Milwaukee, WI, 3-8 August 2008.

Hearne, R. and **C. Kritsky**. Characteristics of Active Water Management Organizations in the Red River Basin. Presented at the Western Agricultural Economics Association Annual Meeting. Big Sky, Mt. June 2008

Hearne, R. 2008. Lessons for Improved Local Water Management. Paper presented at the 2008 Spring Extension Conference. Bismark, ND. March 2008.

Hearne, R. and D. Torpen. Stakeholder Preferences for Water Management Alternatives in the Red River Basin. Paper Presented at the W-2133 Annual Meeting Kona Hi., February 2008.

Jin, Y.;***** Lohstreter, S.; Wu, M., Parisien, J.; Zhao, X. Preparation of luminescent silica nanoparticles with controllable sizes. In 100th North Dakota Academy of Science Annual Meeting, Grand Forks, ND, April 24, 2008. (Oral)
Yuhui Jin got the Denison Award, first place award for Graduate student presentation, in the 2008 North Dakota Academy Sciences Annual Meeting.

Jin, Y.;***** Parisien, J., Wu, M., Zhao, X. Multiple bacteria detection using multicolor fluorescent silica nanoparticles based on FRET. In North Dakota Water Resources Research Institute conference, Bismark, ND, April 15, 2008. (Oral)

Jin, Y.;***** Lohstreter, S.; Wu, M., Parisien, J.; Zhao, X. Manipulation of silica nanoparticles on the continuous spectrum. In The Pittsburgh Conference, New Orleans, LA, March 2, 2008. (Oral)

Kalita, H., Chisholm, B., J., Bezbaruah, A., N. "Ion-imprinted Polymers: A new Approach to Remove Arsenic from Drinking Water". AWWA, Surface Water Conference, April 2008 (Poster Presentation).

Korom, S. F., Network of in situ mesocosms: Aquifer denitrification, 8th Annual Meeting on Agricultural Contaminants: Sources, Fate, and Transport, USGS, Ames, IA, March 18 – 20, 2008.

Korom, S. F., and **R. J. S. Klapperich**, Electron donor concentrations in eastern North Dakota shale formations. 53rd Annual Midwest Ground Water Conference, September 29 – October 2, 2008, Dubuque, Iowa.

Krajangpan, S., Chishlom, B., Bezbaruah, A., RFT-247, Novel Polymer Modified Iron Nanoparticles for Environmental Remediation, provisional patent application filed Feb. 2009.

Krajangpan, S., Jarabek, L., Jepperson, J., Chisholm, B., Bezbaruah, A. April 10 2008. The Use of Multifunctional Polymers to Effective Deliver Iron Nanoparticles to Subsurface Contaminants. 235th ACS National Meeting, New Orleans, LA. [Poster]

Krajangpan, S., Bezbaruah, A., Chisholm, B. April 2008. Effective Delivery of Modified Iron Nanoparticles by Amphiphilic Polysiloxane Graft Copolymer for Groundwater Remediation. The 2008 Surface Water treatment Workshop, Moorhead, MN. [Poster]

Krajangpan, S., Bezbaruah, A., Chisholm, B. August 2008. Groundwater Remediation using Polymer coated iron nanoparticles. The 2008 2nd Annual Joint Student Environmental Conference. North Dakota, ND. [Presentation]

Krajangpan, S., Bezbaruah, A., Chisholm, B. October 2008. Increased Efficacy of Zero-valent Iron Nanoparticles in Groundwater Remediation: Development of Polymeric Delivery Vehicle. The 2008 International Environmental Nanotechnology Conference: Applications and Implications, Chicago, IL. [Poster]

Krajangpan, S., Bermudez, J.J.E., Bezbaruah, A.N., Chisholm, B.J., Khan, E. August, 2008. Nitrate Removal by Entrapped Zero-Valent Iron Nanoparticles in Calcium Alginate, 12th International Conference on Integrated Diffuse Pollution Management (IWA DIPCON 2008), Khon Kaen University, Thailand. [Presentation]

Maharjan, B., and S. F. Korom, Correlation of Electron Donor Concentrations in Aquifer Sediments with Sediment Properties: USGS ACT Site near New Providence, Iowa, 53rd Annual Midwest Ground Water Conference, September 29 – October 2, 2008, in Dubuque, Iowa:

McEwen, D.C. and Butler, M.G. 2008. Impacts on aquatic invertebrate communities of altered drawdown magnitude and timing of spring refill in a managed reservoir within Voyageurs National Park, Minnesota Presentation given at the 93rd Annual Conference of Ecological Socieity of America Meeting, Milwaukee, WI, 3-8 August 2008.

McEwen, D.C., and M.G. Butler. 2008. Application of metabolic theory to the determination of life-span, growth rate, and secondary production of benthic macroinvertebrates. Presentation given at the Annual Conference of American Society of Limnology and Oceanography, St. Johns, Newfoundland, 8-13 June 2008.

Paradeis, B.L., E.S. DeKeyser, and D.R. Kirby. 2008. Abstract:Assessment of Plant Community Structure and Function of Restored Prairie Pothole Wetlands. Society of Wetland Scientists 29th Annual Meeting, Washington, D.C.

Paradeis, B.L., E.S. DeKeyser, and D.R. Kirby. 2008. Abstract: Plant Community Composition of Restored Prairie and Wetlands in the Prairie Pothole Region. 3rd Western Wetland Monitoring and Assessment Workgroup Training Workshop, Rapid City, SD.

Rabiya Shabnam, Senay Simsek, **Jay M Thompson**, Eakalak Khan, Achintya Bezbaruah. "Contaminant Diffusion and Degradation Studies with Alginate Encapsulated Iron Nanoparticles." American Chemical Society Meeting March 2009, Salt Lake City, Utah. (Poster)

Rabiya Shabnam, Achintya Bezbaruah, Senay Simsek, Eakalak Khan, John McEvoy, Yildirim Bora Suzen. "Use of Biopolymer to Encapsulate Iron Nanoparticles: Diffusion and Treatability Studies." International Environmental Nanotechnology Conference, Chicago, October 2008. http://www.emsus.com/nanotechconf/abstracts_posters_n-z.htm (Poster)

Rabiya Shabnam, Achintya Bezbaruah, Senay Simsek, Eakalak Khan. "Biopolymer Encapsulated Metal Nanoparticles and Microorganisms for Environmental Remediation." Presented at Annual Joint Student Environmental Conference, August 2008.NDSU. (Presentation)

Rabiya Shabnam, Achintya Bezbaruah, Senay Simsek, Eakalak Khan. "Encapsulation of Iron Nano Particles and Microorganisms with Alginate for Environmental Remediation." AWWA Surface Water Conference, Moorhead, MN, April 2008 (Poster).

Wijeyaratne D., Jacob D and Otte M. (2008) Chemical Fingerprinting of Sediments of the Souris River to assess the transport of phosphorous and other pollutants 5th Annual Northern Plains Biological Symposium, April, 2008. Fargo, ND. [Poster]

Institute Publications

Technical Report No. ND08-01 Eben Spencer
Technical Report No. ND08-02 Damion Knudsen
Technical Report No. ND08-03 Thunyalux Ratpukdi
Technical Report No. ND08-04 Jay Thompson
Technical Report No. ND08-05 Breanna Paradeis
Technical Report No. ND08-06 Mary Schuh
Technical Report No. ND08-07 Brent Hanson
Technical Report No. ND08-08 Seth Lynne
Technical Report No. ND08-09 Ryan Klapperich
Technical Report No. ND08-10 Ali Tackette

The above publications can be accessed via the Institute web site: http://www.ndsu.edu/wrri

THESES AND DISSERTATIONS

De Silva, Nirodha. 2008. Assessing the Organizational Effectiveness of Conservation Districts in the Red River Basin in Minnesota and North Dakota. M.S. thesis in Natural Resources Management. North Dakota State University.

