

**North Dakota
Water Resources Research Institute**

**North Dakota State University
University of North Dakota**

ANNUAL REPORT

March 1, 2010 to February 28, 2011

Fiscal Year 2010 Report to the U.S. Geological Survey

June 2011

Annual Report

Fiscal Year 2010 Report to the U.S. Geological Survey

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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, 2010 to February 28, 2011.

The ND WRRI is one of the 54 institutes known collectively 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 Graduate Fellowship research projects. The institute also continued its efforts to enhance communications between the State and Federal agency personnel and university faculty and students. NDWRRI also worked closely with the Environmental and Conservation Sciences program of North Dakota State University (NDSU), Natural Resources Management program of NDSU, Energy and Environmental Research Center at University of North Dakota (UND), the International Water Institute, Fargo, ND, and the North Dakota Experimental Program to Stimulate Competitive Research (ND EPSCoR) of the National Science Foundation (NSF) on water related research issues and collaboration.

Program Management

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

State Appropriation

The State Water Commission continued its support to the 2010 – 2011 federal 104(B) funding for the Graduate Research Fellowship program of NDWRRI. This is seventh year the SWC provided 15% match in support of the Fellowship program.

University Support

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

Institute Location

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

ND Water Resources Research Institute
North Dakota State University
Civil Engineering, Dept. # 2470
Fargo, ND 58108-6050
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 major 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 2010-2011 Graduate Research Fellowship competition were posted on the Institute website in September 2009, 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:

October 14, 2009 It's Happening at State, NDSU

Research fellowships available

The North Dakota Water Resources Research Institute has announced its 2010 Graduate Research Fellowship program.

NDSU and University of North Dakota graduate students who are conducting or planning research in water resources areas may apply for fellowships varying from three summer months to a full year in duration. In the past, fellowship awards for master's degree students have ranged from \$800 to \$1,000 and for doctoral students it has been \$1,000 to \$1,400 per month. The fellowship funds must be applied between March 1, 2010, and Feb. 28, 2011. 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. At the time of applying, applicants should have a plan of study filed and should have a thesis research topic selected. Applications need to be prepared in consultation with advisers. Advisers and the applicant should both sign the applications. Applications from students and advisers who have not met the reporting requirements of their previous fellowship projects will not be considered for funding. The general criteria used for proposal evaluation include scientific merit, originality of research, research related to state or region, and extent of regional, state or local collaboration and co-funding. A panel of faculty members and state water resources research professionals will review the proposals. Announcement of awards will be made by early January.

Visit www.ndsu.edu/wrri for background on the program and guidelines for preparation of applications. Applicants and advisers who are new to the program are urged to contact G. Padmanabhan, institute director, at 1-7043 or g.padmanabhan@ndsu.edu.

Applications are due on Nov. 13 by 5 p.m. Send applications to G. Padmanabhan, North Dakota Water Resources Research Institute, Civil Engineering, CIE 201E, NDSU Dept. 2470, P.O. Box 6050, Fargo, ND 58108-6050.

NDWRRI GRADUATE RESEARCH FELLOWSHIPS

Fellowships ranging from \$3000 to \$12,000 were awarded to ten graduate students from NDSU conducting research in water resources areas. No applications were received from UND. Selection of student Fellows and the award amounts were based on competitive proposals prepared by the students with the guidance of their advisers. Projects proposed for fellowship support should relate to water resources research issues in the state or region. Regional, state, or local collaboration or co-funding is encouraged. Fellowships have a matching requirement of two non-federal dollars to one federal dollar. A panel of state water resource professionals reviews the proposals and selects the Fellows and award amounts based on the quality of proposals and the priority of the proposed projects for the state and region. The general criteria used for proposal evaluation include: scientific merit, originality of research, research related to state and/or region, and extent of regional, state or local collaboration and/or co-funding.

This year, eleven applications were received: seven Ph.D. and four MS students. One MS application was rejected. Highly competitive proposals and limited availability of funds restricted the amount of awards. Five of the Fellowships were renewals, all Ph.D. The renewals are Brianna Schneck, Qigang Chang, Dimuthu Wijeyaratne, Harjyoti Kalita, and Halis Simsek.

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

2010-11 Fellows and their projects

Fellows, areas of study, their advisers and fellowship research projects are:

Adam Guy, soil science, Tom DeSutter, “The Impact of Rural and Urban Flooding on Water and Soil Quality in the Red River Valley of the North”

Andrea Hanson, biological Sciences, Mark Sheridan, “Uptake and effects of environmental estrogens on growth of fish”

Anusha Balngoda, civil engineering, Wei Lin, “Studies of Seasonal Succession of Cyanobacteria and Green alga Heinrich-Martin Impoundemtn, North Dakota”

Brianna Schneck, biological sciences, John McEvoy and Mark Clark, “Source Tracking of Cryptosporidium in Rural Watersheds”

Dhritikshama Roy, civil engineering, Achintya Bezbaruah and Eakalak Khan, “Plant-based Biopolymers for Entrapping Metal Nanoparticles for Arsenic Removal: Biodegradation and Treatability Studies”

Dimuthu Wijeyaratne, environmental and conservation sciences, Marinus Otte, “Chemical Fingerprinting of Sediments and Water of the Souris River for Identification of Diffuse Pollution Sources”

