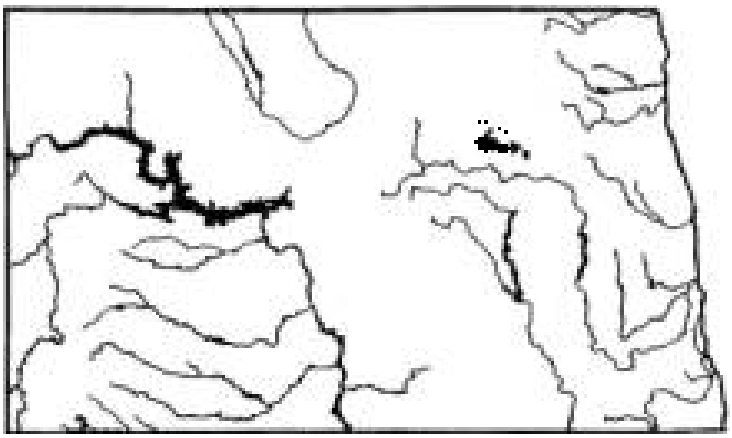

North Dakota
Water Resources Research Institute

North Dakota State University
University of North Dakota

ANNUAL REPORT

For the Period March 2007 to February 2008

Fiscal Year 2007 Report to the U.S. Geological Survey

June 2008

Annual Report

Fiscal Year 2007 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

June 2008

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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, 2007 to February 29, 2008.

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. One proposal was submitted by the faculty for the National Competitive 104(G) grant program. It was not funded. NDWRRI also worked closely with the Environmental and Conservation Sciences program of North Dakota State University (NDSU), Energy and Environmental Research Center at University of North Dakota (UND), and the International Water Institute, Fargo, ND on water related research issues and collaboration. NDWRRI co-sponsored an international conference on water, March 13-15, 2007 with the International Water Institute, Fargo, North Dakota. The Director organized and chaired two sessions creating a forum for presentation of the WRRI Fellowship research to the public. Several WRRI Fellows and their advisors participated.

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 two universities, North Dakota State University and University of North Dakota.

State Appropriation

The State Water Commission continued again this year its support to the 2007 – 2008 federal 104(B) funding for the Graduate Research Fellowship program of NDWRRI. This is fourth 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 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 2006, 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 Calls for Applications for Graduate Research Fellowships

The North Dakota Water Resources Research Institute (ND WRRI) has announced its 2007 Graduate Research Fellowship program. NDSU and University of North Dakota 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 $800-$1,000 range and for doctoral students $1,000-$1,400 per month. The fellowship funds must be utilized between March 1, 2007, and Feb. 29, 2008.

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 advisors. Advisors of the applicant should co-sign the applications.

Applications are due in the office of the director by 5:00 p.m., November 17, 2006. The proposals will be reviewed by a panel of faculty and state water resources research professionals. Announcement of awards will be made by early January.

Consult the ND WRRI website, http://www.ndsu.edu/wrri, for background on the program, and guidelines for preparation of applications. Applicants and advisors who are new to the program are urged to contact ND WRRI Director, G. Padmanabhan, at 231-7043, or G.Padmanabhan@ndsu.nodak.edu.

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

NDWRRI GRADUATE RESEARCH FELLOWSHIPS

Eleven fellowships were awarded in FY2007. The titles of the fellowship projects awarded are given below and details are provided for each project under separate project sections. Five of the Fellowships are renewals, two M.S. and three Ph.D. The renewals are Mary Schuh, Ryan Klapperich, Yuhui Jin, Dan McEwen, and Wei Zheng.

2007-08 Fellows and their projects:

Graduate Student	Project Title	Advisor
William Clark, Ph.D Biological Sciences, NDSU	The examination of Life History Variation in White Sucker (Catostomus commersoni) Populations in North Dakota and Minnesota Drainages	Dr. Mark Clark, Assistant Professor, Department of Biological Sciences, NDSU
Yuhui Jin, Ph.D. Chemistry, UND	Rapid and Sensitive Determination of Bacteria in Water Using Nanoparticles	Dr. Julia Zhao, Assistant Professor, Department of Chemistry, UND
Ryan Klapperich, M.S. Geology , UND	Analysis of Associated Bedrock-Aquifer System Sediments: Origins of Electron Donor-Rich Aquifers in Eastern North Dakota	Dr. Scott Korom, Professor, Geology and Geological Engineering, UND
Damion Knudsen, M.S. in Environmental and Conservation Sciences, NDSU	An Investigation into Subsurface Sampling and Characterization Efficiency Using a High Resolution GIS Based Earth System	Dr. Bernhart Saini-Eidukat, Assistant Professor, Department of Geosciences, NDSU
Sita Krajangpan, Ph.D Civil Engineering, NDSU	Effective Delivery of Iron Nanoparticles by Amphiphilic Polysiloxane Graft Copolymeric Vehicles for Groundwater Remediation	Dr. Achintya Bezbaruah, Assistant Professor, Department of Civil Engineering, NDSU
Dan McEwen, Ph.D Biological Sciences, NDSU	Stoichiometry and the transfer of mercury from benthic macroinvertebrates into game fish	Dr. Malcolm Butler, Professor of Zoology Department of Biological Sciences, NDSU
Breanna Paradeis, M.S. Natural Resources Management, NDSU	Plant Species Composition of Wetlands Located in Restored Native Prairie	Dr. Donald Kirby, Director School of Natural Resources Sciences, NDSU
Thunyalux Ratpukdi, Ph.D. Civil Engineering , NDSU	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	Dr. Eakalak Khan, Assistant Professor, Civil Engineering, NDSU
Mary Schuh, M.S. Soil Science, NDSU	Farm-scale reconnaissance of estrogens in subsurface waters	Dr. Frank Casey, Assistant Professor of Soil Physics, NDSU
Jay M. Thompson, M.S. Environmental Engineering, NDSU	Iron Nanoparticles for the Treatment of the Herbicides Atrazine, Alachlor and Dicamba in Groundwater	Dr. Achintya Bezbaruah, Assistant Professor, Department of Civil Engineering, NDSU
Wei Zheng, Ph.D. Biological Sciences, NDSU	Classification of Macroinvertebrate Communities across Red River Drainage Basin	Dr. Malcolm Butler, Professor of Zoology Department of Biological Sciences, NDSU

NATIONAL COMPETITIVE PROGRAM (104-G)

One proposal from UND was submitted through the ND Institute. The proposal was not funded. 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.

NDWRRI co-sponsored the Third International Water Conference titled "Research Education in an International Watershed: Implications for Decision Making" in Grand Forks, North Dakota, in March 13-15, 2007. The conference organized by the International Water Institute brought administrators, researchers, professionals and educators to Grand Forks, North Dakota to discuss water resources, flood control and water quality management issues related to the Red River of the North. The WRRI Director worked with the IWI in the planning and organization of the conference. He developed and chaired two sessions in the conference which provided a forum for presentation of the WRRI Fellowship research to the public. Several WRRI Fellows and their advisors participated. Ten past and present WRRI Fellows and three advisers made presentations at the conference. The Institute affiliate faculty chaired three sessions in all: 4C, 6A and 6C as listed below. The faculty and fellows' names are in bold letters.

The presentations by the Fellows and Institute affiliate faculty can be viewed at the International Water Institute's web site:

http://www.internationalwaterinstitute.org/2007proceed.htm

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

Concurrent Session 4C: **Water Quality in Rivers and Streams**
*Moderated by **G. Padmanabhan**, Director, ND Water Resources Research Institute, North Dakota State University, Fargo, ND.*

1. Upper Souris River TMDL Background Study. ***Wei Lin**, Civil Engineering and Environmental and Conservation Sciences, **Bernhardt Saini-Eidukat**, Geosciences and Environmental and Conservation Sciences, Joseph Super, Environmental and Conservation Sciences, North Dakota State University, Fargo, ND, and Michael Ell, Environmental Administrator, North Dakota Department of Health, Bismarck, ND.*

2. Simulation of Constituent Transport in the Red River of the North Basin, North Dakota and Minnesota, During Unsteady-Flow Conditions, 1977 and 2003-04. ***R.A. Nustad**, Environmental Engineer, USGS, North Dakota Water Science Center, Grand Forks, ND, and J.D. Bales, Hydrologist, USGS, North Carolina Water Science Center, Raleigh, NC*

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3. Application of Entrapped Cell Systems for Treatment of Anaerobic Sludge Digester Supernatant. ***Christopher Hill** and **Eakalak Khan**, Associate Professor, Department of Civil Engineering and Construction, North Dakota State University, Fargo, ND.*

Concurrent Session 6A: **Soils, Bacteria and Wastewater Treatment.**
*Moderated by **G. Padmanabhan**, Director, ND Water Resources Research Institute, North Dakota State University, Fargo, ND.*

1. The Fate of Manure-borne, Land-Applied Hormones. ***Francis Casey**, Associate Professor, **Mary Schuh**, graduate student, Dept. of Soil Science, Gerald L. Larsen, Research Chemist/Research Leader, Heldur Hakk, Research Chemist, Bioscience Research Lab, USDA-ARS, Fargo, ND, Zhaosheng Fan, graduate student, Dept. of Soil Science, North Dakota State University, Fargo, ND.*

2. Denitrification in the Red River Basin and Beyond: How Aquifer Sediments Influence Water Quality. ***Scott F. Korom**, Associate Professor, Department of Geology and Geological Engineering, University of North Dakota, Grand Forks, ND.*

3. Sensitive Determinatrion of Bacterial Cells Using Fluorescent Nanoparticles. ***Yuhui Jin**, graduate student, Dept. of Chemistry, Jenna Parisien, student, Dept of Chemistry, Min Wu, Assistant Professor, Dept. of Biochemistry, School of Medicine and Health, and **Julia Xiaojun Zhao**, Associate Professor, Dept. of Chemistry, University of North Dakota, Grand Forks, ND.*

Concurrent Session 6C: **Flood, Droughts and Water Management.** *Moderated by **Phil Gerla**, Professor, Department of Geology and Geological Engineering, University of North Dakota, Grand Forks, ND.*

1. Characteristics of Effective Local Water Management Organizations in the Red River Basin. ***Craig C. Kritsky**, graduate student and **Robert R. Hearne**, Assistant Professor, Department of Agribusiness and applied Economics, North Dakota State University, Fargo, ND*

2. The Red River Management Consortium. *Daniel J. Stepan, Senior Research Manager, Energy & Environment Research Center, University of North Dakota, Grand Forks, ND.*

PUBLICATIONS AND PRESENTATIONS

Fellows and advisers

Publications

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., Kannan, S., Wu, M., **Zhao, X**. (2007) Toxicity of luminescent silica nanoparticles to living cells. Chem. Res. Toxicol. Published on web 07/13/07.