Hanson, Brent. 2008. The Use of Channel Characteristics for the Calibration of Index Velocity Ratings for Acoustic Doppler Velocity Meters. MS Thesis. May 2008. North Dakota State University.

Klapperich, R. J., Salinas. 2008. Electron donor potential of Eastern North Dakota shale formations. MS Thesis. University of North Dakota, 103 pp.

Kritsky, Craig. 2008. Identifying Beneficial Attributes of Water Management Organizations. M.S. Paper in Agribusiness and Applied Economics. North Dakota State University.

Maharjan, B., 2008. Correlation of electron donor concentrations in sediments with sediment properties: New Providence, Iowa. MS Thesis. University of North Dakota, 52 pp.

McEwen, Daniel Clayton. 2008. Impacts of Water Level Regulation on Macroinvertebrate Communities in the Littoral Zone of Lakes. Ph. D. Dissertation. December 2008. North Dakota State University.

Paradeis, Breanna. 2008. Plant Community Composition of Wetlands Located on Restored and Native Prairie. MS Thesis. May 2008. North Dakota State University.

Schuh, Mary. 2008. Farm-Scale Reconnaissance of Estrogens in Subsurface Waters. MS Thesis. November 2008. North Dakota State University

Tackett, Ali. 2008. Genetic distribution and diversity of the Johnny darter (Etheostoma nigrum, Rafinesque) in the upper midwest. MS Thesis. May 2008. North Dakota State University.

Thompson, Jay. 2008. Chlorinated Pesticide Remediation Using Zero-valent Iron Nanoparticles. MS Thesis. May 2008. North Dakota State University.

ABSTRACT

Thompson, Jay Michael, M.S., Program of Environmental Engineering, College of Engineering and Architecture, North Dakota State University, July 2008.

Chlorinated Pesticide Remediation Using Zero-valent Iron Nanoparticles.

Major Professor: Dr. Achintya N. Bezbaruah.

Pesticide contamination of groundwater is a major concern in agricultural areas. Of the many remediation technologies developed in the last decade, zero-valent iron is among the most studied. Nanoscale zero-valent iron (nZVI), with its unique properties and high surface area, enhances many of the advantages of traditional iron remediation. Unfortunately, studies comprehensively examining the utility of iron nanoparticles for pesticide remediation are lacking. The intent of this work is to survey the effectiveness of iron nanoparticles for several common chlorinated pesticides and to comprehensively study the reaction kinetics.

Specifically, this study examined the effectiveness of iron nanoparticles for the treatment of the herbicides alachlor, atrazine, dicamba and picloram. Iron nanoparticles were synthesized by the borohydride reduction method and characterized using transmission electron microscopy, X-ray diffraction and Brunauer-Emmett-Teller (BET) specific surface area analysis. The resulting particles had an average diameter of 35 nm and a N_2-BET specific surface area of 25 m^2 g^{-1}. Of the compounds studied, only alachlor degraded in the presence of nZVI.

The surface area normalized pseudo first-order rate constant (k_{SA}) for alachlor dechlorination by nZVI was found to be 38.5 x 10^{-5} L h^{-1} m^{-2} (R^2 = 0.999). The primary reaction by-product was identified as dechlorinated alachlor. The effect of mass transfer and ionic strength was also examined. The results suggested that nZVI may be a viable option for both site remediation and low volume, high concentration pesticide waste treatment.

ABSTRACT

De Silva, Kapuwella Vidanege Nirodha Sudershini Buddhika, M.S., Natural Resource Management, College of Graduate and Interdisciplinary Studies, North Dakota State University, December 2008. Assessing the Organizational Effectiveness of the Conservation Districts in the Red River Basin in Minnesota and North Dakota. Major Professor: Dr. Robert R. Hearne.

The overall objective of this study was to assess the effectiveness of local water management agencies in the Red River basin in North Dakota and Minnesota. The study estimated the technical efficiency scores of 23 conservation districts. Specifically, this study identified the most successful characteristics of the technical efficiency of education, conservation practices, and the tree planting practices. The results implied that the board member experience does not increase the educational activities, conservation practices, and tree-planting projects of the conservation districts. Moreover, the study showed that the conservation districts in Minnesota are relatively more efficient than those in North Dakota. Furthermore, the research indicated that the organizations which have more meetings are relatively more efficient than those with fewer meetings. These findings can assist the local management of water resources and soil resources by providing policy makers and the agencies at the local level with a better understanding of the characteristics of successful local water organizations.

ABSTRACT

Kritsky, Craig Charles; M.S.; Department of Agribusiness and Applied Economics; College of Agriculture, Food Systems, and Natural Resources; North Dakota University; May 2008. Identifying Beneficial Attributes of Water Management Organizations. Major Professor: Dr. Robert R. Hearne

Water Management Organizations (WMOs) have evolved from their inception in the early 1900s and continue to evolve today. Recently, WMOs have increased their awareness of water quality and environmental issues. WMOs evolve at different rates due to local social, economic, and political norms. The Red River creates the border for Minnesota and North Dakota. This makes the Red River Basin ideal for WMO and institutional research.

The objective of this research is to identify the characteristics of WMOs that are more successful at adopting activities considered positive to local water management as well as basin management. These activities include collaboration and water quality improvement efforts.

Results demonstrate that board member experience positively impacts several traditional WMO activities, including water movement projects, stream flow clearing efforts, wetlands restoration, and tree sales. Board member experience negatively impacts collaboration, conservation contracts, water retention projects, and education and outreach. Board member attendance at annual water conferences had a positive correlation with total grant funding and conservation contracts. Cooperative extension training for board members positively correlates with conservation contracts and joint powers agreements.

ASTRACT

Torpen, David Randal, M.S., Department of Agribusiness and Applied Economics, College of Agriculture, Food, and Natural Resources, North Dakota State University, December 2007. Stakeholder Preference for Water Quality Alternatives in the Red River Basin. Major Professor: Dr. Robert R. Hearne.

The objective of this research is to estimate stakeholder preferences for management alternatives within the Red River of the North basin. Specifically, this thesis analyzes preferences related to water quality, water-based recreation, water supply, and institution. Results are estimated using choice experiments. Data show that residents are willing to pay approximately $84 per year for wetland restoration, $76 per year for additional bike trails, and $117 for enhanced fishery management. Taken to an aggregate level of all counties with land in the basin, willingness to pay is approximately $24 million for wetlands, $22 million for bike trails, and $34 million for enhanced fishery management. These values can assist institutions and policy-makers in making decisions related to the basin's water resources.

Graduate student: Brijesh Maharjan
Adviser: Scott Korom

ABSTRACT

The concentrations of electron donors in aquifer sediments are important in understanding the fate and transport of redox-sensitive constituents in ground water, such as nitrate. In this study, 50 sediment samples were collected from below the water table from 11 boreholes at the US Geological Survey Agricultural Chemicals Transport site near New Providence, Iowa. All samples were analyzed for gravel, sand (coarse, medium, and fine), silt, clay, inorganic carbon contents and for the following electron donors: organic carbon, ferrous iron, and inorganic sulfide. A subset of sediment samples was analyzed for organic sulfur, but all of the 14 samples were below detection; therefore this potential electron donor was not considered further. Nonparametric correlation analysis was done with the data for the other three electron donor concentrations, inorganic carbon concentrations, sediment grain sizes, and sediment depths. The major finding was that electron donor concentrations are positively correlated to the smaller grain sizes and to each other. These findings suggest that most aquifer denitrification at this site takes place in zones having lower hydraulic conductivities.