Halis Simsek, civil engineering, Eakalak Khan, “Fate of Biodegradable Dissolved Organic Nitrogen in Fargo Waste Water”

Harjyoti Kalita, materials and nanotechnology, Achintya Bezbaruah and Bret Chisholm, “Iron Imprinted Polymer for Removal and Monitoring of Arsenic”

Ishara Rijal, agriucultural and biosystems engineering, Xinhua Jia, “Reference Evapotranspiration and Actual Evapotranspiration Measurements in North Dakota”

Qigang Chang, environmental and conservation sciences, Wei Lin, “Development of GAC-NZVI Adsorbent for Arsenic Removal”

The Impact of Rural and Urban Flooding on Water and Soil Quality in the Red River Valley of the North

Project Number: 2010ND211B

Fellow: Adam Guy

Adviser: Thomas DeSutter

Start Date: 3/1/2010

End Date: 2/28/2011

Publication:

Abstract

Guy, A., T. DeSutter, F. Casey, R. Kolka, and J. Leitch. 2011. Impacts of major flooding on an urban environment. 54th Annual Manitoba Soil Science Society Conference. Winnipeg, MB, Canada.

Progress:

Adam has successfully defended his thesis (April 2011) and is finishing his thesis edits. Adam recently **presented** his research at the 54th Annual Manitoba Soil Science Society Conference. Winnipeg, MB, Canada. The most **significant research results** are:

- 1) The urban area of Fargo, ND and Moorhead, MN (F-M) did not negatively impact water quality during the 2009 flood event,
- 2) About 28 and 4,500 Mg of phosphorus and total sediment, respectively, were deposited within the F-M area during the flooding event,
- 3) 17beta-estradiol was detected in nine of 24 water samples with an average concentration of 0.61 ng/L and estrone was not detected in any sample,
- 4) Concentrations of total N and total C between sediment and soil were variable and averaged about 2,900 and 3,200 mg/kg and 47 and 46 g/kg, respectively, across all samples,
- 5) No gasoline range organics were detected, but diesel range organics ranged from about 17 to 41 µg/g in the sediment and were significantly greater within the sediment compared to the soil. Overall, diesel range organics were present in 26 out of the 27 sediment samples analyzed,
- 6) Total Hg in the sediment and soil across all samples ranged from about 43 to 67 ng/g and 47 to 81 ng/g, respectively, and
- 7) Analysis of both sediment and soil for 22 trace elements yielded no concentrations greater than one would expect for uncontaminated soil,
- 8) Results were presented to both NDSU students and to graduate students at Chulalongkorn University (Bangkok, Thailand) by DeSutter through his international teaching, and
- 9) DeSutter promoted this research to River Keepers personnel and their education activities. River Keepers is a non-profit organization whose mission statement revolves around the sustainable use of the Red River within the Fargo and Moorhead city limits.

The **practical application** of these results is that the quality of the sediment remaining after flooding waters recede would not be considered harmful. Thus, human activity, including recreation and gardening, would be safe. **In addition**, the deposition of high concentrations of carbon, phosphorus, and nitrogen by flooding waters and sediments should lead to a decreased demand for synthetic fertilizers in these flooded areas, which would reduce any negative water quality impacts from fertilizers to the Red River.

Uptake and effects of environmental estrogens on growth of fish

Project Number: 2010ND215B

Fellow: Andrea Hanson

Adviser: Mark Sheridan

Start Date: 3/1/2010

End Date: 2/28/2011

Publication:

Hanson, A., Kittilson, J.D., McCormick, S.D., Sheridan, M.A., 2011. Effects of 17 β -estradiol, 4-nonylphenol, and β -sitosterol on the growth hormone-insulin-like growth factor system and seawater adaptation of rainbow trout (*Oncorhynchus mykiss*). *Aquaculture, in press*.

Hanson, A., Kittilson, J.D., Sheridan, M.A., 2011. Environmental estrogens inhibit growth of rainbow trout (*Oncorhynchus mykiss*) by modulating the growth-hormone insulin-like growth factor system. *In preparation*.

Hanson, A. and Sheridan, M.A. Effects of Environmental Estrogens on Organismal Growth and the Growth Hormone-Insulin-Like-Growth Factor System of Rainbow Trout. Annual Meeting of the Society for Integrative and Comparative Biology, Salt Lake City, UT, January 4-7, 2011.

Progress:

Activities and Findings

The aim of this project is to advance our understanding of the fate of environmental estrogens in aquatic ecosystems by measuring their uptake and metabolism and evaluating the impact as assessed by organismal growth. The overall hypothesis of this project is that environmental estrogens are taken up by rainbow trout from water and alter postembryonic growth by modulating the growth hormone (GH)-insulin-like growth factor-1 (IGF-1) system.

First, we have evaluated the effects of environmental estrogens on feeding and food conversion, and on postembryonic growth rate. In terms of overall organismal growth, the environmental estrogens, estradiol (E2), β -sitosterol (β S), and nonylphenol (NP) were shown to lead to decreased organismal growth in terms of relative growth (both weight and length) compared to controls.