Schuh, M., F.X.M. Casey, and H. Hakk. 2007. Farm-Scale Reconnaissance of Estrogens in Subsurface Waters. In Annual Meetings Abstracts [CD- ROM]. ASA, CSSA, and SSSA, Madison, WI.

Klapperich, R. J. S., and S. F. Korom, (2007) Electron donor potential of eastern North Dakota shale formations. EOS, Transactions, American Geophysical Union, 88(52), Fall Meeting Supplement, Abstract H13G-1676, 2007.

Gibbs, P. S., R. Kasa. **J. Newbrey**, S. R. Petermann, R. E. Wooley. H. Vinson, and **W. Reed**. (2007) Identification, antimicrobial resistance profiles, and virulence of members from the family *Enterobacteriaceae* from the feces of yellow-headed blackbirds (*Xanthocephalus xanthocephalus*) in North Dakota. *Journal of Avian Diseases* 51:649-655.

Hearne, R. 2007. "Evolving Water Management Institutions in the Red River Basin." *Environmental Management.* 40(6):842-852.

Presentations

Jay Thompson, **Achintya N. Bezbaruah, Bret J. Chisholm**, **2007**, Rapid Dechlorination of the Herbicide Alachlor by Zero Valent Iron Nanoparticles. ISNEPP 2007, Nanotechnology in Environmental Protection and Pollution, 11-13 December. Ft. Lauderdale, FL (Presentation)

Jay Thompson, **Achintya N. Bezbaruah, Bret J. Chisholm**, **2007**, Iron Nanoparticles for the Treatment of the Herbicides Atrazine, Alachlor and Dicamba in Groundwater. 2 nd International Conference on Environment, 2-5 August. Athens, Greece (Presentation)

Jay Thompson , **Achintya N. Bezbaruah, Bret J. Chisholm**, **2007**, Laboratory Scale Study to Determine the Effectiveness of Iron Nanoparticles for Selected Pesticide Remediation. 2007 AWRA Summer Specialty Conference, Emerging Contaminants of Concern in the Environment: Issues, Investigations, and Solutions, 25-27 June. Vail, CO (Poster)

Jin, Y., Wu, M., **Zhao, X**. 2007. Simultaneous detection of multiple bacterial cells using fluorescent nanoparticles. The Pittsburgh Conference, Chicago, Illinois. February 25 - March 2.

Jin, Y., Wu, M., **Zhao, X**. 2007. Cytotoxic properties of luminescent nanomaterials. The Pittsburgh Conference, Chicago, Illinois. February 25 - March 2.

Krajangpan, S. , Jarabek, L., Jepperson, J., **Chisholm, B., Bezbaruah**, A. September 7 2007. Protecting Iron Nanoparticles from Oxidation by Non-target Compounds and Their Effective Subsurface Delivery Using Amphiphilic Polysiloxane Graft Copolymers, ND/SD ESPCoR 6th Biennial Joint Conference 2007, Fargo, ND. [Poster]

Krajangpan, S. , Chisholm, B., Bezbaruah, A., December 11 2007. Comparative Studies of Colloidal Stability of Bare and Amphiphilic Polysiloxane Graft Copolymer Coated Iron Nanoparticles and Their TCE Degradation Kinetics. ISNEPP 2007 Nanotechnology in Environmental Protection and Pollution, Ft. Lauderdale, FL. [Presentation]

Krajangpan, S., Elorza, J., **Bezbaruah, A., Khan, E., Chisholm, B**., December 11 2007. Nitrate Removal by Zero-Valent Iron Nanoparticles Entrapped in Calcium Alginate. ISNEPP 2007 Nanotechnology in Environmental Protection and Pollution, Ft. Lauderdale, FL. [Presentation]

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

Institute Publications

Gerla, Philip J. and William Lenarz (2007) Effect of Land Cover and Pattern on the Quality of Groundwater Discharged from Springs and Seeps at Pigeon Point, Southeastern North Dakota, Technical Report No: ND07 – 01, North Dakota Water Resources Research Institute, June 2007.

Newbrey, Jennifer L. and Wendy L. Reed (2007) West Nile Virus Antibodies in Free-Living North Dakota Icterids, Technical Report No: ND07 – 02, North Dakota Water Resources Research Institute, June 2007.

Hill, Christopher B. and Eakalak Khan (2007) A Comparative Study of Immobilized Nitrifying and Co-immobilized Nitrifying and Denitrifying Bacteria for Ammonia Removal of Sludge Digester Supernatant, Technical Report No: ND07 – 03, North Dakota Water Resources Research Institute, July 2007.

Newbrey, Michael G. and Allan Ashworth (2007) Climate Change and Evolution of Growth in North American Hiodontidae, Esocidae, and Percidae, Technical Report No: ND07 – 04, North Dakota Water Resources Research Institute, July 2007.

Goltz, Kendall and Jay A. Leitch (2007) Implicit Prices of Wetlands, Wetland Easements, and Recreational Sales of Farmland in North Dakota, Technical Report No: ND07 – 05, North Dakota Water Resources Research Institute, December 2007.

Shultz, Steven (2007) The Impact of Rural Water Supply Systems on Property Values, USGS/NIWR 104G Project: # 2005NE83G, North Dakota Water Resources Research Institute and Nebraska Water Resources Center, August 2007.

THESES AND DISSERTATIONS

Goltz, Kendall. December 2007. M.S. Thesis: "Implicit prices of wetlands, wetland easements, hunting/recreational sales, and other attributes of farmland in four counties in North Dakota" Natural Resources Management Program, North Dakota State University, Fargo, ND 58105.

Newbrey, Michael G. July 2007. Ph. D Dissertation: "Climate Change and Evolution of Growth in North American Hiodontidae, Esocidae, and Percidae" Biological Sciences Department, North Dakota State University, Fargo, ND 58105

Newbrey, Jennifer. July 2007. Ph. D Dissertation: "Maternal condition, carotenoids and reproduction in yellow-headed blackbirds" Biological Sciences Department, North Dakota State University, Fargo, ND 58105

Torpen, David. December 2007. M.S. Thesis: "Stakeholder Preferences for Water Quality Alternatives in the Red River Basin" Agribusiness and Applied Economics program, North Dakota State University, Fargo, ND 58105

PROJECTS (104-B: Fellowship)

Description of WRRI Graduate Research Fellowship and 104(G) projects follow:

The Examination of Life History Variation in White Sucker Populations in North Dakota and Minnesota Drainages

GRF Project 2005ND78B
Fellow: William Clark
Adviser: Mark Clark
Department of Biological Sciences
North Dakota State University
Fargo, ND 58105

Regional Water Problem

In the Midwest, extensive landscape modifications of prairie habitat, due to agricultural practices, has altered the hydrology of most river basins; yet, identifying the proximate mechanisms by which these landscape changes are passed to the species inhabiting these river basins remains elusive. Changes in turbidity, water chemistry, and temperature accompany changes in river hydrology and represent major changes to the environment of fish inhabiting these rivers. In North Dakota, millions of State dollars are spent on maintaining productive fisheries for revenue and recreation. North Dakota's fishery managers have two main goals when managing aquatic systems: 1) enhancing fish production and 2) maintaining fish community structure. Research on the mechanisms of habitat alteration on life history traits such as growth, age at maturation, fecundity, immune function, and longevity provide managers with the data and tools to better conserve ecological communities.

Scope and Objectives

I propose a research program that examines variation in individual growth (size at age, length-weight ratio, body lipid levels), reproductive effort (gonad: body mass ratio, age at maturation, tubercle development) and physiology (metabolic rate, immune function) in white sucker populations distributed in North Dakota and Minnesota. In addition, I will quantify relationships among watershed landcover, hydrology, and temperature and variation in white sucker life-history traits.

Results to date

Currently I have finished my second field season and am in the process of working on analysis of growth rates, immune system components, and reproductive effort. In 2007 I collected fish from 28 watersheds in North Dakota and intend to sample the same tributaries in 2008.

Parasite load and H:L ratio

One underutilized index of stress is the ratio of heterophils to lymphocytes. Changes in H/L ratio is a measurement of chronic stress and may prove useful in the evaluation of habitat effects on aquatic vertebrates. We used H/L ratios to evaluate the effects of parasite load on white suckers. Our preliminary results suggest that fish with parasites have a higher H/L ratio or a higher level of chronic stress (figure 2). Furthermore the results also indicate that there is no direct correlation between parasite load and H/L ratio (figure 3). In conclusion, the data suggests that chronic stress levels are higher in fish with parasites however H/L ratios are not affected by number of parasites.

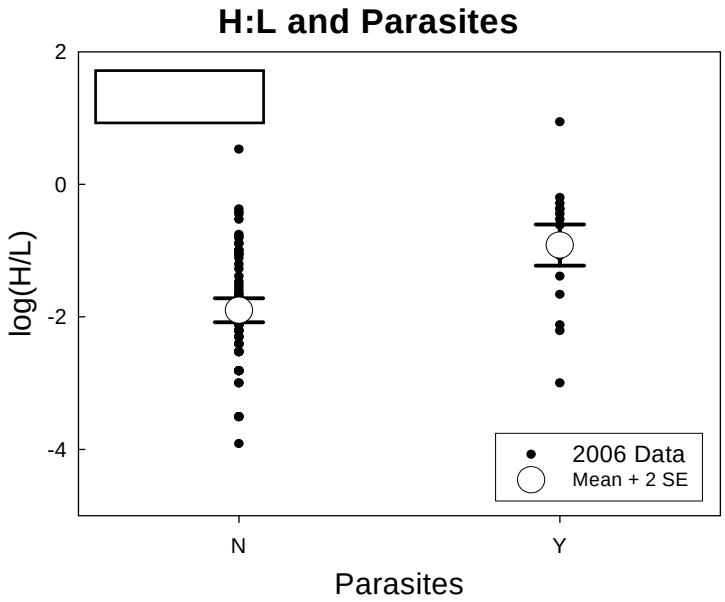

Figure 2: This figure shows the relationship between presence of parasite (x-axis) and the chronic stress level of a fish (y-axis). The results show that fish with parasites (Y) have a high H/L ratio then fish without parasites (N).