ABSTRACT

McEwen, Daniel Clayton, Ph.D., Department of Biological Sciences, College of Science and Mathematics, North Dakota State University, December 2008. Impacts of Water Level Regulation on Macroinvertebrate Communities in the Littoral Zone of Lakes. Major Professor: Dr. Malcolm G. Butler.

Altering the magnitude and timing of water-level drawdown can change important structural and functional properties of aquatic communities in temperate lakes. In the first two chapters, entitled "Macrobenthic community responses to changes in water-level management at Voyageurs National Park, Minnesota" and "Network structure in aquatic food webs resulting from hydroelectric dam operations", I describe changes in the benthic community that occurred in concert with alteration of the timing and magnitude of water-level drawdown in Voyageurs National Park (VOYA). I detected change from a community dominated by small-bodied invertebrates to one comprised of more large invertebrates and higher overall trophic diversity. From a network perspective, taxa such as predatory macroinvertebrates and dipterans played a greater role in community connectance of than did smaller, non-dipteran invertebrates. In a third chapter entitled "Spatially explicit Bayesian before-after control-impact (BACI) designs using proper distributional assumptions", I introduce a Bayesian analog to the traditional BACI experimental design often used to assess the response of populations to impacts. I show how ignoring spatial dimensions of populations within sampling periods can lead to wrong conclusions. Different distributional assumptions are contrasted, including those appealing to zero-inflation factors. I show that distributional assumptions matter, and specifically that a negative binomial or zero-inflated negative binomial should be a first choice when estimating benthic populations. I use these empirical findings in a fourth chapter entitled "Potential mechanisms for changes in macrobenthic communities impacted by regulated water-levels". In Chapter 4 I fit production models to population dynamics of a typical benthic invertebrate. Using assumptions from the Metabolic Theory of Ecology, I generate plausible mechanisms to explain the empirical findings from the VOYA study. I found that simulated impacts on benthos production had their greatest impact on phenology - when during the year production occurred. I was able to recover differences in production based on animal size, such as was found at VOYA, only by increasing extra-winter mortality on large animals. Together, these four chapters provide new insight into impacts of water-level fluctuation on aquatic ecosystems, especially macroinvertebrate communities.

Fellow: Ali Tackett
Major Adviser: Craig Stockwell

ABSTRACT

This novel study examined the existing phylogeography of Etheostoma nigrum(Johnny darter, Rafinesque) in the Upper Midwest. Four microsatellite loci were chosen to examine eight populations of E. nigrum, a non-migratory, benthic fish, from three drainage basins: the Red River of the North, the upper Missouri River, and the upper Mississippi River. These systems provide an excellent opportunity for phylogeographic studies as they have only been recently available to colonization by ichthyofauna, I applied four microsatellite loci to examine population structure within and among these major watersheds. Using AMOVA, strong evidence of a watershed effect was observed with 31% of the genetic variance among watersheds. Variance between populations within drainages accounted for 9% of the total variation. This observation was further supported using a Bayesian analysis which identified five well-supported assemblages which roughly agreed with watershed assignment. One notable exception to this pattern was observed for Lake Ida. This isolated lake is located in the Red River drainage; however, the population more closely aligned with populations from the upper Mississippi River. Because Johnny darters show considerable geographic genetic structure, they provide a good model to compare with other species that have been translocated within and among drainages.

Fellow: Brent Hanson
Adviser: Wei Lin

ABSTRACT

Acoustic Doppler Velocity Meters (ADVMs) have become popular for estimating discharge in rivers exhibiting complex flow characteristics. To use the ADVMs for estimating channel discharge, a relation needs to be developed between the mean channel velocity and the index velocity provided by the ADVM. In the past, this relation was primarily developed empirically. To improve the accuracy of ADVM discharge estimates, a more theoretical approach was developed for defining the relationship between a river's mean channel velocity and the ADVM's index velocity. The approach involves using the channel's geometry at a single cross-section to more accurately define the mean channel velocity to index velocity relation by means of fewer discharge measurements. The use of the channel geometry allows for prediction whether the mean-index velocity relation within a channel is linear or parabolic, allowing for more accurate extrapolation of the rating.

ABSTRACT

Schuh, Mary Cecilia, M.S., Department of Soil Science, College of Agriculture, Food Systems, and Natural Resources, North Dakota State University, September 2008. Farm-scale Reconnaissance of Estrogens in Subsurface Waters: A Field Study. Major Professor: Dr. Frank Casey.

17ß-estradiol (E2) is a natural estrogenic hormone found in animal manure and urine. It has been reported to dissipate rapidly in soil laboratory studies but is frequently detected in the environment at concentrations that could potentially have adverse affects on wildlife. The objective of this study was to assess the persistence and detections of manureborne E2 in soil on a farm-scale. Soil cores were taken from various locations at a swine (*Sus scrofa*) farm over 2006 and 2007. The producer applied liquid manure slurry to one of the selected sites each year. Cores were taken to the depth of the water table and separated into 15-cm increments. Porewater was extracted and analyzed for E2, using a combination of liquid chromatrography and tandem mass spectrometry (LC/MS-MS). Estradiol was detected at all sites but was highly variable. Estradiol was detected in 249 out of 589 extractions (42.3%), and concentrations ranged from 0 to 733 ng-E2 kg^{-1}-dry soil (or 0- 7,712 ng L^{-1} porewater equivalents). Analysis of variance indicated a significant difference between sites and time (p!0.05). Beginning in Spring 2006, concentrations trended upward, reaching a maximum in the Spring of 2007, and then declined. Manure slurry surface application did not appear to have a significant affect on the amount of E2 extracted. A similar range of concentrations was detected on all sites, and non-application site detections followed similar trends to application sites. Detection trends appeared to be related to climate, possibly to precipitation. Where E2 was detected, highest concentrations favored the upper profile, while the greatest frequency of detections was in the lower profile and near the water table.

ABSTRACT

Paradeis, Breanna Lyn, M.S., Program of Natural Resources Management, Department of Soil Science, College of Graduate and Interdisciplinary Studies, North Dakota State University, April 2008. Plant Community Composition of Wetlands Located on Restored and Native Prairie. Major Professor: Dr. Edward Shawn DeKeyser.

The goal of this study was to evaluate the species composition and physical characteristics of restored prairie pothole wetlands. Plant communities of restored and native temporary, seasonal, and semi-permanent wetlands were evaluated using the Index of Plant Community Integrity approach, a transect method, and a Floristic Quality Index. Wetland functions were evaluated using the Hydrogeomorphic approach. Data were analyzed using Nonmetric Multidimensional Scaling ordination and the Multi-Response Permutation Procedure. This study compared restored and native plant communities located on Tewaukon National Wildlife Refuge and Lostwood National Wildlife Refuge. Plant communities were grouped according to refuge location and land-use history. In general, the restored plant communities were found to have less species richness and diversity than the native plant communities located on the same national wildlife refuge. In addition, plant communities located on Lostwood National Wildlife Refuge were found to be higher in species richness and diversity than the plant communities on Tewaukon National Wildlife Refuge. However, restoration attempts have been successful in returning certain native species to formerly degraded areas. Restored communities are expected to improve over time with proper management. The results of these analyses may be used to identify the potential composition of restored wetland communities and to evaluate the success of restoration efforts throughout the Prairie Pothole Region.