Next, we have completed work examining the effects of environmental estrogens on the GH-IGF system *in vivo*. All environmental estrogens were shown to decrease hepatic sensitivity to GH, as assessed by GH receptor 1 (GHR 1) mRNA expression. In addition to decreasing hepatic sensitivity, it was also determined that hepatic production of IGF-1 and IGF-2 decreased in environmental estrogen-treated fish. In gill, E2 reduced

expression of mRNAs encoding GHR2, IGF-1, IGF-2, and IGFR1A, whereas NP reduced the expression of GHR 1, GHR 2, IGF1, IGF-2, and IGFR1A mRNAs. β S had no significant effect on the expression of any GH-IGF system component in gill filaments. The effects of EE on levels of GHR 1, GHR 2, IGFR1A and IGFR1B mRNA in red muscle and white muscle were somewhat variable. β S and NP decreased GHR 1 in red muscle, while GHR 2 mRNA expression decreased in white muscle. High concentrations of E2 reduced levels of IGFR1A in white muscle and of IGFR1B in red muscle, whereas NP reduced the expression of IGFR1A and IGFR1B mRNAs in red muscle.

These data support the hypothesis that EE reduce growth in fish by modulating the GH-IGF system in terms of GH sensitivity, IGF production, and IGF sensitivity in a tissue-specific manner at the molecular level and in terms of overall organismal growth.

Experiments have been initiated to examine the effects of environmental estrogens on the GH-IGF system *in vitro* as assessed by mRNA expression of GHR1/2, IGF-1/2, and IGFR1A/B in liver or gill. E2, β S, and NP were not observed to affect the expression of GHRs in any tissues examined. However, decreased expression of both IGF-1 and IGF-2 in a time- and concentration-dependent manner was observed in the liver. Potency and efficacy of each of the environmental estrogens varied with E2 and NP eliciting the greatest response. Similar results were observed in gill. Currently, experiments are being conducted examining the *in vitro* response in muscle tissue of rainbow trout.

These current data, in addition to the muscle data, will allow us to fully characterize the time course and efficacy of EE on IGF-1 binding characteristics and on the growth-promoting actions of IGF-1 in target tissues.

Studies of Seasonal Succession of Cyanobacteria and Green Algae at Heinrich-Martin Impoundment, ND

Project Number: 2010ND212B

Fellow: Anusha Balangoda

Adviser: Wei Lin

Start Date: 3/1/2010

End Date: 2/28/2011

Publication:

Balangoda, A., "Seasonal Succession of Phytoplankton Population at Heinrich-Martin Impoundment, North Dakota" ND WPCC state conference, October, 2010 [Poster].

Progress:

The purpose of this study is to identify population variation of cyanobacteria and green algae in relation to their growth requirements. The specific objectives are; (1) To collect water and phytoplankton samples to determine seasonal variation of nutrients level and phytoplankton abundance; (2) To determine seasonal variation of total phytoplankton biomass and relative abundance of cyanobacteria; and, (3) To determine the factors that affect on growth of phytoplankton, especially the seasonal growth and succession of cyanobacteria.

This progress report discusses the progress I have made from March 1, 2010 to February 28, 2011. Water samples were collected at the Heinrich Martin Impoundment, (HMD) which is located in north central Lamoure County, ND on biweekly schedule at four depths of four sampling sites over the summer, 2010. Water samples were analyzed for nutrients, TSS, VSS, and biological parameters; chlorophyll-*a* and phytoplankton counting and identification. Further; DO, DO saturation, water temperature, specific conductance, turbidity, pH, and secchi depth were measured on site.

Average water temperature in the HMD varied between a minimum of 13°C to a maximum of 24.5°C from June to October, 2010. Spatial and vertical variations of water temperature were not observed due to aeration in deeper part and wind mixing in the shallow part of the impoundment. According to observed TP concentration ($\geq 100 \mu\text{g/L}$), secchi depth reading ($< 3\text{m}$), and chlorophyll-*a* concentration (10-100 mg/L) the HMD showed hypertrophic condition. Low TDN (370 $\mu\text{g/L}$) to SRP (180 $\mu\text{g/L}$) ratio was observed over the summer 2010. It is suggested that the HMD is a N-limiting impoundment. Seasonal variation of phytoplankton community structure was observed in the HMD. Total phytoplankton cell densities were varied along the depths and spatially. Eight phytoplankton divisions were counted and identified up to genus level. Among them; Bacillariophyta, Crptophyta, and Dinophyta were important of the phytoplankton community during much of the sampling period and contributed greatly to the total phytoplankton cell density at all depths. In addition, Chlorophyta and Cyanophyta were also observed at all depths, contributed relatively little to total phytoplankton cell density.

The factors that affect growth of phytoplankton, especially the seasonal growth and succession of cyanobacteria are in progress.

Source Tracking of *Cryptosporidium* in Rural Watersheds

Project Number: 2009ND183B

Fellow: Brianna Schneck-Stenger

Adviser: John McEvoy and Mark Clark

Start Date: 3/1/2010

End Date: 2/28/2011

Publication:

Stenger, B.L., Pennil, C. C., Clark, M.E., Lanctot, V. , Giddings, C.W., and McEvoy, J.M. “*Cryptosporidium* transport in the Red River Valley during major spring floods” North Dakota State EPSCoR Conference, Grand Forks, ND, 2010.

Schneck, B.L., Pennil, C. C., Clark, M.E., Lanctot, V. , Giddings, C.W., and McEvoy, J.M. “*Cryptosporidium* transport in the Red River Valley during major spring floods” Summer COBRE poster presentation in Fargo, ND, 2010.