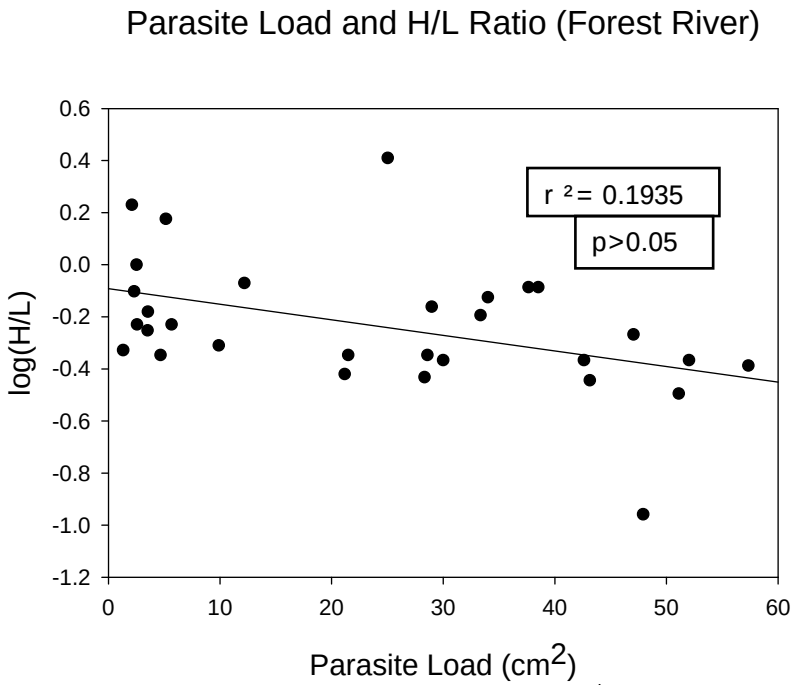

Figure 3: This figure shows the relationship between parasite load (cm^2)(x-axis) and H/L ratios (y-axis). These results show that there is not a significant correlation between number of parasites and chronic stress level.

Rapid and Sensitive Determination of Bacteria in Water Using Nanoparticles

GRF Project 2006ND98B
Fellow: Yuhui Jin
Adviser: Julia Xiaojun Zhao
Department of Chemistry
University of North Dakota
Grand Forks, ND 58202

1. 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.

2. 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).

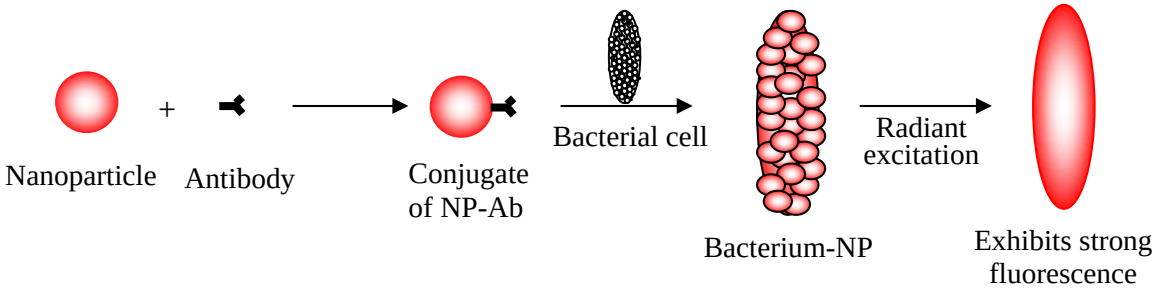

Figure 1 Schematic diagram of determination of bacteria using fluorescent nanoparticles

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 will focus 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.

2. Progress

During the last two years, some significant progress has been made by the applicant. Basically, the project has three goals. G**oal 1** of the development of multiple colored nanoparticles has been achieved in the first year (2006). G**oal 2** of the determination of target bacterial cells using nanoparticles has been accomplished in the second year (2007)

Analysis of Associated Bedrock-Aquifer System Sediments: Origins of Electron Donor-Rich Aquifers in Eastern North Dakota

GRF Project 2006ND101B
Fellow: Ryan Klapperich
Adviser: Scott Korom
Department of Geology and Geological Engineering
University of North Dakota
Grand Forks, ND 58202

Project Background

Nitrate pollution has long been recognized as the most prevalent form of groundwater pollution. The only effective process to remediate nitrate contaminants is denitrification, typically through natural attenuation. This process reduces nitrate (NO_3^-) to harmless nitrogen gas. The process occurs naturally, requiring only an oxygen-limited environment, the presence of nitrogen digesting bacteria, and the availability of electron donors. The three most common electron donors are organic carbon, sulfide (typically as pyrite, FeS_2), and ferrous iron minerals. Research has also shown that the controlling factor in this reaction has typically been the availability of suitable electron donors within the aquifer sediments.

The long-term goal of this research is to develop an aquifer nitrate vulnerability index based on the supply of electron donors in the aquifer sediments. This project contributes toward that goal by considering the abundance of electron donors in the likely parent materials comprising the aquifer sediments. Based on the experience of previous UND denitrification research and literature reports, shale units are more likely to have large supplies of electron donors than other regional rock types. Shale is relatively soft and easily weathered and comprises much of the bedrock in eastern North Dakota. Therefore, shale units are the most likely contributors to sediments in nearby aquifers. My hypothesis is that regional bedrock units rich in electron donors should correlate to nearby aquifer sediments that are potentially rich in electron donors. The practical utility of this work is that an initial list of aquifers with potentially high denitrification capacities in North Dakota may be made using geological investigations. Later, more extensive and more expensive geochemical analyses would be necessary to confirm the denitrification capacity of specific aquifers and specific aquifer sites. However, much of the initial work could be done with data already available and in conjunction with future drilling performed by the North Dakota State Water Commission (NDSWC).

Progress

Geochemical analysis is ongoing. The bedrock samples were collected this previous summer in conjunction with the State Water Commission. They were collected in a general east to west transect across Stustman, Foster, and Steele counties. Two to three samples were collected when the shale was penetrated, representing an upper and lower, and occasionally mid-level sample. Samples from Kidder, Benson, Nelson, and Cass Counties have also been provided from other drilling projects. In total there are 39 samples representing 21 different sites and seven lithologic units. XRD analysis has been preformed on many of the samples and shows that the shale units are rich in quartz, clay minerals, and occasionally calcite, as was expected. Pyrite, micas, and iron bearing minerals have also been detected. XRD has also verified that the lithologic units are generally uniform in space and depth, meaning a single sample can be considered representative. Organic carbon analysis shows distinct differences between the formations. The Carlisle and Greenhorn formations have significantly higher values of OC than the Pierre or Niobrara formations. Inorganic sulfide analysis to date also suggests some formations have significant quantities of sulfide (as S-) available. This data suggests the shales contain similar levels of electron donors as nearby aquifers.

Significance:

This research will investigate the link between the denitrification capacities of eastern North Dakota aquifers with the electron donor composition of the surrounding bedrock. If such a link is possible, a qualitative index (low, medium, and high) of aquifer denitrification capacity based on the probable source of the parent material will be developed. This index could then be used to focus, in a cost-effective fashion, more extensive and expensive geochemical analysis on specific aquifers or zones in specific aquifers.

An Investigation into Subsurface Sampling and Characterization Efficiency Using a High Resolution GIS Based Earth System

GRF Project 2007ND148B
Fellow: Damion Knudsen
Adviser: Bernhardt Saini-Eidukat
Department of Geosciences
North Dakota State University
Fargo, ND 58105

Research:

Groundwater polycyclic aromatic and chlorinated hydrocarbon containing non aqueous phase liquid contamination is a major issue affecting people's health and the vast amount of money being used to remediate it. The majority of investigators of non aqueous phase liquid contaminated sites currently use traditional sampling methods such as hollow stem auger coring, hand held photo-ionization detectors, visual confirmation, and laboratory analysis to determine the extent of a subsurface contaminant source zone. These methods are time consuming, costly, and can create large amounts of waste. Improving upon traditional site characterization methods using direct sensing instruments such as laser induced fluorescence can greatly reduce the time and budget constraints of site characterization. Investigators may now be able to understand the extent of contamination and create draft or preliminary 3-D models in situ and in real time while still in the field. Shallow subsurface direct sensing instruments are comparable to measurement while drilling and geophysical wire line bore hole instruments used in the oil and mining industry. Direct sensing, measurement while drilling, and wire line instruments usually collect large amounts of data preceded or followed by traditional sampling methods used for calibration and data verification. Many times in environmental investigations both direct sensing instruments and traditional sampling methods will be operating on a site at the same time with direct sensing instruments finding hotspots in order to guide traditional sampling methods.

These concepts are in agreement with a growing movement of site characterization experts at the Environmental Protection Agency, who emphasize that a greater number of lower cost, higher density measurements such as directly sensed data, followed by lesser amounts of higher cost traditional sampling, is more effective in the characterization of source zone groundwater contamination. With direct sensing instruments such as laser induced fluorescence between 4,000 and 40,000 semi-qualitative and semi-quantitative measurements are collected depending on the size of the site and the degree of accuracy of the characterization desired by the site investigator. This is in comparison to at most a few dozen core samples that might be taken from a site using traditional sampling methods. In current practice, sample boring locations are often based on little more than gut-feel with pen and paper maps. Alternatively, computer derived or guided sample

locations would be expected to decrease source zone interpolation uncertainty and optimize sampling locations. The combination of intelligent location selection and real time feedback via direct sensing instruments should produce a significantly more efficient site characterization. This is important in light of the budgetary, time, and spatial limitations investigators are often dealt. Direct sensing instruments are of higher resolution than traditional sampling methods and provide a more resolute model of the contaminant source zone.

Objectives and Methods :

1. Conduct a literature review on different methods, instrumentation, and geostatistics of subsurface site characterization.
2. Characterize using modern geostatistical theory and geographic information systems, directly sensed groundwater contaminant data from Morton and McKenzie County, North Dakota, and a site in Codington County, South Dakota.
3. As high resolution three dimensional models of subsurface contaminant distributions are created, computer simulations will investigate different 3-D sampling densities and provide an optimized method or workflow for investigators while also providing economic constraints given certain model accuracy values.

Progress to Date:

I have produced high resolution three dimensional models of subsurface contaminant distributions to be used in the simulator. Computer simulations are underway investigating different 3-D sampling densities. Budgets are being given to the different simulated sampling methods in attempts to quantify model accuracy versus total project cost.