PROJECTS (104-B: Fellowship)

Description of WRRI Graduate Research Fellowship projects follow:

RAPID AND SENSITIVE DETERMINATION OF BACTERIA IN WATER USING NANOPARTICLES

GRF Project 2008ND162B
Fellow: Yuhui Jin
Adviser: Julia Xiaojun Zhao
Department of Chemistry
University of North Dakota
Grand Forks, ND 58202

Significance of the project

Sensitive and Rapid Detection of Bacteria in Drinking Water

Bacteria can grow or re-grow in distribution systems of drinking water. In fact, potable water is a major source of some bacterial colonization[7,8]: for example, *L. pneumophila* and *E coli.* etc. The *L. pneumophila* in potable water can replicate rapidly and increase in virulence.[9] The British Communicable Disease Surveillance Center reported that 19 of 20 hospital outbreaks of Legionnaires' Disease in the United Kingdom from 1980 to 1992 were attributed to the *Legionella*-contaminated potable water.[10] Given the low infectious dose of pathogenic bacteria, the presence of even a single bacterium in potable water may pose a serious health risk. Therefore, sensitive and rapid detection of bacteria in water is critical.

However, the current definitive method for the detection of bacteria is the culture of the organism, which requires about 24 hours for bacterial growth.[11] This method is too slow to meet the public need. The PCR-based method can detect bacteria within six hours, but the method requires pre-enrichment of the target bacteria. The proposed method will be able to specifically identify pathogenic bacteria at a single bacterium level within 30 minutes in water samples. The method will be accurate, rapid and sensitive to meet the public need.

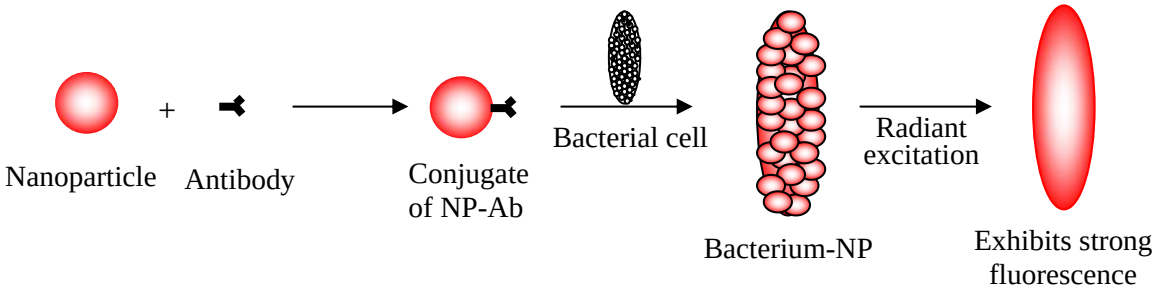
Application of Nanotechnology in North Dakota

Nanotechnology has been a rapidly developing area in recent years and is becoming a hot topic worldwide. However, it is an area that is underdeveloped in North Dakota. At the University of North Dakota, Dr. Zhao is the first faculty member working in the nanotechnology area. There is a great need to develop emerging nanotechnology in North Dakota to advance the economic and educational development of the state. Four students in Dr. Zhao's group have participated in the proposed project: a postdoctoral research associate, a Ph.D. student, and two American Indian undergraduate students. The proposal will undoubtedly benefit the development of North Dakota, both in terms of economy and education.

Project Description and Objectives

The objective of this proposal is to develop a rapid and ultrasensitive method for the specific identification and quantitative determination of pathogenic bacteria in water. The major feature of the proposed method is the employment of fluorescent nanoparticles as target bacteria identifiers that could
emit strong fluorescent signals. The method will consist of three major steps. First, the nanoparticles will react with a specific antibody to form a conjugate of nanoparticle-antibody (NP-Ab). Second, based on the antibody-antigen reaction, the NP-Ab conjugates will identify target bacteria cells from a sample by
attaching the NP-Ab to the bacteria surface antigen. Third, target bacteria will be qualitatively and quantitatively determined by measuring the fluorescence intensity and wavelength (Figure 1).

Figure 1 Schematic diagram of determination of bacteria using fluorescent nanoparticles



The method will have three major advantages.

(A) High sensitivity. The nanoparticles will be synthesized using organic dye molecules. Thousands of dye molecules will be encapsulated within a single nanoparticle. Traditional dye labeling method for the determination of bacteria only links one dye molecule to an antibody, which reacts with a single antigen. The proposed method links one nanoparticle, rather than one dye molecule, to each antibody. The advantage is that a single nanoparticle contains thousands of dye molecules, resulting in a highly amplified fluorescent signal. Furthermore, because a bacterial surface contains a number of antigens, a single bacteria cell can be linked with multiple highly fluorescent nanoparticles, making the determination of single bacteria possible.

(B) High specificity and accuracy. The high specificity and accuracy will come from two factors. (1) The identification of the target bacteria will be based on the antibody-antigen reaction. The selected antibody will only specifically recognize a target bacterial antigen. (2) Due to the strong fluorescent signals provided by nanoparticles, the signal difference between target and non-target cells is significant even in the presence of only a single target bacterium. Thus, the false positive reading will be reduced dramatically.

(C) Rapid determination. The size of the nanoparticles is adjustable in the range of 10 nm to 60 nm in diameter. The small size makes nanoparticles highly mobile, which enables them to easily reach target bacteria in a matrix. According to our previous study, the assay will take less than 30 minutes to complete the sample preparation and the determination of bacteria. Compared to the traditional bacteria detection method, plate counting, which takes about 24 hours, the proposed assay will significantly reduce the bacteria determination time.

This proposal focused on following three specific goals.

Goal 1: Development of Quantum Dot-like Highly Fluorescent Nanoparticles (Goal 1 has been achieved during the initial stage of the project. See 2006 progress report)

Goal 2: Specific, Rapid and Sensitive Identification of Target Bacteria (Goal 2 has been achieved during 2007 under the support of NDWRRI. See attached progress report.)

Goal 3: Simultaneous Determination of Multiple Pathogenic Bacteria

The final goal of this proposal is to simultaneously determine multiple bacteria using differently colored nanoparticles. Three kinds of bacteria will be simultaneously detected: *Klepsiella pneumoniae, Psudomonas aeruginosa,* and *L. pneumophila*. It is difficult to differentiate these bacteria from their physical appearances, but their virulence is drastically different. These bacteria will be accurately identified by differently colored nanoparticles and quantitatively determined via fluorescence intensity measurements. It is expected that the principles discovered in this study could be extended to the determinations of various pathogenic bacteria.

Tasks accomplished

In the first step, the quantum dot-like luminescent silica nanoparticles were developed. These luminescent silica nanoparticles can be excited by a single wavelength excitation source, and give out light with different emission wavelength. This property will benefit the simultaneously detection of different kind of bacteria targets.

In the second step, lab-made bacteria samples have been detected by these quantum dot-like luminescent silica nanoparticles by spectro-fluorometer and fluorescence microscope.

Finally, samples which are collected from North Dakota water system were studied by using this method.

Significant outcomes:

The rapid and sensitive determination of pathogenic bacteria is extremely important in biotechnology, medical diagnosis, and bacteria sample analysis. Current methods either lack ultrasensitivity or take a long time for analysis. The bioconjugated nanoparticles-based assay can be used for in situ pathogen quantification, and provides a fast and sensitive technique for bacteria determination.