Schneck, B.L., Pennil, C.C., Lanctot, V.T., Giddings, C.W., Clark, M.E., and McEvoy, J.M. “*Cryptosporidium* genotypes in Midwestern mammals” Presented at the 7th Northern Plains Biological Sciences Symposium in Fargo, ND, 2010.

Progress:

Cryptosporidium are ubiquitous pathogenic parasites that can reside in water sources and may pose a threat to public health. We sampled the Red River and its tributaries during major flooding events in 2009 and 2010 for *Cryptosporidium*. Spring flooding results in the movement of *Cryptosporidium* from the fields of North Dakota, South Dakota and Minnesota to the Red River. Livestock contributed significantly to *Cryptosporidium* contamination in the Red River during major spring floods. Cattle were the primary source of surface water contamination. We estimated the flow of oocysts during peak flooding in 2010 at 728,000 per second, based on our oocyst counts and a river flow of 560,000L per second. This is significant when less than 100 oocysts are needed to infect a host.

***Cryptosporidium* transport in the Red River Valley during major spring floods**

Key findings:

- *Cryptosporidium* was detected in 9 of 13 (69%) samples from the 2009 flood.
- Cattle adapted *Cryptosporidium andersoni* was detected in 7 out of 9 samples.
- Pig adapted *Cryptosporidium suis* was detected in 1 out of 9 samples.
- Wildlife adapted Deer Mouse Genotype III was detected in an overland flow sample.
- *Cryptosporidium* was detected in 14 of 17 (82%) samples from the 2010 flood.
- Cattle adapted *Cryptosporidium andersoni* was the primary species detected in samples from the 2010 flood.

- We identified a vole-specific genotype in one river sample.
- The average number of oocysts per liter from the 17 samples was 0.8.
- The average number of oocysts per liter four days before the flood, at crest, and one week after the crest was 1.1, 1.3, and 0.3, respectively.

Empirical evidence supports host adaptation and a limited host range for most *Cryptosporidium* species and genotypes. This knowledge is critical to track sources of water contamination and characterize human health risk; however, the factors affecting host range remain unclear. Small mammals are hosts to various genotypes of *Cryptosporidium*. We are using small mammals as a model to study the effect of factors such as host population density, diversity and behavior on the host range of *Cryptosporidium* genotypes. The prevalence of *Cryptosporidium* from more than 600 animal samples is approximately 40%. We've identified at least 14 *Cryptosporidium* genotypes/species in 10 wildlife host species. We have identified a novel genotype of *Cryptosporidium* in Eastern chipmunks and are planning to publish the findings once further molecular characterization and microscopic analysis is complete. Two species of *Cryptosporidium*, *C. parvum* and *C. ubiquitum*, are considered human pathogens and were found in a number of wildlife samples. We have also identified *Cryptosporidium* in 3 previously unreported host species; black-tailed prairie dogs, woodland voles, and cotton rats.

***Cryptosporidium* in Midwestern mammals**

Key findings:

- A single species/genotype was identified in most positive samples, with the exception of a deer mouse sample and grey squirrel sample, which were positive for both *C. parvum* and *C. ubiquitum*.
- Genotype names may be misleading. For example, Muskrat I and Muskrat II are more prevalent in voles.
- W12, previously identified in surface water, is associated with the meadow vole.
- W18 is associated with Northern short-tailed shrews.
- *C. ubiquitum* and *C. parvum*, known human pathogens, were associated with squirrels and deer mice.
- The extent of host adaptation in *Cryptosporidium* is likely to vary, with some species/genotypes having a broad host range.
- A number of *Cryptosporidium* genotypes were found in multiple host species. For example, we found Muskrat II genotype in 4 host species.
- Many host species can harbor multiple types of *Cryptosporidium*. For example, we detected at least 4 *Cryptosporidium* genotypes in meadow voles, deer mice, and northern short-tailed shrews.
- Multiple types of *Cryptosporidium* can be found in a specific area at a given time.

Plant-based Biopolymers for Entrapping Metal Nanoparticles for Arsenic removal: Biodegradation and Treatability Studies

Project Number: 2010ND213B

Fellow: Dhritikshama Roy

Adviser: Achintya Bezbaruah and Eakalak Khan

Start Date: 3/1/2010

End Date: 2/28/2011

Publication:

1. Roy, D., Bezbaruah, A., and Khan, E. Biodegradation of Biopolymers used for Surface Modification of Metal Nanoparticles. Poster presented at the Annual AWWA Surface Water Treatment Workshop. Fargo, North Dakota. April 27, 2010.
2. Roy, D., Bezbaruah, A., and Khan, E. Biodegradation of Polydimethylsiloxane (PDMS) in Aqueous Environment. Poster presented at ND EPSCoR. Annual Conference, Grand Forks, North Dakota. September 29, 2010.
3. Roy, D.; Bezbaruah, A., and Khan, E. Biodegradation of Polydimethylsiloxane (PDMS) in Water Environment. Poster presented at the 1st North Dakota Water Pollution Control Conference, Fargo, North Dakota. October 13, 2010.
4. Roy, D., Khan, E., and Bezbaruah, A. 2010. Microbial Degradation of Polysiloxane in Aqueous Environment - A Laboratory Scale Study. Paper presented at the Eastern South Dakota Water Conference, South Dakota State University, Brookings, South Dakota, November 9-10, 2010.