Significance:

I am researching improvements that can be made by merging old and new technology with regards to site characterization and management of three dimensional subsurface analyte distributions. Groundwater contamination has been indicated in community increases of certain rare cancers and health issues. One example of this would be Love Canal in New York in which many people were exposed to toxic fumes from hazardous waste that migrated with groundwater through the subsurface into living areas. In 2004 the EPA published a report stating that much research still needs to be done on understanding dense non aqueous phase liquid groundwater contamination with regards to not only the transportation of these dissolved chemicals through the subsurface but also of their free phase source zones. New research and observations as of late have led to statements that source zone depletion is becoming an even more effective method of groundwater remediation instead of just treating the dissolved phase constituents of groundwater contamination.

Effective Delivery of Iron Nanoparticles by Amphiphilic Polysiloxane Graft Copolymeric Vehicles for Groundwater Remediation

GRF Project 2007ND150B
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

An increasing number of laboratory and field studies illustrate the potential of metal particles for degrading organic and inorganic species susceptible to reduction reactions [1-8]. Nanoparticles are attractive for remediation of various contaminants because of their unique physiochemical properties [9, 10]. Various chlorinated aliphatic hydrocarbons [11] and toxic metals [12, 13] can be remediated using metal nanoparticles such as zero-valent iron nanoparticles (nZVI). Metal particles/nanoparticles have also been used for the remediation of groundwater contaminated with chemicals used in explosives [14-19] and arsenic [19-22].

The effectiveness nZVI for groundwater remediation depends upon the effective delivery of the nanoparticles to the water/contaminate interface without flocculation and severe oxidation. To accomplish effective delivery of nZVI, a delivery system that provides for dispersability and colloidal stability of individual nanoparticles in water is required. In addition, the delivery system should protect the nZVI from severe oxidation by dissolved oxygen and water and provide an affinity for the water/contaminate interface.

Colloidal stability of nZVI has been accomplished using surfactants [23]. The hydrophobic "tails" of the surfactants physically absorb onto the nZVI surface while the hydrophilic "heads" inhibit flocculation and allow for suspension in the aqueous medium. While surfactants provide colloidal stability in water, the highly reversible nature of surfactant absorption limits its application as a delivery system for ground water decontamination since desorption will be favored when the nanoparticles are transported through surfactant-free ground water. In contrast, high molecular weight, amphiphilic polymers show essentially irreversible absorption and, thus, are more suitable as a delivery system for ground water remediation [24, 25].

Saleh *et al*. [26] have shown that amphiphilic triblock copolymers with an A-B-C triblock microstructure are effective delivery systems for nZVI. The triblock copolymers were produced using atom transfer radical polymerization (ATRP) in conjunction with a post-polymerization ester-hydrolysis step and a post-polymerization sulfonation step. The results of the research demonstrated enhanced colloidal stability and an increased affinity for a water/organic interface provided by the amphiphilic triblock copolymer. The amphiphilic triblock copolymers synthesized and evaluated by Saleh *et al*. [26] showed promising results with respect to enhanced colloidal stability of nZVI and the creation of a thermodynamic affinity of the nanoparticles for the water/contaminant interface. However, kinetic studies showed a decrease in the rate of contaminant degradation by the polymer-modified nZVI as compared to unmodified nZVI [27]. The reduction in

contaminant degradation rate was attributed to low permeability of the contaminant through the film absorbed onto the nZVI. In addition to issues associated with contaminant degradation rate, the synthesis method required to produce the triblock copolymer structure is quite sensitive to impurities and oxygen and quite slow. Further, catalyst residues can be difficult to remove. Despite 15 years of intense research, ATRP is not being practiced commercially to any great extent. As a result, there exists a need to prepare tailored, multifunctional polymeric materials using a cost-effective, commercially-viable synthetic route that could serve as a highly effective delivery system for nZVI.

Considering the requirements of an effective delivery system for nZVI, functionalized amphiphilic polysiloxanes are an ideal class of polymers for the application. **Figure 1** provides a schematic representation of amphiphilic polysiloxane graft copolymers (APGCs) that could be easily synthesized and evaluated.

The hydrophobicity of the polysiloxane polymer backbone will protect 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 as illustrated schematically in **Figure 2**. Since polysiloxanes have a very low glass transition temperature (-120°C) and are highly soluble in most hydrocarbons, they will readily allow permeation of organic contaminants such as arsenic to the nZVI surface providing fast, efficient contaminent remediation. Additionally, the versatility of the hydrosilylation reaction enables tailoring of the polysiloxane polymer backbone chemical structure to enhance contaminant specificity.

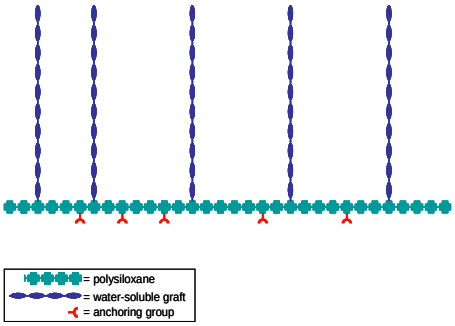

Figure 1. A schematic representation of amphiphilic polysiloxane graft copolymers (APGC)

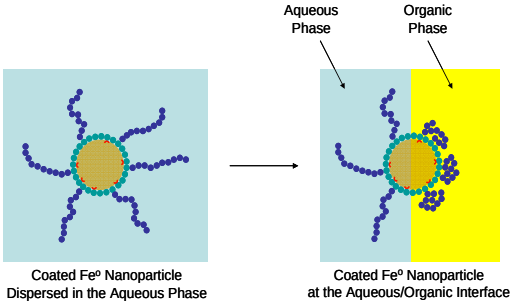

Figure 2. A schematic representation of the polymer coated nanoparticles in water and at the water/contaminant interface.

In addition to possessing the ideal characteristics for nZVI delivery system, this class of polymers can be easily synthesized from a wide variety of commercially available starting materials. For example, Gelest® Inc. sells a variety of poly(dimethylsiloxane-co-methylhydrosiloxanes) copolymers with varying methylhydrosiloxane content and molecular weights as well as poly(methylhydrosiloxane) homopolymers of varying molecular weight. With regard to precursors for the generation of hydrophilic polymer grafts, Clariant® sells an array of monovinyl-terminated PEGs of varying molecular weight. Thus, with this class of graft copolymers, extensive structure-property relationships can be developed by varying polysiloxane backbone molecular weight, hydrophilic polymer graft content and molecular weight, and anchoring group content.

Description of the Critical State or Regional Water Problem to be Investigated

Arsenic compounds are often found in contaminated groundwater [28]. A trivalent arsenic [As(III)] contamination is a major concern in southeast North Dakota (568 sq mile area in Sargent, Ransom and Richland counties are affected) [29]. The contaminated area is primarily comprised of farmland and a few small cites including Hankingson, Lindrud, Wyndmere, and Milnor. Sampling done since 1979 in that area indicated arsenic concentration as high as 1.5 mg/L. Remedial investigation completed by North Dakota Department of Health between 1982 and 1986 indicated widespread occurrence of elevated groundwater arsenic concentration. The elevated concentration of arsenic was attributed to, in part, to the use of arsenic-laced grasshopper bait used in the 1930s and 1940s to control grasshopper population. Arsenic trioxide, sodium arsenate, Paris Green, and other arsenic compounds were mixed with bait material (e.g. oats) and applied to farm field.

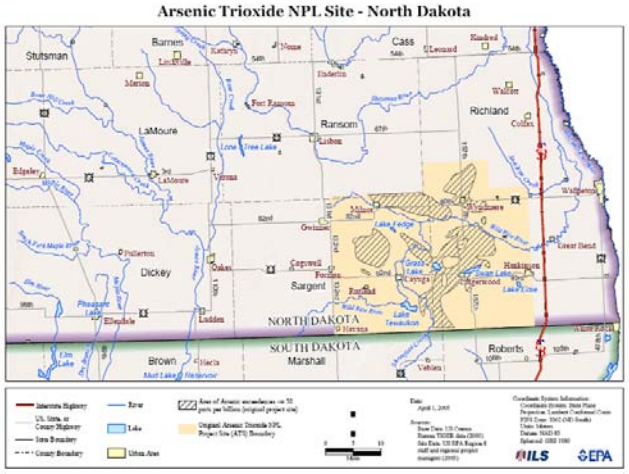

Figure 3. Arsenic Contaminated Area in SE North Dakota [29]

In addition, there are concerns about the TCE in North Dakota and Minnesota, especially, at the Baytown Ground Water Contamination Site in Washington County, Minnesota. They have looked at nZVI as a potential remedy for source zone and at-well applications [30]. RDX is a common nitramine explosive and one of the major groundwater contaminants in military facilities. RDX, explosive, when ingested, is known to cause tremors and convulsions leading to death. Though presently not reported in alarming level at the Air Force Base at Minot (ND) it may also be major of the concerns in the future.

Research Progress

The progress is summarized below:

Task I: *Synthesis and characterization of APGCs*

Carboxylic acid-functional APGCs containing polyethylene glycol grafts (PDMS/PEG/AA) were successfully synthesized. The APGCs were synthesized by

hydrosilylation using PtO_2 as a catalyst**.** The proton absorption peaks at δ 0.4-0.5 ppm and δ 1.4-1.6 ppm in the ^{1}H NMR spectrum (**Figure 4a**) correspond to methylene protons created as a result of successful hydrosilylation of the vinyl functional precursors to the hydride functional polysiloxane copolymer.

The carbon absorption ^{13}C NMR spectrum (**Figure 4b**), has verified that the hyrosilylation reaction has occurred. The Carbonyl peak has a quartet at δ 158.0-158.9 ppm. Poly(ethylenglycol) peaks appear between δ 59 ppm and 78 ppm. The tert-butyl carbonyl and its methylene carbon are located at δ 150.6 ppm, and δ 29.0 ppm, respectively. The same procedure was used to produce APGC varying the relative molar concentration of carboxylic acid groups to PEG grafts. With the varied ratios, all five formulations of PDMS/PEG/AA, A (70/25/5), B (62/36/2), C (72.5/21/6.8), D (67/29/4), and E (65/32/3), were successfully synthesized and characterized.

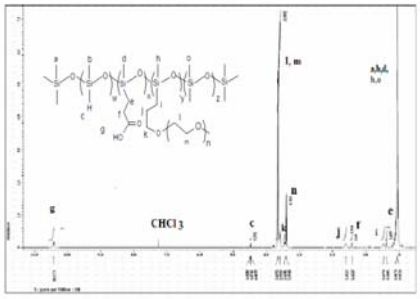

Figure 4a. A proton NMR spectrum of APGC.