Modification of Iron Nanoparticles by Amphiphilic Polysiloxane Graft Co-Polymer for Arsenic, TCE, and RDX Remediation

GRF Project: 2008ND 164B
Fellow: Sita Krajangpan
Adviser: Achintya Bezbaruah and Bret Chisholm
Department of Civil Engineering and
Center for Nanoscale Science and Engineering
North Dakota State University
Fargo, ND 58105

Introduction/ Background on Research Topic

Zero-valent iron nanoparticles (nZVI) have been used for groundwater remediation of various contaminants because of their unique physiochemical properties. Various chlorinated aliphatic hydrocarbons, explosives, and metals have been successfully decontaminated with nZVI. However, nZVI are not only highly reactive with the contaminants, but also rapidly react with surrounding media in the subsurface (dissolved oxygen and/or water) and other non-target compounds. Thus, significant loss of nZVI reactivity occurs before the particles reach the target contaminants. Additionally, strong magnetic interactions between particles cause agglomeration, limiting colloidal stability and reduction in reactive surface area. For nZVI to effective, the particles should remain dispersed, protected from non-target compounds, and suspended for longer time. The inherent problems associated with bare nZVI can be overcome by designing a delivery vehicle. Considering the requirements of an effective delivery vehicle for nZVI, functionalized amphiphilic polysiloxanes are an ideal class of polymers for this application. Amphiphilic polysiloxane graft co-polymers (APGC) have been synthesized by hydrosilylation of hydride-functional polysiloxanes, poly ethylene glycol (PEG) and *tert*-butyl acrylate (tBA) (supported by 2007 NDWRRI fellowship). The water-soluble grafts, PEG, allow for dispersibility and colloidal stability in an aqueous medium. The hydrophobicity of the polysiloxane polymer backbone protects the nZVI from excessive oxidation by creating a barrier to water while also creating an affinity of the coated nZVI for the water/contaminant interface. The polymer also readily allows permeation of contaminants to the nZVI surface.

This year's research is in continuation of the work proposed for the 2007 NDWRRI program.

Project Objectives:

1. Synthesize and characterize the nZVI using transmission electron microscopy (TEM), scanning electron microscopy with Energy Dispersive Spectroscopy or X-ray microanalysis (SEM/ EDS), X-ray diffraction (XRD), and BET surface area analysis. **Completed**.
2. Synthesize APGC by hydrosilylation and characterize the APGC using nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy techniques. **Completed**.
3. Study colloidal stability of APGC coated nZVI and compare with uncoated (bare) nZVI. **Completed**.
4. Compare the degree of oxidation of APGC coated and bare nZVI by non-target compounds. **In progress.**
5. Study of reaction kinetics for APGC coated nZVI mediated degradation of various contaminants [As, TCE and RDX] and compare with bare nZVI. **In progress**.
6. Identification of As, TCE, and RDX degradation by-products. Inductively coupled plasma mass spectroscopy (ICP-MS), gas chromatography (GC), and High performance liquid chromatography (HPLC), respectively, will be used in As, TCE, and RDX studies. **In progress**.

Progress as of date:

The nZVI, APGC, and CnZVI were successfully synthesized and characterized. The colloidal stability comparison between CnZVI and bare nZVI were completed. Batch experiments using CnZVI were conducted with replications and showed promising results in As, TCE, and NO3--N removal as compare to nZVI. Shelf-life of CnZVI (over 7 month-periods) showed stable colloidal stability. Ionic strength study showed no significant change in colloidal stability and TCE removal. SEM/EDX was used to study surface corrosion of the metal particles. The results indicate that CnZVI markedly protects nZVI surface from undesired corrosion.

Significance:

Successful development of a delivery vehicle for iron nanoparticles will have broader ramifications in the field of groundwater remediation. The synthesis, characterization, and analysis phases of the polymeric delivery vehicle development process have and will result in fundamental knowledge on the behavior of the polymer coated nanoparticles. Kinetic studies for As/ TCE/ RDX will help us in quantifying the advantages and disadvantages of using polymer coated iron nanoparticles for remediation. Identification and analysis of degradation by-products will also help in identifying future research directions in this area. The results of this research will be useful for the pilot tested to create a reactive barrier/wall to contain the arsenic trioxide plume in southeast North Dakota. The results from this project will stimulate further research for the development of target specific delivery vehicles for contaminants of environmental concern.

Interactions between Microorganisms and Metal Nanoparticles: A New Approach for Groundwater Remediation

GRF Project: 2008ND171B
Fellow: Rabiya Shabnam
Adviser: Achintya Bezbaruah
Department of Civil Engineering
North Dakota State University
Fargo, ND 58105

Introduction and Background:

Nanoparticles are attractive for remediation of various contaminants because of their unique physico-chemical properties. Zero-valent iron (nZVI) is the most popular among the metal nanoparticles used in environmental remediation. Though nZVI have been extensively used for remediation, their efficacy has been evaluated excluding their possible interactions with environmental microorganisms. The present research is based on the hypothesis that symbiotic relationships develop between introduced nZVI and microorganisms. Nanoparticles can reduce a contaminant as the first step in the degradation process and microorganism can preferentially take over the process and reduce/oxidize the degradation by-product(s) to benign end products or vice-versa. Reported work on interactions between nanoparticles and microorganisms is limited, specifically in the area of environmental engineering. The purpose of this study is to experimentally prove that microorganisms and nanoparticles develop symbiotic relationships or such relationships can be simulated under specific environmental conditions. The study will also explore possible uses of such relationships for enhanced environmental contaminant removal. Experiments will be conducted in 'micro-reactors' made of biopolymers (e.g. alginate). Biopolymers are used in environmental remediation for cell entrapment and in immobilization of enzymes. It is proposed to encapsulate nZVI and specific microorganisms in alginate microcapsules to study their interactions. The encapsulated microorganisms will be studied for their growth and viability. TCE will be used as the target contaminant in the initial studies. Other contaminants of concern will be used based on the results from the initial studies.

Project Objectives:

The main objective of this study is to investigate the interactions between iron nanoparticles and microorganisms. The specific objectives include:

- Design, production and characterization of alginate microcapsules
- Entrapment of nZVI and specific microorganisms in calcium alginate microcapsules

- Study nZVI-microorganism interactions in terms of microbial growth and their behavioral changes
- Conduct degradation studies for specific contaminants (e.g., TCE)

Progress:

Some progress has been made in design and production of alginate microcapsules. The capsules have been optimized for their size and properties (e.g., membrane thickness, bursting strength) for various alginate concentrations, dropping velocities, and gelation times . Entrapment of nZVI and sample microorganisms into alginate capsules has been achieved. Tracer studies using nitrate, ammonia, various polysaccharides and pesticides are underway. The tracer study results will be used to develop mathematical models for diffusion of contaminants into and out of the alginate capsules (i.e., contaminant availability for the encapsulated nZVI and microorganisms, and degradation by-product transport).

Significance:

Environmental nanoscience is one of the fastest emerging areas in the field of contaminant remediation. Successful entrapment of iron nanoparticles and microorganisms in alginate capsules will lead to possible use of these micro reactors for degrade contaminated groundwater plumes when used as permeable reactive barriers. The results of this project will also be useful for the development of household treatment system for drinking water. Most importantly this study will elucidate the nZVI-microorganism relationship that can be exploited further in other areas of science and technology.

Development of GAC-NZVI Adsorbent for Arsenic Removal

GRF Project: 2008ND168B
Fellow: Qigang Chang
Adviser: Wei Lin
Department of Civil Engineering
North Dakota State University
Fargo, ND 58105

Background:

From the 1890s to 1940s, arsenic-laced bait was used extensively throughout North Dakota to combat grasshopper infestations. The bait, which included arsenic trioxide, sodium arsenate, Paris Green and other arsenic compounds, was commonly applied to farm fields. Unused materials were often buried or dumped in pits and low-lying areas. Groundwater was heavily contaminated with arsenic. A superfund site, located in parts of Ransom, Richland, and Sargent counties, was approved in 1983. Intensive remedy efforts were taken, and in 1996, this site was removed from the National Priority List. On January 22, 2001, the USEPA revised the maximum contaminant level (MCL) of arsenic downward from 50μg/L to 10μg/L. All the remedy facilities in this former superfund site are no longer able to protect people's health under the new MCL of arsenic.