Progress:

Introduction: Due to their high surface area ($22\text{--}54\text{ m}^2\text{g}^{-1}$), reactivity and zero-valent iron (ZVI) core-hydrous oxide shell structure, the use of nanoscale zero-valent iron (NZVI) particles has been attractive for remediation of various contaminants including arsenic. However, they agglomerate in aqueous environment and get oxidized by non-target compounds, and lose their unique characteristics. While polymers are successfully used to overcome the problem of agglomeration and/or uncontrolled oxidation, most polymers so far used are not biodegradable and they themselves may become 'pollutants'. This project studied biodegradability of polymers used for coating NZVI, and will experiment with a few new biopolymers and use them for contaminant (e.g., arsenic) remediation.

Progress Made: Biodegradation batch studies with polydimethylsiloxane (PDMS), polyethylene glycol (PEG), and acrylic acid (AA) and PDMS(-PEG-AA)-based copolymer have been conducted using mixed bacterial cultures (activated sludge) for up to one month under aqueous environmental conditions. Composting of PDMS and PDMS-based copolymers has been conducted to see microbial growth. Very limited

biodegradation has been observed in aqueous environment but fungal growth has been observed under composting environment.

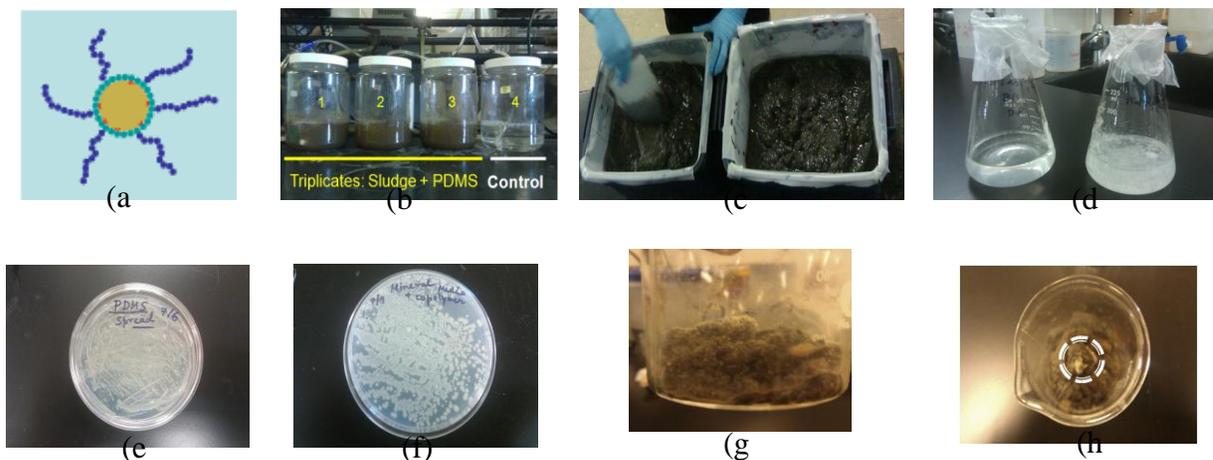


FIGURE (A)-(H). (A) PDMS-PEG-AA COPOLYMER COATED NZVI; (B) AEROBIC DEGRADATION STUDIES FOR THE COPOLYMER; (C) COMPOSTING STUDIES OF THE COPOLYMER; (D) GROWTH STUDIES OF COPOLYMER/PDMS DEGRADING MICROORGANISMS; (E) MICROBIAL PLATE COUNT FOR MICROORGANISMS FROM PDMS DEGRADATION REACTOR; (F) MICROBIAL PLATE COUNT FOR MICROORGANISMS FROM PDMS-PEG-AA COPOLYMER DEGRADATION REACTOR; (G) LONG-TERM COMPOSTING EXPERIMENT; AND (H) FUNGAL GROWTH IN PDMS COMPOSTED FOR MORE THAN SIX MONTHS. ISOLATION OF COPOLYMER/PDMS DEGRADING MICROORGANISMS IS UNDER WAY.

Experiments Underway: Respirometric studies for PDMS and PDMS-based copolymers are underway and new biopolymers are being tried.

Expected Outcomes from this Study: (a) Development of environmentally safe biopolymer entrapped NZVI system of aqueous arsenic removal; (b) Isolation of specific bacteria responsible for the degradation of polymers used to coated NZVI.

Deliverables: The proposed research already resulted in the a few presentations and posters. At least three peer reviewed journal articles, a number of conference papers and reports to NDWRRI are expected from this study.

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

Project Number: 2009ND189B

Fellow: Dimuthu Wijeyaratne

Adviser: Marinus L. Otte

Start Date: 3/1/2010

End Date: 2/28/2011

Publication:

Wijeyaratne D., Jacob D and Otte M April 2010. Chemical fingerprinting and determination of tributary contribution of trace elements in the upper Souris River, ND 7th Annual Northern Plains Biological Symposium, 2010. Fargo, ND. [Poster]

Progress:

The multi-element fingerprinting technique uses natural tracers in combination with field data collection, laboratory analyses of sediments, and statistical modeling techniques to identify sediment source areas in a watershed. In this technique natural tracers are identified and measured for both sediment sources and sediment mixtures collected at the watershed to identify the potential source areas of sediments.