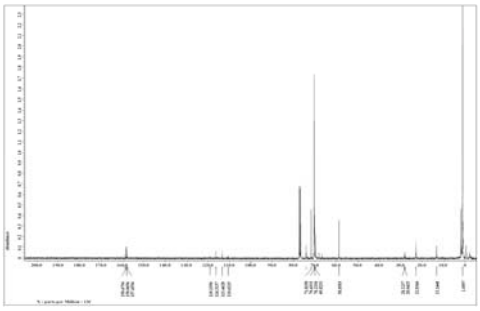

Figure 4b. A carbon NMR spectrum of APGC.

Task II: *Synthesis and characterization of nZVI*

Iron nanoparticles (nZVI) were successfully synthesized as per method laid out in my 2007 award proposal. The synthesized nZVI has average particle size of 35 nm. The particles sizes were analyzed by transmission electron microscope (TEM) over 300 particles (**Figure 5a, 5b**). BET specific surface was determined to be $25 m^2/g$. SEM/EDS data indicate that iron is the most abandon mineral (84.34%), with, a smaller amount of oxygen (15.66%, in the oxide shell) on the nZVI (**Figure 6**). The shell prevents particles from spontaneously igniting in the atmosphere, yet allows contaminant access to nZVI in solution [31].

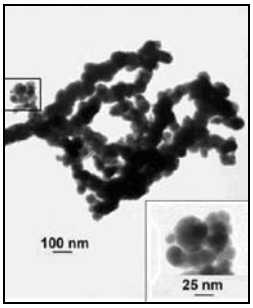

Figure 5a. TEM image of nZVI synthesized by the researcher's group.

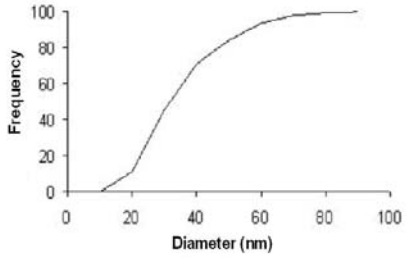

Figure5b. Size distribution curve for synthesized nZVI

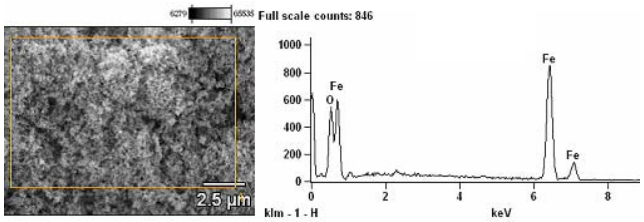

Figure 6. SEM/EDX image of fresh nZVI synthesized in the laboratory. The EDX result indicates 84.34 %iron and 15.66 %oxygen on nZVI.

Task III: *Polymer coating of nZVI and sedimentation rate measurements*

Aqueous slurry of nZVI was combined with 5, 10, and 15 g/L APGC polymer solutions of all five formulations. The mixture was sonicated for 30 min followed by gentle end-over-end rotation for 72 h to disperse the nanoparticles and allow the polymer to absorb on the surface of the nanoparticles. The APGC coated nZVI were then filtered and washed multiple times to remove any excess non-adsorbed APGC.

The colloidal stability of the APGC coated nZVI was then evaluated by measuring sedimentation rates of nanoparticle suspensions using a UV-spectrometer (at a wavelength of 508 nm). The sedimentation studies were done with five replications for each batch. **Figure 7** displays representative data illustrating the effect of APGC composition on colliodal stability of nZVI. From the figure, it can be seen that modification of the APGC coated nZVI have decreased sedimentation rate and the magnitude of the decrease was a function of APGC composition. The APGC with the highest concentration of carboxylic acid anchoring groups provided the highest colloidal stability. These results confirm that the proposed approach for enhancing nZVI colloidal stability is valid as is the synthetic process for creating novel carboxylic acid-functionalized APGC.

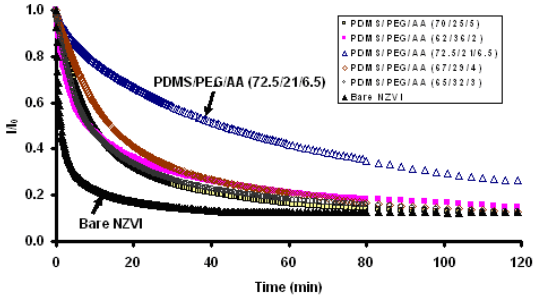

Figure 7. Sedimentation studies of APGC coated nZVI (PEG = polyethylene glycol and AA = acrylic acid). Ratio represents weight percent of each component. Marked decrease in sedimentation rate was observed for APGC modified nZVI as compared to bare nZVI.

Task IV: *Degree of oxidation by non-target compound*

The degree of oxidation was determined by quantitative SEM-EDX peak area. The EDX peak area analysis provides an approximate surface corrosion by percent Fe:O elemental composition. The analyses show 84.34:15.66, 49.71:50.29, and 68.03:31.97 for fresh nZVI, bare nZVI and APGC coated nZVI, respectively (**Figure 6, 8, 9**). The results indicate using APGC coated nZVI had significantly decreased nZVI surface corrion. However, excess oxidation might have occurred during the washing process. Therefore, sample preparation needs to be modified and this study needs to be repeated.

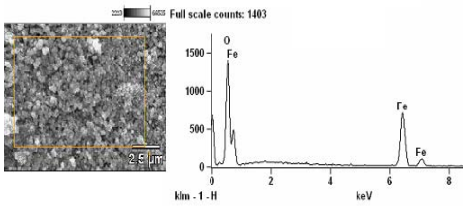

Figure 8 SEM/EDX image of bare nZVI in aqueous solution. The EDX result indicates 49.71 %iron and 50.29 %oxygen in the nZVI.

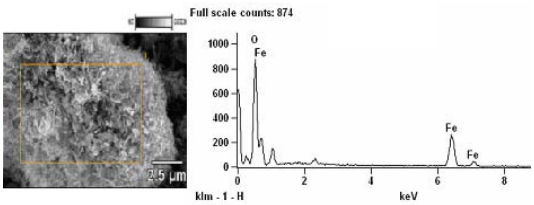

Figure 9 SEM/EDX image of APGC coated nZVI in aqueous solution. The EDX result indicates 68.03 %iron and 31.97 %oxygen in the nZVI.

Mercury Accumulation in Chironomus Dilutus Reared on Nutrient-Limited Food

GRF Project 2007ND153B
Fellow: Dan McEwen
Adviser: Malcolm G. Butler
Department of Biological Sciences
North Dakota State University
Fargo, ND 58105

Research

Mercury (Hg) damages the central nervous system, altering the way that nerves conduct electrical impulses and divide, leading to lowered cognitive and metal functioning or in especially acute circumstances cerebral palsy, mental retardation or death. Its effects are especially harmful to fetuses or infants during development of the nervous system. Hg emissions have continued to increase since the industrial revolution, entering aquatic food chains via atmospheric precipitation where they suspend in the water column and are taken up by phytoplankton or settle to the bottom where they become available to bacteria. Phytoplankton, with acquired Hg, is either ingested by zooplankton or sinks to the substrate as detritus. In turn, detritus and bacteria provide a food source to macroinvertebrate benthic organisms (i.e., benthos) and bioaccumulation occurs up through trophic levels eventually to game fish that are consumed by humans. As a result, the EPA and various state agencies issue advisories for fish consumption where impairment occurs. The North Dakota Department of Health currently has consumption advisories listed for Devils Lake, Red River, Lake Oahe/Missouri River, Lake Sakakawea, and other water bodies. Research is prposed for addressing taxonomy, stoichiometry, and benthic-pelagic coupling in the context of benthic contribution to Hg accumulation to fisheries in Minnesota and North Dakota lakes along a trophic gradient from oligotrophic to eutrophic.

Objectives and Methods

The objectives of this study are as follows:

1. Characterize the benthic community of lakes under a variety of nutrient regimes
2. Quantify the biomass of the constituent members of the benthic communities in those lakes
3. Quantify carbon, nitrogen, phosphorus, and mercury ratios for those communities as a whole

4. Model how those ratios impact rates of mercury accumulation and concentrations in piscivorous game fish likely to inhabit those lakes (e.g., lake trout, walleye, smallmouth bass, northern pike, etc.)
5. Use appropriate regression models to test whether there is a relationship between Hg and P (as a limiting nutrient) in the benthos
6. Provide applicable information for managers of mercury-susceptible systems

Project Progress

A culture of *Scenedesmus obliquus* (TOW 9/21 P-1W) has been obtained from an unnamed pond in Itasca State Park, Minnesota (from M.W. Fawley). *Chironomus dilutus* culture has been established with larvae from a regional wetland, with culture methods adapted from Townsend et al. (1979). Preliminary growth experiments are in progress, using a high nutrient food source (i.e., Tetramin B) to determine methodology for maintaining cultures and sustaining low mortality. We are also in the process of growing batch cultures of algae at desired nutrient levels to feed *Chironomus*.

Significance of Research

This research will provide a better understanding of factors contributing to the bioaccumulation of mercury in aquatic ecosystems.

Plant Species Composition of Wetlands Located in Restored Native Prairie

GRF Project 2007ND147B
Fellow: Breanna Paradeis
Adviser: Donald Kirby
School Of Natural Resources Sciences
North Dakota State University
Fargo, ND 58105

Research:

Wetlands are an important landscape feature in the Prairie Pothole Region (PPR) of the Northern Great Plains. Wetlands impart several benefits including the maintenance or improvement of water quality, groundwater recharge, flood attenuation and the provision of habitat and/or forage to wildlife and livestock (Kirby et. al 2002a,b). However, wetlands have been impacted in the Prairie Pothole Region by various human activities including agricultural practices. These impacts have lead to the decline of wetland functions and water quality (Detenbeck et. al 2002). Restoring species richness and diversity and managing native prairie wetland complexes in a way that mimics natural disturbance processes while minimizing negative human impacts will improve wetland functions and water quality.

In recent years, several large-scale restorations of native grasslands have occurred throughout the state of North Dakota. Many of these restorations, often on large tracts of publicly owned land such as National Wildlife Refuges, have focused on restoring native plant species diversity and richness in the surrounding prairie areas rather than within the wetlands themselves. However, it is likely that the wetlands have functionally benefited from the restoration and improved management of the surrounding uplands. Evaluation of the plant species composition of the restored wetland and upland areas and of the subsequent management regimes, will give insight towards the hydrological functions and processes occurring within these wetlands, i.e. water storage, improvement of water quality, and sedimentation.