Western North Dakota also has elevated arsenic in groundwater. The arsenic level is approximately 24μg/L in all three wells supplying drinking water at Oakes and is around 40 μg/L at Devils Lake. The new regulation presents a major compliance challenge to the existing water supply systems, especially the small rural community systems that until recently had few regulation requirements. Some small communities are attempting to apply for regulatory exemptions due to the high costs associated with meeting the new MCL. While exemptions offer temporary cost savings, they do not defend the population from possible negative health impacts. There is an urgent need to develop safe and affordable technologies to meet the new drinking water standard in small rural communities in North Dakota.
Granular Activated Carbon (GAC) is an excellent stable adsorbent widely used in water treatment process, especially for organic contaminants. But GAC alone only exhibits limited adsorption capacity to arsenic. Research found that arsenic adsorption capacity increases significantly after activated carbon is impregnated with iron

The proposed research hypothesizes that GAC-NZVI (nano zero valent iron) could be synthesized with desired amount of nano iron which are stable and highly reactive. GAC-NZVI could be a promising adsorbent to treat trace arsenic in drinking water by inheriting advantages from GAC and NZVI while avoid their drawbacks. GAC-NZVI could be directly used in existing GAC fix-bed system without additional

extension and separation. Organic compounds may still have access to the huge specific surface of GAC so that GAC-NZVI will retain the ability to remove odor, taste, and color.

Project Objectives:

The primary goal of this research is to develop GAC-NZVI adsorbent to treat arsenic to meet current stringent drinking water standard at an affordable cost for rural communities in North Dakota. The specific objectives are as follows:

1. To develop a method to synthesize GAC-NZVI adsorbent with desirable characteristics for arsenic removal;
2. To determine the adsorption capacity and kinetic for arsenic removal using GAC-NZVI adsorbent;
3. To study the mechanisms of arsenic removal and factors that affect arsenic removal capacities and efficiency by GAC-NZVI adsorbent; and
4. To predict the performance of the GAC-NZVI adsorbents at various chemical conditions through model simulations.

Experimental and analytical studies will be carried out to achieve the above objectives. Groundwater samples from several locations of North Dakota, including Lidgerwood, Richland and Oakes, will be used to evaluate the performance of GAC-NZVI.

Progress :

The principle hypothesis has been proved that high amounts of iron could be impregnated in GAC with an even-distribution. A new impregnation method has been developed and 12.62% and 8.52% iron were impregnated in GAC Darco 20×50 and Norit RX3 EXTRA, respectively.

GAC-Iron has been characterized by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray unit. SEM analyses indicated that 12.62% iron evenly distributes inside GAC Darco 20×50. And nano-level iron particles were observed in SEM images. X-ray Diffraction analyses indicated that iron exists inside GAC both in crystal structure (α-FeOOH) and amorphous status.

Arsenate synthetic water was used in adsorption tests. The pH of isotherm tests were controlled neutral by using bicarbonate buffer solution so as to keep conditions close to the natural water. Three levels of iron content in GAC-Iron Darco 20×50, 1.48%, 5.92% and 12.13%, were used to conduct arsenate isotherm tests to determine the arsenate adsorption capacities. The Langmuir model (Equation 1) fits the isotherm curves better than the Freundlich model.

$$q = \frac{q_{max}(b c_e)}{1 + b c_e} \quad (1)$$

GAC-Iron with 5.92% and 12.13% iron content exhibited much higher arsenate adsorption capacity than GAC-Iron with 1.48% iron content. In the Langmuir model,

parameter b represents the affinity of adsorbent for arsenate. In present research, GAC-Iron showed a higher affinity for arsenate than other research in literature, such as 1.12 L/mg reported by Gu et al.(2005) and 0.18L/mg reported by Chen et al.(2007). In addition, GAC-Iron exhibits the comparative adsorption capacity at low arsenate concentration (<200μg/L), which represents most real-world cases. Challenges were encountered in arsenate adsorption tests. No difference of adsorption capacity was observed between GAC-Iron with 5.92% and 12.13% iron. The reasons are not clear, and further research will identify impact factors and modify the synthesizing method to produce GAC-Iron that has enhanced arsenate adsorption capacity.

Significance:

GAC-NZVI will be a promising adsorbent that could be used to remove arsenic from drinking water at existing facilities without further expansion. The GAC-NZVI adsorbent could meet the stringent drinking water standard of arsenic at affordable cost and help rural communities of North Dakota to comply with federal regulations. In addition to the benefits to North Dakota, sharing of knowledge from this research will benefit the environmental community as a whole and encourage additional research to create new technologies by combination of latest technologies with conventional technologies.

Selected Pesticide Remediation with Iron Nanoparticles: Modeling and Barrier Applications

GRF Project: 2008ND165B
Fellow: Jay Thompson
Adviser: Achintya Bezbaruah
Department of Civil Engineering
North Dakota State University
Fargo, ND 58105

Research:

Pesticide contamination of groundwater remains an ongoing area of concern. One promising pesticide remediation technology is reductive dechlorination by iron filings or powder. This technology has been successful in both the lab and field. However, limitations inherent in this process have limited its use.

Recent research has shown that nanoscale zero valent iron (nZVI), with its high surface area and reactivity, can overcome many of these limitations. Although particle properties can vary greatly with synthesis method, typical particles have diameters less than 100 nm. This property results in extremely high specific surface area, which greatly speeds reactions and can eliminate potentially harmful byproducts. Additionally, nZVI can be injected directly into an aquifer, eliminating the need for the expensive excavation associated with iron filings.

Research completed with support of the 2007 NDWRRI program has successfully characterized the synthesized nZVI and described pesticide (alachlor) degradation as a pseudo-first order reaction. However, the proposed model does not account for changes in nZVI surface chemistry, due to oxidation and possibly boron content. This research will attempt to create a more mechanistic model that can be applied to a broader set of applications. Further, environmentally-benign, alginate-based delivery technologies will be evaluated for agricultural applications.

Project objectives:

1) Synthesize and characterize nZVI. Characterization techniques include X-ray diffraction (XRD), transmission electron microscopy (TEM), and BET surface area analysis. **Complete**

2) Conduct kinetic degradation trials on the selected pesticides with both nano and micro scale iron. Compare reaction kinetics and byproducts. **Complete**

3) Fully characterize the surface composition of manufactured microscale iron, manufactured nanoscale iron and borohydride synthesized nanoscale iron by X-ray photoelectron spectroscopy (XPS). Mathematically describe the pseudo-first order reaction rate constant in terms of surface area, surface chemistry and degree of agglomeration. **In progress**

4) Assess the utility of nanoscale iron entrapment and encapsulation (E/E) for pesticide remediation. Compare the kinetic and hydraulic characteristics of E/E nZVI with bare nZVI. **In progress**

Progress:

The nZVI characterization and kinetic trials proposed in the 2007 NDWRRI program are complete. A manuscript describing this work is currently in review for publication. Kinetic trials on E/E nZVI are underway; preliminary results are promising. Column studies and analysis were completed.

Significance:

The proposed research will be useful for the development of an nZVI permeable reactive barrier with improved hydraulic characteristics. This is significant because research on practical, inexpensive applications of nZVI is scarce. Furthermore, the proposed (and completed) research may have applications in the development of an inexpensive on-site pesticide waste treatment system. Such a system could potentially treat low-volume, high-concentration pesticide wastewater and rinsewater much more economically than the centralized treatment system used presently.