This study was carried out in two watersheds in North Dakota, the Souris River and the Turtle River. The aim of this study was to develop multi-element fingerprints of the Souris River and Turtle River sediments and to evaluate the suitability of these fingerprints to assess the geographic origin of potential pollutants of the two rivers. In the initial step of this study, existing sediment samples of the Souris River from a previous project were analyzed for multiple elements. This study showed statistically significant variations in element concentrations of surface sediments at different sites and therefore it was confirmed that the multi-element fingerprinting can be used to assess the sediment and contaminant loading patterns.

In the multiple element fingerprinting studies the linear mixing of elements and the absence of enrichments and depletions of elements are assumed. Two laboratory experiments were performed to assess the validity of these assumptions. The results of these experiments verified the assumptions and showed that there is a statistically significant spatial and temporal variation in the element concentrations depending on their mobility and re-deposition.

Field studies were conducted in the Souris River and Turtle River to assess the variation of element concentrations in the top riverbed samples along the main rivers and their tributaries. The sediment contribution from the tributaries and the phosphorus concentrations in the main channel were used to calculate the phosphorus contributions from the tributary sediments to the Souris River. The larger tributaries of the Lower

Souris River showed higher phosphorus contribution compared to the smaller tributaries of the Upper Souris River. The differences in phosphorus contributions were related to land use, underlying geology, and the size of the watersheds of the tributaries in the Souris River watershed. Similar analysis was used in the Turtle River to calculate Arsenic, Cadmium and Selenium contribution from the tributaries to the Turtle River. The differences in the contribution of these elements were related to the underlying geology and the size of the watersheds.

This study provides a detailed analysis of element concentrations along the Souris and Turtle Rivers in North Dakota and provides information about relative sediments and element loading rates from the tributaries to the main rivers. Also this study helps to identify the sources and sinks of potentially enriched elements in the two rivers. The multi-element fingerprinting technique can be successfully used as a tool to identify the relative contribution of sediments and assessing and tracing pollution sources in rivers. Multi-element fingerprinting provides a relatively low cost, rapid tool for sediment tracking, without the need for addition of exotic chemicals such radio-tracers or dyes to natural ecosystems.

Fate of Biodegradable Dissolved Organic Nitrogen in Fargo Wastewater

Project Number: 2009ND191B

Fellow: Halis Simsek

Adviser: Khan Eakalak

Start Date: 3/1/2010

End Date: 2/28/2011

Publication:

Conference Publications

1. Simsek, H., Kasi, M., Blonigen, M., and Khan, E. (2010) Fate of Dissolved Organic Nitrogen in Two Stage Trickling Filter Process. In *Proceeding 83rd Annual Water Environment Federation Technical Exposition and Conference*, Oct. 2-6, 2010, New Orleans, LA, Water Environment Federation.

Presentations

1. Simsek, H., Kasi, M., Blonigen, M., and Khan, E. (2010) Fate of Dissolved Organic Nitrogen in Two Stage Trickling Filter Process. Presented at the *83rd Annual Water Environment Federation Technical Exposition and Conference*, Oct. 2-6, 2010, New Orleans, LA.
2. Simsek, H., Kasi, M., Blonigen, M., and Khan, E. (2010) Fate of Dissolved Organic Nitrogen in Two Stage Trickling Filter Process. Presented at the *International Student Prairie Conference*, Jun. 7-8, 2010, University of Manitoba, Winnipeg, Manitoba, Canada.
3. Simsek, H., Kasi, M., Blonigen, M., and Khan, E. (2010) Fate of Biodegradable/Bioavailable Dissolved Organic Nitrogen in Two Stage Trickling Filter Process. Poster presented at *the 82nd Annual Meeting of the North Dakota Water and Pollution Control Conference*, Oct. 12-14, 2010, Fargo, North Dakota.
4. Simsek, H., Kasi, M., Blonigen, M., and Khan, E. (2010) Biodegradable Dissolved Organic Nitrogen Removal in Wastewater Treatment Plant with Two Stage Trickling Filter Process. Poster presented at *the 2010 North Dakota EPSCoR Conference*, Sept. 29, 2010, Grand Forks, North Dakota.

Progress:

Recent advances in the treatment processes and increasingly demanding regulations require the reduction of dissolved organic nitrogen (DON) portion of total dissolved nitrogen (TDN) in the wastewater effluent. Removal of biodegradable portion of DON

(BDON) through biological treatment processes can contribute to effluent DON reduction. Previous studies showed that about 25% to 80% of the treatment plant effluent TDN is DON. In this study, fate and characteristics of DON and BDON through a two-stage trickling filter wastewater treatment plant in Fargo, North Dakota were investigated. A year-round, bi-weekly sampling program along the treatment train from influent to effluent was implemented from August 10, 2009 to August 22, 2010. The sampling locations were as follows: Before primary clarifiers (treatment plant influent, raw wastewater), after primary clarifiers, after biochemical oxygen demand (BOD) trickling filters, after intermediate clarifiers, after nitrification filters, after final clarifiers, after chlorination basin, and after dechlorination (final effluent before being discharged to the Red River).