Project Objectives:

The goal of this study is to evaluate plant community composition and physical characteristics of prairie pothole wetlands in restored native prairie areas and to incorporate the data obtained into a model that predicts wetland condition and function based on environmental variables. This study will also compare and evaluate restoration and management techniques employed in restored native prairie areas, and their effect on the plant species composition, physical characteristics, and functional capacity of wetland ecosystems.

Project Progress

Restored wetland study sites were selected based on restoration techniques and time since restoration. Native sites were selected based on distance from restored sites for comparative purposes. Wetland vegetation data was collected using an Index of Plant Community Integrity (IPCI) method for native and restored wetlands located throughout the Prairie Pothole Region. In the surrounding upland areas, vegetation data was collected along several transects placed at mid-slope and top-slope positions within the watershed.

The physical and functional characteristics of each wetland were evaluated using the Hydrogeomorphic (HGM) model as developed by the U.S. Corps of Engineers. The HGM model provides a means for direct comparison of the landscape and hydrological function of wetlands in different hydrologic regimes and diverse environmental conditions. Similarly, landscape information, i.e. upland land use, was obtained for each wetland and its surrounding catchment basin. Information and records pertaining to the restoration techniques employed were obtained (when available) for each wetland included in the study. Similarly, management records were obtained for both the native and restored wetlands.

Significance:

This project will assess the condition of wetland and upland plant communities in restored areas in order to relate the function of prairie pothole wetlands to environmental conditions. This project will also provide valuable insight on the functional capacity of restored wetlands in various states throughout the region in order to evaluate restoration attempts and management techniques. The results of this study could be used to help guide future management and restoration efforts in ways that further improve wetland functions.

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

GRF Project 2007ND142B
Fellow: Thunyalux Ratpukdi
Adviser: Eakalak Khan
Department of Civil Engineering
North Dakota State University
Fargo, ND 58105

Research Problem

In the drinking water field, the presence of Natural organic matter (NOM) is a concern because it can cause several impacts on water quality and treatment processes. The reactivity of NOM is closely related to its physicochemical properties such as molecular weight, aromaticity, elemental composition, and functional group content. However, it is not well understood due to heterogeneous properties of bulk NOM . To overcome the complexity of NOM, isolation or fractionation is often required in order to obtain more uniform material for further characterization as well as to provide the link between NOM properties and its behavior when subjected to treatment processes.

Recently, I have developed a new NOM fractionation procedure using pre-packed solid phase extraction (SPE) sorbents to fractionate NOM into six fractions includes hydrophobic acid, hydrophobic base, hydrophobic neutral, hydrophilic acid, hydrophilic base, and hydrophilic neutral. With this novel technique, the fractionation time could be reduced to about 6 hours (compared to 24 hours for existing technique).

The Moorhead Water Treatment Plant (MWTP) uses the Red River water as a primary source to produce drinking water for residents of city of Moorhead, MN. Understanding the characteristic and composition of NOM in the drinking water source is helpful for the identification the problematic NOM fractions (the NOM fractions that have potential to form carcinogenic disinfection byproducts). Currently, fractionation and characterization NOM from the Red River never been investigated. Total organic carbon (TOC) is used to measure performance of NOM removal at different treatment stages at MWTP. However, the TOC values of bulk water can only indicate the organic content but do not provide information on the treatability of the different types of organic molecules in NOM. NOM fractionation technique could elucidate the effect of water treatment processes at MWTP on NOM composition.

Project objectives:

The main scope of this study is to fractionate and characterize NOM from the Red River and to investigate the removal of each NOM fraction along the treatment train of MWTP. The specific objectives of the study are as follows:

1. To fractionate NOM in water from the Red River;
2. To characterize the isolated NOM fractions by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR).
3. To investigate the effect of water treatment processes at MWTP on NOM composition.

Progress:

NOM from the Red River has been fractionated and characterized. The Effect of treatment processes at MWTP on NOM composition has been investigated. This study is close to completion.

Significance:

For the first time, the application of the novel SPE technique will be demonstrated and NOM in the Red River water will be fractionated. The fate of different NOM fractions through the treatment train of MWTP will be elucidated. Deliverables from this project include the information on the composition and characteristics of NOM in the Red River water and the efficiency of treatment units at MWTP for removal of NOM fractions.

Farm-Scale Reconnaissance of Estrogens in Subsurface Waters

GRF Project 2006ND145B
Fellow: Mary Schuh
Adviser: Francis Casey
Department of Soil Sciences
North Dakota State University
Fargo, ND 58105

Research Problem

Estrogens are very potent endocrine disrupting chemicals and are naturally present in animal manures applied to the soil. In areas where there are concentrated animals, such as at confined feeding operations, there is increasing concern on both state and regional levels that hormones may be transported to surface water or to groundwater. Research has shown that parts per trillion 17ß-estradiol concentrations can cause male fish to express female characteristics. Humans are not as toxicologically sensitive to hormones compared to aquatic organisms, yet the amount of environmental exposure to hormones is still unknown. Because of this, the fate and transport of estrogens and quantification of estrogens introduced into the environment from animal operations is an important problem of state, national, and international concern.

Previous to this study, work was done at a swine (*Sus scrofa*) farm in North Dakota, including the installation of lysimeters to monitor the amount of 17ß-estradiol leached through soil and the installation of wells to monitor the surficial aquifer. For this reason, the above location was elected as the research site for this project. In a prior study various types of manure were applied to the surface of lysimeter plots. Based on known application rates in manure and laboratory-determined degradation rates, it was anticipated that most of the hormones would be metabolized or bound to the top 0.10 m of soil. Instead, data (unpublished) consistently shows low amounts of 17ß-estradiol leached through the soil and detected in lysimeter water (0.6 m below the surface; Fig. 1) and in the surficial aquifer (~0.5 – 3m below the surface; Fig. 2). 17ß-Estradiol was even found beneath a control plot, where no manure was applied, which provided evidence for the antecedent existence of this hormone in the soil or that it was leached from somewhere else.

Objectives

The objective of this project is to identify the causes of the unexpected detections of 17ß-estradiol. It is known that the farmer injects his swine liquid manure slurry from a lagoon holding pond into the field soil at this research location. It has also been determined that the soils in this area are aquic and exhibit redoximorphic features (i.e. faint mottling) within 0.16 m of the soil surface, suggesting large fluctuations in the water table. These high water tables are more prevalent in the springtime when the temperatures are still low. The combination of cool and wet anaerobic conditions inhibit microbial activity that is necessary to degrade these hormones and may promote their persistence in the soil. Moreover, these soils are derived from water deposited sand, which decreases the

sorption of 17ß-estradiol and further exacerbates the transport of this hormone. The following hypotheses were proposed for causes: (1) There exists high levels of background 17ß-estradiol from the lagoon material the farmer injected in the field; (2) High water-table conditions cause a cool and anaerobic environment in which 17ß-estradiol persists; and (3) The ground water that contains the 17ß-estradiol is transporting exogenous hormones into the lysimeters in the soil horizon.

Project progress

A sampling strategy was formulated to allow the comparison of spatial and temporal variability of 17ß-estradiol in soil at the swine farm selected for this research. Five locations for soil cores were chosen in and around a field where liquid lagoon slurry was to be injected as fertilizer. The soil core sites were chosen based on nearness to regularly monitored wells – so soil concentrations could be easily compared to groundwater concentrations – and contact with surface conditions deemed as having potential to compromise groundwater quality, i.e. next to an uncovered compost heap, near a holding pond for lagoon slurry, and in a field injected with lagoon material. Also, samples were taken through time to observe any temporal fluctuations in 17ß-estradiol concentration due to temperature and high water tables, or manure application.
Cores were taken to the depth of the water table and separated into 6-inch increments. Pore water was extracted from each section and sent to a lab to be analyzed for concentrations of 17ß-estradiol and its main metabolite, estrone, using a combination of mass spectrometry and dual liquid chromatography (LC/MS-MS). Data from cores taken in 2006 is available. Extractions have been completed for cores taken in 2007. These samples have been prepared for analysis and results are expected by August 2007.
Dissipation study: A side experiment was completed to test the rate of dissipation of 17ß-estradiol in soil obtained from the research site. This was done, because little to no estradiol was detected in the first analyzed extracts; however, estradiol's primary metabolic product, estrone, was being detected. A known amount of 17ß-estradiol was applied to soil columns and extracted at different times. This work was completed in May 2007. Extracts are currently awaiting analysis at the USDA-ARS lab.

Expected benefits and results

The data obtained from this study will allow the mechanisms of 17ß-estradiol and its metabolites to be studied more effectively. It will help to connect the ongoing field and laboratory research on this subject, and it will help to assess the effectiveness of the natural restorative processes in the environment.

The knowledge that is obtained will also help to further discern the factors that control the retention and transport 17ß-estradiol, and thus may be useful in the development of remediation or manure handling strategies.

Another important outcome is to quantify the amount 17ß-estradiol contributed to the environment, and whether this amount is a concern to human and animal health. This research will provide new information on 17ß-estradiol and will be valuable for risk evaluation of this estrogen as well as related hormones.

Iron Nanoparticles for the Treatment of the Herbicides Atrazine, Alachlor and Dicamba in Groundwater

GRF Project 2007ND149B
Fellow: Jay Thompson
Adviser: Achintya Bezbaruah
Department of Civil Engineering
North Dakota State University
Fargo, ND 58105

Introduction/Background on Research Topic

Iron metal has been used for the remediation of contaminated groundwater for about two decades [20]. The most common mode of contaminant degradation by iron is reductive dehalogenation, which can be explained by the relationship below [20, 35].

$$R\text{-}Cl + Fe^0 (s) + H^+ \rightarrow Fe^{2+} + R\text{-}H + Cl^-$$

Typically, iron for remediation is in the form of filings or microscale powder. In this manner, iron has been used in the field and laboratory to remediate water contaminated with chlorinated ethanes [11, 22], chlorinated methanes [20], arsenic [19], and pesticides [5, 8, 14, 26, 28]. The advantages of iron metal for remediation include its non-toxicity, economy, and faster reaction rates than biological processes. The above reaction has been shown to be surface area dependant [35]. Because of the relatively low surface area of iron filings and powder, reactions may be slow or incomplete, resulting in possibly toxic degradation by-products [11].