Iron imprinted polymer for Removal and Monitoring of Arsenic

GRF Project: 2008ND169B
Fellow: Harjyoti Kalita
Adviser: Achintya Bezbaruah and Bret Chisholm
Department of Civil Engineering and Center for Nanoscale Science and Engineering
North Dakota State University
Fargo, ND 58105

Introduction and Background:

Arsenic present in water is a serious environmental and health concern because of the toxicity of arsenic on human and on other living organisms. Arsenic usually occurs naturally in groundwater although some arsenic based pesticides and preservatives may also contribute. The U.S. EPA has set 0.010 parts per million (10 µg/L) as the arsenic standard for drinking water in 2006. The maximum contaminant level or MCL of 10 µg/L has created an urgent need of new technology for arsenic removal from water and sensing.

Arsenic is present in water in tri- and penta-valent forms. Different Processes are presently used to remove arsenic. However, most of the conventional arsenic removal processes can not remove As(III) and As(V) simultaneously. They can treat either As(III) or As(V), and, hence, a pretreatment in the form of oxidation or reduction is needed. The need for an additional unit process adds to the capital and operation costs of treatment.

To overcome this limitation it is proposed to synthesize ion-imprinted polymer for the removal of both As(III) and As(V) simultaneously. Cross-linkers will be used in the polymer which can bind both As(III) and As(V) and reduce As(V) to As(III). Hence, arsenic removal could be done in one step. This research will proceed further on to develop sensors with low response time and high arsenic detection efficiency.

Project Objectives:

- Preparation of an ion imprinted polymer (IIP) for selective removal of arsenic from water
- Selectivity study of the IIP in presence of different ionic particles
- Determine the reusability time and number for effective removal of arsenic
- Preparation of a new ion imprinted potentiometric sensor for arsenic metal ion

Progress:

The progress made is summarized below:

Task I: Ternary complex formation: Thiol- arsenic complex was synthesized.
Task II: Synthesis of polymer: The complex formed in task I was imprinted in

styrene-divinyl benzene copolymer (Figure 1).
Task III: Preparation of IIP: The polymer material was filtered and then dried in vacuum to get the IIP (Figure 2).

The effects of various parameters (e.g., pH, temperature, different cross-linker, reaction time) ware analyzed to find out the optimal conditions. ICP-OES analysis was carried out to see the binding of arsenic with the polymer.

Figure 1. Thiol- arsenic complex synthesized.

Figure 2. Arsenic ion-imprinted polymer synthesized.

Significance:

The outcome from this work will have a universal appeal and will be very relevant to North Dakota. Arsenic contamination is a major concern in southeast North Dakota (568 sq mile area in Sargent, Ransom and Richland counties are affected). The IIP developed will find potential use in large and small water treatment plants including point-of-use treatment units. Ion-imprinted chemical sensor technology will have potential applications in clinical diagnostics, environmental and food analyses as well as in illicit drugs detection, genotoxicity and chemical weapons.

Chemical Fingerprinting of Sediments and Water of the Souris River for Identification of Diffuse Pollution Sources

GRF Project: 2008ND170B
Fellow: Dimuthu Wijeyaratne
Adviser: Marinus Otte, Professor
Department of Biological Sciences
North Dakota State University
Fargo, ND 58105

Introduction and Background:

Sediments are a valuable source of information regarding the occurrence, magnitude and trend of human-associated environmental contaminants because they integrate erosion products from throughout the catchment area. Sediments consist of a large number of elements, many potentially contributing to water pollution. Sediment quality is an important environmental concern because sediments may act both as a sink and a source of constituents to the overlying water column and biota.

Chemical fingerprinting identifies the distribution of chemical elements within a matrix and thus defines its unique signature in comparison to similar matrices. It provides a sediment profile, which can then be used for direct sediment source tracing.

This project will consist of three major research tasks as follows:

Task 1- determine the chemical fingerprint for the Souris River sediments by assessing the surface and depth variation in sediment signature

Task 2- use the fingerprinting technique to identify sediment transport (source and sink sites) along the Souris River

Task 3 - apply the chemical fingerprinting technique to determine sources and sinks of P and other significant elements.

Project Objectives:

1. To obtain a chemical fingerprint of sediments and water at selected sampling sites in the Souris River.
2. To assess the concentration of phosphate in sediments and water at selected sites of the Souris River and identify potential sources of phosphate pollution.

3. To assess the spatial variations in element concentrations in water and sediments and relate them to the land use patterns and phosphorous loading in the Souris River.
4. To assess the biogeochemical behavior of elements in water and sediments of the selected areas of the Souris River.
5. To geographically model the variation of the concentration of the elements along the Souris River.
6. To geographically model potential sediment and associated pollutant sources along the Souris River.

Progress to date:

In August 2008, sediment samples from the top layer of the riverbed were collected from small tributaries along the Upper Souris River. The samples were taken from inside tributaries, and from 50 m upstream and 50 m downstream in the Souris River. The homogenized sediment samples were acid digested and analyzed using a Spectro genesis ICP-OES for about 53 elements. The fingerprints were developed for each site sampled in August 2008 and development of a model to describe data is in progress.

PROJECT (104-B: Information Dissemination)

Information Dissemination and Communication

Project: 2008ND172B
PI: G. Padmanabhan

Activities to disseminate institute and other research under this project included:

1. Maintaining a web site
2. Publishing a newsletter
3. Publication of Fellowship and other research done through the Institute
4. Presentation of research results to state and federal water agencies
5. Sponsor or co-sponsor local or regional conferences

The website of the Institute was updated at least quarterly, and more often when a research project wished to provide updates or when a Fellow graduates. The website provides additional details on the research. The list of Institute Affiliate Faculty with their expertise was updated. Research reports published by the institute were placed on this web site as and when they became available. The institute web site is http://www.ndsu.edu/wrri.

The Institute continued its annual newsletter, which highlights the graduate research fellowship program, the research grants associated with it, and general summaries of ongoing research. The newsletter profiled institute research and researchers and published other newsworthy water issues in the State

The Institute continued its off-campus seminar series, designed to enhance communication between the State and Federal agency personnel and university faculty and students. Advisors and fellows presented their research results to State and Federal professionals in Bismarck (200 mi from Fargo). The Institute also encouraged its Fellows and faculty to attend seminars and conferences held in the region. Modest support for travel was provided by the institute whenever appropriate.

The Institute continued to work toward establishing the Institute as a clearinghouse for information on water resources research expertise of faculty and staff at NDSU and UND.

PROJECTS (104-G: National Competitive Program)

ASSESSING THE EFFECTIVENESS OF LOCAL WATER INSTITUTIONS IN WATER MANAGEMENT

GRF Project 2005ND86G (104-G)
PI: Robert Hearne
Department of Agricultural Economics
North Dakota State University
Fargo, ND 58105

1 Synopsis and Planned Goals:

This research will focus on the Red River of the North Basin in Minnesota and North Dakota although some assessment of Manitoba's institutions will be included. The analysis generated by this research should support decision makers throughout the North America. Specific objectives of the research include:

1) Develop a set of objective and subjective criteria and indicators to evaluate the effectiveness of local water management institutions;
2) Review the different governmental and nongovernmental institutions in the basin, classify their current goals and activities as well as their chartered purposes, and identify overlaps as well as functions that are not being addressed;
3) Identify and evaluate the characteristics of local water institutions that have a demonstrated capability to meet local goals and wider goals of the greater river basin, including water quality monitoring and participation in the establishing TMDLs;
4) Assess the use of: 1) scientific and technical information provided by USGS and other agencies; 2) extension education and training programs; and 3) other support provided by governmental and non-governmental agencies and organizations;
5) Analyze institutions' and agencies' likely behavior in a decision-making situation, such as watershed and basin planning, or conflict resolution and further develop decision-making support tools;
6) Identify the characteristics of institutions that successfully evolve to meet new challenges;
7) Analyze preferences of a sample of residents and stakeholders toward watershed management issues and the types of institutions they trust; and
8) Disseminate results to various forums including local workshops, extension materials, and scientific journals.