Results showed that the average TDN in the plant influent was 33.1 mg/L as N while that in the effluent was 25.2 mg/L as N. Although the treatment plant was not equipped with a nutrient removal process, it achieved 24% removal of the influent TDN mainly via cell uptake. The removal was observed mainly through the BOD and nitrification trickling filters. Average influent and effluent DON concentrations were 9.02 and 3.44 mg/L as N, respectively. Major DON removal was observed in the biological processes of the plant. The BOD and nitrification trickling filters provided the same removal of DON at 37%. The BDON profile had a similar trend as that of the DON profile along the treatment train. BDON removal occurred mainly in the trickling filters. BDON in the raw wastewater and plant effluent were 6.1 and 1.7 mg/L as N respectively corresponding to 72% removal. The BOD trickling filters removed 43% of BDON and the nitrification trickling filters also removed 43% of BDON. The BDON was found to be between 51% and 69% of DON after various treatment units in the plant. In other words, there was 31% or more of BDON that was not treated by any processes along the treatment train.

A season effect (summer, April to October versus winter, November to March) on the BDON profile was examined. The plant has an operational change between the winter and the summer months. The plant does not disinfect during the winter months. Overall, the plant achieved higher BDON removal during the winter months. Modeling the fate of DON and BDON through the plant was attempted. The Biowin modeling process was selected and calibrated with the comprehensive data collected. Simulation of ammonia, DON and BDON through the plant showed perfect matching between the model results and the measured values. The model was found to be most sensitive to dissolved oxygen and particulate organic nitrogen hydrolysis rate. The model could potentially be used to optimize operational and control parameters of the plant to achieve better DON and BDON removal performances.

Ion Imprinted Polymer for Removal and Monitoring of Arsenic

Project Number: 2009ND188B

Fellow: Harjyoti Kalita

Adviser: Achintya Nayan Bezbaruah, Bret Chisholm

Start Date: 3/1/2010

End Date: 2/28/2011

Publications:

1. Kalita, H.; Chisholm, B.; Bezbaruah, A.N. Use of Ion-imprinted polymer to remove simultaneously As(III) and As(V) from water, The 2010 Surface Water Treatment Workshop, American Water Works Association, Fargo, ND April, 2010.
2. Kalita, H.; Bezbaruah, A.N. Ion-imprinted Polymers to As(III) and As(V) from Drinking Water, The International Student Prairie Conference on Environmental Issues, Winnipeg, Canada, June, 2010.
3. Kalita, H., Chisholm, B., and Bezbaruah, A.N. (2010) (Poster) Removal of Aqueous Arsenic with Reusable Ion-imprinted Polymer (IIP), ND EPSCoR 2010 State Conference, Grand Forks, ND September 2010.
4. Kalita, H.; Chisholm, B.; Bezbaruah, A.N. Synthesis of Ion-imprinted Polymers to Remove As(III) and As(V) from Drinking Water, 2010 Eastern South Dakota Water Conference, Brookings, SD, November, 2010.
5. Bezbaruah, A.N.; Kalita, H. Sensors and Biosensors for Endocrine Disrupting Chemicals: State-of-the-Art and Future Trends in *Treatment of Micropollutants in Water and Wastewater* (Eds: Virkutyte, J., Varma, R.S., Jegatheesan, V.), International Water Association, London, U.K., pp. 93-115, 2010, ISBN: 9781843393160.

Patent:

1. Kalita, H., Chisholm, B., J., Bezbaruah, A., N. Patent Application for "Synthesis of Ion Imprinting Polymer for Removal of Arsenic." is under preparation.

Progress:

Introduction: Arsenic contamination of drinking water is a serious environmental and health concern. In drinking water supplies, arsenic occurs naturally although some pesticides and preservatives also may contribute. With the U.S. Environmental Protection Agency (U.S. EPA) and World Health Organization's (WHO) lowered maximum containment level (MCL) for arsenic in drinking water (10 ppb), there is an urgent need to develop low capital and less technology intensive processes for arsenic removal. Oxidation of As(III) to As(V), coprecipitation and adsorption, adsorption onto sorptive media, ion exchange methods, and membrane filtration are the available technologies to remove arsenic from water. However, most of the available methods cannot remove As(III) unless it is oxidized to As(V) and there is a need effective novel method to remove both As(III) and As(V) species, preferably simultaneously, from water. Such methods can be very useful for household purposes and in small water treatment plants. This new method/methods should be able to remove arsenic to below 10 ppb at a relatively low cost. Solid phase extraction is one of the most promising technologies for the removal of various contaminants from water. The main advantages of solid phase extraction are: (a) high enrichment factor, (b) low cost (c) use of relatively less hazardous materials, and (d) flexibility in the method. While there are conventional solid phase adsorbents such as use of activated carbon, cellulose, silica gel, and glass beads, to name a few, they are difficult to be regenerated/reactivated. There is a need to developed cost effective solid phase extraction media which can be reused for a number of times using less technology intensive regeneration process. Ion imprinted polymers (IIP) are potential candidates to achieve these needs. These are cheaper, environmentally compatible, and have high selectivity relative to the conventional solid sorbents.

Progress : Thiol- arsenic complex has been synthesized and combined with sodium arsenate as a source of As(V). A solid white colored thiol- arsenic complex compound was formed. Binding of arsenic allyl mercaptal was seen from the FTIR spectra analysis. The solid white colored complex formed was imprinted in styrene-divinyl benzene copolymer. The copolymer was dried and leaching studies were conducted. ICP-OES analysis was carried out to see the binding and elution of arsenic to/from the polymer during the synthesis of the IIP of arsenic. More than 99 % arsenic was bound to the allyl mercaptan. A technique to synthesize IIPs for aqueous arsenic removal has been successfully developed.