With the development of nanoscale zero-valent iron (nZVI) for environmental remediation, many of the problems associated with iron filings were resolved [37]. Iron nanoparticles are typically 1-100 nm in diameter. This results in specific surface areas on the order of 20-30 m^2/g [18, 23] compared to about 0.05 and 5 m^2/g for iron filings and lab-grade iron micropowder, respectively [11, 36].

Research has shown that nZVI can successfully degrade chlorinated ethenes [34], chlorinated methanes [17], PCBs [34], arsenic [13], and other metals [23] in anoxic environments. Additionally, a recent study has shown that some pesticides can be treated by nZVI in oxic conditions [12]. Advantages of nZVI over microparticles include improved economics of direct injection into the aquifer, very fast reaction rates and more complete reactions.

Pesticides, including herbicides, insecticides and fungicides, are among the many contaminants successfully treated by conventional iron powder or iron filings. Numerous studies have demonstrated success on the bench scale and field scale. Research has shown that pesticides, when applied and handled properly, will not accumulate to high levels in groundwater [16]. However, accidents and spills can and do happen, often resulting in very high pesticide concentrations [2]. Iron nanoparticles have shown potential to remediate such spills.

While the proposed nZVI/pesticide trials have been largely successful in the laboratory (see "*Research Progress Made*"), the final goal of the work proposed in the 2007 NDWRRI program was a small-scale pesticide spill remediation technology. To achieve this, a delivery vehicle is needed. Polymeric delivery vehicles have been developed that both disperse nZVI and protect it from non-target species [27]. Unfortunately, these polymeric coatings are synthetic and thus, may not be desirable in

the subsurface. While this may be an acceptable trade-off for highly toxic and recalcitrant chlorinated solvent sites, this is an unsuitable approach for smaller, less toxic pesticide spills.

For the proposed application, the delivery vehicle must be biodegradable, economic and relatively simple to use. Calcium alginate is an ideal candidate for this application. This work aims to entrap and encapsulate (two distinct technologies) nZVI in calcium alginate with the end goal being a product that can be easily emplaced in a trench or bore hole for site remediation. Alginate entrapment/encapsulation is a process where nZVI is captured in an alginate matrix (entrapment) or encapsulated in a thin-walled alginate capsule (encapsulation). Although the entrapped/encapsulated nZVI (E/E nZVI) will lack many of the specialized properties of more advanced polymeric vehicles, it will be biodegradable, inexpensive, and simple to emplace.

Description of the Critical State or Regional Water Problem to be Investigated

Clean, safe groundwater for drinking is critical for North Dakota. Sixty percent of North Dakota's population use groundwater as their drinking water source [24]. In rural areas, where pesticide contamination is more likely to occur, 97% of the population depends on groundwater [45]. Protection of this resource is of vital interest to the people of North Dakota.

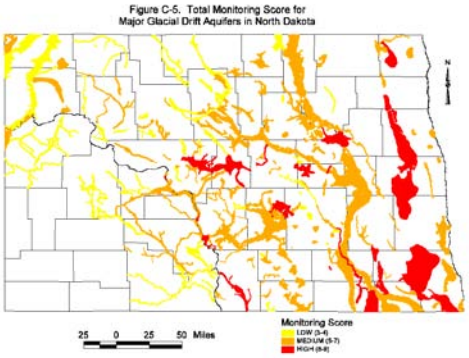

Figure 1: Aquifers in North Dakota Vulnerable to Pesticide Contamination. [24]

Modern agricultural practice has prevented high-level non-point source contamination of ground water [16]. While vigilance must be maintained on non-point source contamination, a more immediate problem is the point source contamination of groundwater at agricultural chemical retail outlets and pesticide storage, mixing, and loading facilities on farms. North Dakota water quality officials cite the release of the herbicides used to control leafy spurge, such as dicamba, at these retail outlets [3]. In Minnesota, the most common pesticide contamination scenario is the accidental release of corn herbicides at agricultural chemical retail outlets [33]. The North Dakota Department of Health has conducted a study on the vulnerability of groundwater to pesticide contamination. The results are summarized in **Figure 1**. Note that the vulnerable aquifers of the southeast coincide with the state's highest concentration of corn acreage and thus chloroacetanilide consumption [10]. Although this work is focused on state environmental issues, pesticide contamination is national [15, 32] and even global [30] concern.

Research Progress Made

A short progress summary is provided below. Please note that the new work proposed for the 2008 program has begun as well.

nZVI Synthesis and Characterization

Particles were successfully synthesized in the manner proposed in the 2007 submission. Particles were characterized by transmission electron microscopy, X-ray

diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface area analysis. Average particle diameter and specific surface area were determined to be 35 nm and 25 m^2 g^{-1}, respectively. Typical nZVI morphology is presented in **Figure 2**.

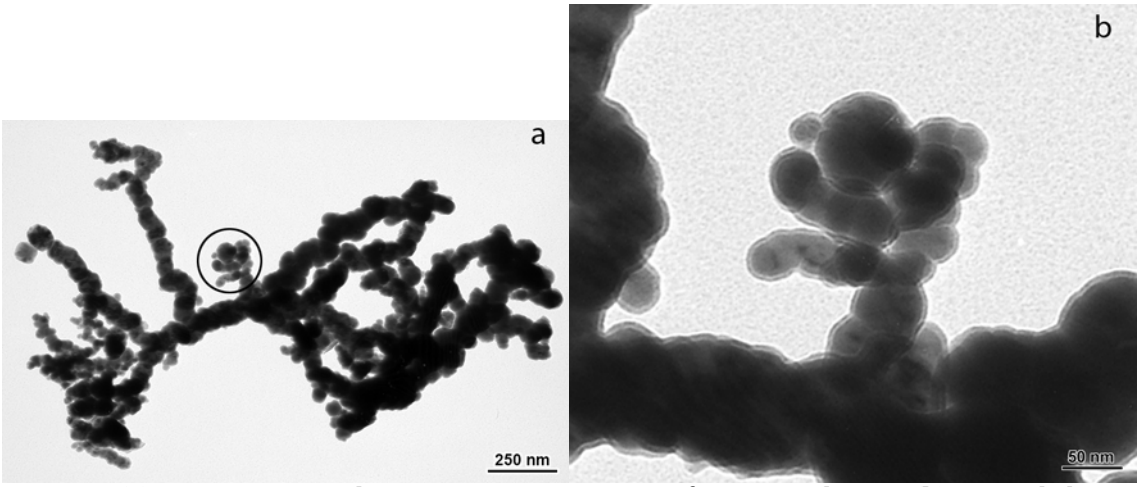

Figure 2 (a): Transmission electron microscopy image of an nZVI cluster. **(b)** Expanded image of area indicated in **(a)**.

Degradation Batch Trials

As proposed, atrazine and alachlor degradation trials were conducted. Atrazine degradation was found not to occur in the presence of nZVI. A variety of buffer and acid injection conditions were attempted to facilitate dechlorination, however, none yielded atrazine degradation. While further acid injection would likely allow nZVI mediated reduction [7], such a system would not have practical applications. Thus, atrazine trials were concluded.

Alachlor (2-Chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide) degradation trials using nZVI were conducted as proposed. Alachlor dechlorination proceeded rapidly and was complete. First order kinetics adequately described the nZVI mediated degradation of alachlor (R^2 = 0.999). The following pseudo first order rate equation was proposed:

$$\frac{dC}{dt} = k_{SA}\rho_A C$$

where C is alachlor concentration (mg L^{-1}), k_{SA} is the surface area normalized rate constant (38.5 x 10^{-5} L m^{-2} hr^{-1}) and ρ_A is the iron surface area concentration (m^2 L^{-1}). Experimental and modeling results are presented in **Figure 3**.

The degradation byproduct of the above reaction was determined by GC-MS to be dechlorinated alachlor (N-(2,6-Diethylphenyl)-N-(methoxymethyl)acetamide). This finding was confirmed by the stoichiometric transfer of chlorine from alachlor to chloride ions as the reaction progressed (**Figure 4**). Although the toxicology and persistence of this compound are unknown, the dechlorinated species of metoachlor, a structurally similar herbicide, was found to be roughly five times more biodegradable than its parent

compound [6, 31]. Thus, it is likely that the byproduct of the observed reaction is a more environmentally benign compound than its parent.

A comparison of microscale and nanoscale zero valent iron for alachlor degradation was also conducted. As expected, nZVI mediated reactions progressed more quickly than microscale iron on a mass normalized basis. Perhaps less expectedly, nZVI performed 5-10 times better than microscale iron a surface area normalized basis. It is assumed that the higher ratio of active to inactive surface area in nZVI accounted for this difference. One goal of the mechanistic studies proposed in this document is to better elucidate this phenomenon.

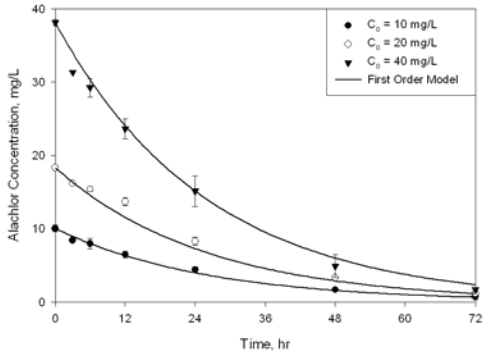

Figure 3: Alachlor degradation and modeling results in the presence of nZVI at differing initial concentrations. Iron mass loading: 4 g L^{-1}. Error bars represent ± standard error. Controls (not shown) do not display appreciable alachlor degradation.

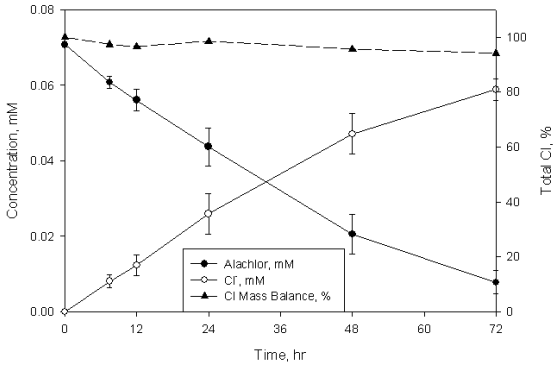

Figure 4: Cl^- evolution during alachlor degradation. Iron mass loading: 4 g L^{-1}. Error bars represent ± standard error. Dotted line represents the percentage of Cl (alachlor + Cl^-) recovered in IC and HPLC analyses.