2. Progress Towards Goals:

Two surveys were completed. Three M.S. theses were completed. All objectives except number 5, have been completed. Objective 5 was not possible because the operational expenses and travel of USGS employees collaborating with the project were not allowed. The survey data are currently being used to develop further research articles for additional objectives such as assessing organizational effectiveness. .

3. Information Transfer

Scientific journals and extension reports; professional, extension, and public meeting presentations have been used in information transfer. Much of these meetings were in the preliminary stages of the research. For instance public input was important in the survey design. Results have been presented and discussed at local meetings within the Red River Bain as well as professional conferences.

4. Students Supported

David Torpen defended his thesis "Stakeholder Preferences for Water Quality Alternatives in the Red River Basin" for an M.S. degree in Agribusiness and Applied Economics in December 2007. A coauthored paper has been submitted for publication and is under review in the *Journal of Natural Resources Policy Research.*

Craig Kritsky defended his Plan B paper "Identifying Beneficial Attributes of Water Management Organizations." For a M.S. degree in Agribusiness and Applied Economics in 2008. A coauthored paper has been accepted for publication in Water Policy.

Nirodha de Silva defended her thesis "Assessing the Organizational Effectiveness of Conservation Districts in the Red River Basin in Minnesota and North Dakota" for an M.S. degree in Natural Resources Management. A coauthored abstract from this work has been accepted as a selected poster for the Agricultural and Applied Economics Association meeting in July 2009.

COLLABORATIVE RESEARCH ON IN SITU DENITRIFICATION AND GLYPHOSATE TRANSFORMATION IN GROUND WATER: NAWQA EASTERN IOWA BASINS STUDY UNIT

GRF Project 2006ND126G (104-G)
PI: Scott Korom
Co-PI: Capel, Paul D. (USGS)
Department of Geology and Geological Engineering
University of North Dakota
Grand Forks, ND 58202

1. Synopsis. Contamination of ground water by nitrate and pesticides is widespread in some areas of the country and can threaten drinking water supplies. It is well known that the most important removal mechanism of nitrate and most pesticides from ground water is biodegradation, but the *in situ* transformation rates are largely unknown. In this study, two 180-L stainless steel chambers forming *in situ* mesocosms (ISMs) of aquifer sediments will be installed below the water table at the NAWQA agricultural chemicals study sites in the glaciated region of Iowa. This work will extend the use of this technique to examine denitrification in an area characterized by high dissolved iron concentrations and to measure the transformation rate of the extensively-used herbicide, glyphosate. The objectives for the research are the following:

1. Measure the denitrification and glyphosate transformation rates in the two ISMs.
2. Determine whether the denitrification is better fit by zero-order or first-order reaction rates.
3. Determine what donors are contributing electrons for the denitrification and their relative amounts.
4. Incorporate the results of the two ISMs into the existing databank of nine other ISM sites in glacial outwash aquifers in the Upper Midwest.
5. Update the available data of the apparent isotopic enrichment factor for ^{15}N in nitrate versus denitrification rate among of ISM sites.
6. Update the nitrate vulnerability index and extrapolate the findings to similar, unmonitored agricultural and environmental settings.

Aquifer sediment samples will be collected from the Iowa site and analyzed for grain-size distributions, mineralogy, and major e^- donors (organic carbon, inorganic sulfide, organic sulfur, and ferrous iron) to determine optimum locations for installation of the ISMs, provide insights on the types and heterogeneity of e^- donors at the site, and provide the e^- donor supply data at the Iowa site that can be compared to previous ISM studies in the Upper Midwest. After the ISM chambers are installed, they will be purged and then amended with nitrate and bromide, which serves as a tracer for nitrate. The ISMs will be sampled over time (months) and the decreases in nitrate concentrations compared to bromide concentrations will be used to calculate rates of denitrification. Modeling of the evolution of the geochemistry in the ISMs will provide insights into what e^- donors contributed electrons to the denitrification and their relative amounts. The field experiment will be repeated a second time; however, in addition to nitrate and bromide, glyphosate will be added. The attenuation and transformation of glyphosate (with the

dominate metabolite, AMPA) will be studied in both the presence and absence of nitrate to determine the fate of glyphosate in oxidizing and reducing conditions. The results of this study will provide site-specific transformation rates for nitrate and glyphosate and extend the aquifer nitrate vulnerability index that was developed in earlier studies. This information is vital for the development of tools and quantitative methods to characterize the transport and fate of agricultural chemicals in the Eastern Iowa Basins Study Unit, the Upper Midwest, and beyond.

2. Progress report. The starting date for the grant was August 1, 2006; the previous progress report was written in June, 2008. Since then, a trip was taken to the field site in October to purge the shallower in situ mesocosm ("ISM S") and amend it a second time, only this time glyphosate was included in the amendment. The first tracer test in the deeper ISM ("ISM D") continued uninterrupted. Both ISMs were sampled about every month. This project officially ends on July 31, 2009; however, the ISMs are expected to be sampled through the current growing season. Therefore analytical results will continue to be produced from the various laboratories involved, including those for glyphosate and for isotopes of nitrate (^{15}N and ^{18}O).

Based on results through April, 2009, denitrification measured in ISM D had a zero-order rate (that is, independent of concentration) of 0.018 mg/L/day ($R^2 = 0.98$) and a first-order rate (concentration-dependent) of 0.00051/day ($R^2 = 0.96$). Denitrification for the first tracer test in ISM S had a zero-order rate of (0.0070 mg/L/day ($R^2 = 0.84$) and a first-order rate of 0.00015/day ($R^2 = 0.72$). These rates are at the low end of the range for the ISM network we have in Iowa, Minnesota, and North Dakota. Nitrate concentrations in the second tracer test for ISM S increased slightly, which indicates that native groundwater diluting the amended water during the test apparently had nitrate in it. For the tests that showed denitrification, sulfate concentrations did not increase, which indicates that sulfide (as pyrite) did not serve as an electron donor. Therefore, organic carbon and/or ferrous-iron minerals are the likely source of electrons for the reactions. However, at these low denitrification rates, it is not yet known if there is enough of a denitrification "signature" in the water for geochemical modeling to indicate the likely mix of electron donors contributing to the nitrate reduction.

Analysis of the core samples showed low concentrations of organic carbon (0.13% ± 0.31%, ± 1 standard deviation used throughout), inorganic sulfide (0.033% ±0.046%), and ferrous iron (0.24% ± 0.19%). A subset of 14 samples measured for organic sulfur were all < 0.01%, which was the detection limit. With respect to the electron donor concentrations in the sediments, the nonparametric Spearman rank coefficient test showed the following correlations:

1) Organic C was positively correlated to silt and clay (both at $\alpha = 0.01$).
2) Inorganic S was positively correlated to clay ($\alpha = 0.05$).
3) Fe(II) was positively correlated to silt and clay (both at $\alpha = 0.05$).

Therefore, electron donors tend to be more available in the finer sediment textures. Coupling this finding with others that showed that finer-grained sediments are more reactive suggests that finer-grained sediments at the Iowa site would have a greater denitrification capacity both because of their smaller sizes and because of their greater contents of electron donors.

3. Students supported and level of support under the project. Mr. Bijesh Maharjan started on the project on January 1, 2007, as a half-time research assistant with a salary of $1,318/month. Bijesh completed an M.S. in Environmental Engineering in December, 2008. Currently he is a PhD student in Land and Atmospheric Science at the University of Minnesota.