The 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.

Use of Artificial Substrates and Dipnet for Sampling Aquatic Macroinvertebrates in the Red River of the North

GRF Project 2007ND144B
Fellow: Wei Zheng
Adviser: Malcolm G. Butler
Department of Biological Sciences
North Dakota State University
Fargo, ND 58105

Research Problem

Aquatic macroinvertebrates living in large rivers generally use different habitats and respond differently to the hydrological regime. As one of the major rivers in western United States, the Red River of the North provides multiple uses for local people. However, little is known about the macroinvertebrate fauna of the Red, largely because rivers of this size and type are difficult to sample. Research on macroinvertebrate communities in major habitats of the main-stem Red River is needed to determine what types of animals predominate in the various habitats within this river. Identification of ecologically significant taxa (in term of abundance or functional importance) in the river will aid in selection of candidate indicators for future biomonitoring, a need increasingly recognized by state and national management agencies. Also needed is assessment of sampling techniques that can efficiently monitor those taxa that may be significant indicators of the river's ecological function and condition.

Scope and Objectives

The objectives of this research are to 1). Inventory the macroinvertebrate communities of different habitat conditions in the main stem Red River 2). Explore the temporal changes of these benthic communities through the open water season and 3). Compare the results of outcomes provided by different sampling techniques. These objectives will allow me to evaluate potential relations between aquatic invertebrate communities and environmental conditions.

Project Progress

Drift net sampling was conducted from 27 May to 4 November 2006. Nets were deployed from bridges over the main-stem Red River at three different locations: within Fargo-Moorhead (FM), 26 river-km north of FM, and 38 river-km south of FM. Triplicate nets were deployed overnight at two week intervals. We are now in the process of identifying and quantifying the macroinvertebrates from these drift samples. Infaunal benthos was sampled with a Ponar grab at five cross-channel transects at different sites along the river. We also deployed artificial substrates (standard Hester-Dendy samplers plus a custom-made ash log substrate design) for 5 weeks beginning on 1 Sept 2006.

Preliminary results from the drift nets indicate that drift densities reached a maximum during summer, peaking in late August. Community composition differed between sampling sites and over time. Dominant taxa over the season included chironomid larvae, elmid beetle larvae, adults of several aquatic beetle families, as well as terrestrial Coleoptera. Chironomidae displayed the highest drift rates from August to early September, when other taxa were relatively sparse in the drift. The burrowing mayfly *Ephoron* (Polymitarcidae) had a notable emergence in mid-summer. Several drifting taxa (Chironomidae) were significantly negatively related to discharge, but not to other hydrological parameters. Seasonal variability in drift likely results from the life histories of individual species, as well as fluctuations in discharge. Terrestrial insects made a substantial contribution to invertebrate drift in this river reach.

These drift net samples will provide a unique inventory of the invertebrate fauna of the Red River in the FM area. Although these data will be biased toward insects (due to their emergence behavior) and exclude non-drifting taxa such as unionid mussels, we are impressed at the diversity of the fauna represented – including large numbers of small gastropods and a major contribution by terrestrial arthropods. These data show us which species, at a minimum, live in the river, and will permit a general ranking of each taxon's abundance and potential ecological significance. The drift data also point to important issues for continued investigation. Our transect samples of the river channel produced very low densities of only a few species, and the microhabitats occupied by a majority of the fauna remain undiscovered. For example, the mayfly *Ephoron album* is conspicuous in the drift during its emergence in late July-mid August, but we have yet to collect a single larva from a benthic habitat. The majority of the Chironomidae and other insect taxa probably live on flotsam and organic debris associated with woody snags distributed sporadically along the river. Work in 2007 will focus on determining and quantifying the fauna associated with such habitats, and in seeking unique microhabitats that support other ecologically significant macroinvertebrates.

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

Abstract

There are a variety of formal and informal local institutions that are involved with water resources management in rural areas. These governmental and non-governmental institutions have different objectives, different legal statuses, and different affiliations with state and local governments. Research is needed to assess the roles and effectiveness of local water institutions. As new initiatives to improve water quality are being proposed, it is important to assess the capacity of existing institutions to meet new and evolving needs. The objective of this research is to improve local management of water resources by providing policy makers and agencies with an improved understanding of the characteristics of successful local institutions. This research will focus on the Red River of the North basin in Minnesota and North Dakota although some assessment of Manitobas institutions will be included. The basin is fairly homogeneous in terms of land use and geographic features, but features three completely different sets of water law, which makes it an excellent case study of institutions. The overall objective of this research is to strengthen local water management institutions so that they may better meet evolving local and basin wide needs, especially the maintenance of water quality. Specific objectives of the research include: 1) Develop a set of objective and subjective criteria and indicators to evaluate local water management institutions; 2) Provide a review of the different governmental and nongovernmental institutions in the basin, classify their goals, activities and chartered purposes, and identify overlaps and 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; 4) Assess the use of: scientific and technical information; extension education and training programs; and other support provided by governmental and non-governmental agencies; 5) Analyze institutions and agencies likely behavior in a decision-making situation 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 that they trust; and 8) Disseminate results to various forums including local workshops and scientific journals. Objective and subjective criteria and indicators for local water institutions will be refined for local

circumstances by interviewing and surveying assorted State and Federal agencies who work on water management issues. A survey of local water institutions will be used to: identify goals, activities, and accomplishments; assess their understanding and use of technical information and extension training; and provide an understanding of how these institutions have evolved to meet changing needs. This survey will be supported by another survey of local leaders, county commissioners, and mayors. The Legal-Institutional Analysis Model will be used to assess negotiation strategies. And choice experiments, a stated preference technique that can estimate the non-market value for environmental goods and services, will be used to analyze residents and leaders preferences towards water management programs and institutional frameworks.

Benefits of the Research

By identifying the attributes of local institutions that effectively achieve their own goals and/or further goals of water quality maintenance, this research will:1) ascertain whether existing institutional frameworks should be adapted to meet evolving needs or new institutions should be developed to address emerging issues such as water quality monitoring and enforcement; 2) support local institutions by identifying key characteristics that facilitate effectiveness; 3) assess the benefits and costs associated with having water resource institutions defined along county lines as opposed to watershed lines; 4) support the development of extension and education programs that strengthen local institutions by specifically addressing key characteristics of effectiveness; and 5) help policy makers in the design strategies to monitor and enforce nonpoint source pollution abatement initiatives. Based upon this research and subsequent reviews and comments, recommendations will be made to political leaders and lawmakers, agency officials, and local stakeholders.

Synopsis and Planned First, Second, and Third Year Goals

This project was to assess local water management institutions and organizations in the Red River Basin.

During the first year period of September 2005 – August 2006 planned goals were to:

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; and
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.

During the period of September 2006- August 2007 planned goals included:

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; and
7) Analyze preferences of a sample of residents and stakeholders toward watershed management issues and the types of institutions they trust.

During the period of September 2007- August 2008 planned goals included:

8) Disseminate results to various forums including local workshops, extension materials, and scientific journals.

2. Progress Towards Goals:

A review of water management organizations and institutions has been conducted. The paper was published in *Environmental Management.*

A set of criteria and indicators for effective public water management organizations was developed. These criteria and indicators were used to develop a survey instrument 2006. A surveys of organization managers and board members was conducted in December 2006 – January 2007. Survey data has been analyzed. This analysis: i) identified the characteristics of local water institutions and their boards that have a demonstrated capability to meet local goals and wider goals of the greater river basin; ii) assessed the use of scientific and technical information, extension education and training programs, and other support provided by governmental and non-governmental agencies and organizations; and iii) identified the characteristics of institutions that successfully evolve to meet new challenges. A MS thesis from this work was presented and defended in August 2007. The final disquisition is ongoing. A draft paper from this analysis was presented to the Western Agricultural Economics Association meeting in Big Sky, Mt. in June of 2008. An improved version of this paper will be submitted for publication in 2008. See attached manuscript.

An analysis of institutions' and agencies' likely behavior in a decision-making situation has not been conducted. This objective was to have been completed with the support of USGS personnel from Ft. Collins Research center. However, given that grant funds can not be used for USGS travel, we have not been able to complete this task.

A second survey of informed stakeholders was conducted in late 2007. An MS thesis based upon this work was presented and defended in December 2007. The final disquisition has been accepted. A paper based upon this research has been presented at the W-2133 meeting in Kona, Hawaii in February 2008. An Agribusiness and Applied Economics report (#629) based upon this research has been released. This paper will be submitted for publication in a scientific journal in 2008.

A further analysis of measures of "effectiveness" has been initiated. Data envelopment analysis and the competing values framework will be used to analyze previously collected data. The results of this analysis should be completed by October of 2008.

Collaborative Research on in Situ Denitrification and Glyphosate Transformation in Ground Water: NAWQA E. 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. Project Progress The starting date for the grant was August 1, 2006 and the first progress report was written in June, 2007. Since then, one trip was taken to the Iowa field site in November, 2007, to install the pair of ISMs and one trip was taken to Ames, Iowa, in March, 2008, to attend the 8th Annual USGS Agricultural Chemical Team Meeting. The ISM installation was successful and they have been sampled monthly. Preliminary results indicate that denitrification is progressing in the ISMs, but rates are relatively slow. The ISM protective casings were flooded in June, 2008. Subsequent analyses will determine if the flooding interfered with the ISM tracer tests in-progress, but significant interference is unlikely. From the site, 50 aquifer sediment samples have been analyzed for texture (gravel, coarse sand, medium sand, fine sand, silt, and clay) and the electron donor concentrations: organic carbon, ferrous iron, and inorganic sulfide. Organic sulfur analyses were done on 14 sediment samples, but concentrations were judged to be too low to continue this analysis for the remainder of the samples. Preliminary results indicate little correlation between sediment texture and sample depth and little correlation between electron donor concentrations and sample depth; however the finer grain sizes are positively correlated, and coarser grain sizes negatively correlated, with electron donor concentrations. Further analysis is on-going. Depending on denitrification rates and if, and how much, the flooding influenced the current tracer tests in-progress in the ISMs, we plan to initiate at least one new ISM tracer test later this summer, or early fall, with glyphosate. Ground-water samples for isotopic analysis (^{15}N and possibly ^{18}O for the nitrate remaining in the ISMs) will be sent to The University of Waterloo later this summer.

The project is on schedule based on the timeline given in the project proposal.

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 ($1,312/month). Bijesh is working on an M.S. in Environmental Engineering and hopes to complete his degree by December, 2008.