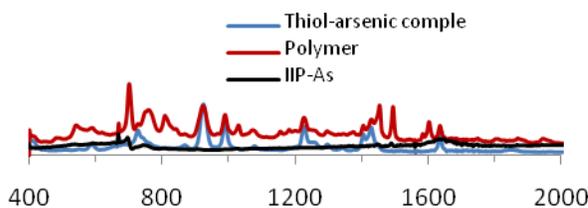


FIGURE 1: FT-IR SPECTRA OF THIOL-ARSENIC COMPLEX, POLYMER AND IIP-AS. THE PEAK AT $\sim 590 \text{ CM}^{-1}$ IS DUE TO THE AS-S STRETCHING. ABSENCE OF PEAK AT $861, 800 \text{ CM}^{-1}$ (AS=O⁻ STRETCH) AND AT $719, \text{ (AS-O STRETCH)}$ CONFIRMED THAT ALL ARSENIC WAS BIND TO THE ALLYL MERCAPTAN.

Table 1: Influence of various parameters on the percent extraction of arsenic onto IIP particle.

WEIGHT OF IIP-AS (G)	EXTRACTION (%)	PRECONCENTRATION TIME (HR)	EXTRACTION (%)	ELUTION TIME (HR)	EXTRACTION (%)
0.05	> 87	1	>97	0.5	>98
0.1	>96	2	>99	1	>99
0.15	>98	3	>99	1.5	>99
0.2	>96	4	>99		
0.25	>97	5	>99		
0.3	>97				

Deliverables: The proposed research already resulted in the a few presentations and posters. At least three peer reviewed journal articles, a number of conference papers and reports to NDWRRI are expected from this study. At least one intellectual property (patent) is expected from this research. The patent application process has been initiated.

Reference Evapotranspiration and Actual Evapotranspiration Measurements in North Dakota

Project Number: 2010ND214B

Fellow: Ishara Rijal

Adviser: Xinhua Jia

Start Date: 3/1/2010

End Date: 2/1/2011

Publications:

Rijal, I., X. Jia, D. D. Steele, T. Scherer, X. Zhang, and X. Pang. 2010. Comparison of evapotranspiration in subsurface drained and undrained field in North Dakota. ASABE 2010 Annual International Meeting, June 20-23, 2010, Pittsburgh, PA. Paper No: 1009554.

Pang, X., X. Jia, T. M. DeSutter, T. F. Scherer, D. D. Steele, and **I. Rijal.** 2010. Effect of subsurface drainage on water availability in the Red River Valley of the North. ASABE 2010 Annual International Meeting, June 20-23, 2010, Pittsburgh, PA. Paper No: 1009921.

Progress:

Evapotranspiration (ET) for both subsurface drained and undrained fields has been evaluated for soybean in 2010. The crop coefficient has been also developed. The reference evapotranspiration has been estimated using ASCE-EWRI 2005 and Jensen Haise methods.

Subsurface drainage (SSD) has been used to remove excess water from agricultural fields. The water leaving from a SSD system can affect both the quality and quantity of a surface water system. Therefore, determination of the water balance components is the first step to study the impact of SSD on water quantity, while evapotranspiration (ET), one of the most important components in the water balance, needs to be accurately measured. In this study, the ET for both the subsurface drained and undrained (UD) fields was measured using eddy covariance system for soybean in 2010. The SSD system showed a good control over the water table depth and provided sufficient water for crop production throughout the growing season. However, the ET values between the SSD and the UD fields did not yield any statistical difference for the entire growing season. In 2010, frequent rainfall events in July have provided sufficient water for soybean growth during its peak growing season.

The reference evapotranspiration (ET_{ref}) was estimated using ASCE-EWRI 2005 (both grass and alfalfa) and Jensen-Haise 1963 methods. The ASCE-EWRI method is considered as the standardized and recommended method, while the Jensen Haise (JH) method is the most widely used method in North Dakota. The ASCE-EWRI method estimated a higher ET_{ref} compared to the JH method. The JH method underestimated the ET values especially during the windiest period in May, October and November.

However, during mild wind conditions, the ET_{ref} rates by the JH method were comparable to that by the ASCE-EWRI (grass) method.

Crop coefficient (K_c) was calculated for soybean under two different field conditions. The K_c was developed using the ET from the eddy covariance system and the ET_{ref} estimated using ASCE-EWRI (alfalfa) method. The soybean K_c curve had its highest values 0.76 for the SSD and 0.65 for the UD in July, representing the highest water demand by soybean during that period. During the early and late growing seasons, the K_c values were about the same in both fields.

Development of GAC-NZVI Adsorbent for Arsenic Removal

Project Number: 2009ND186B

Fellow: Qigang Chang

Adviser: Wei Lin

Start Date: 3/1/2010

End Date: 2/1/2011

Publications:

Publications:

1. **Chang, Q.G.;** Lin, W.; Ying, W.C. (2010) Preparation of iron-impregnated granular activated carbon for arsenic removal from drinking water. *J. Hazard. Mater.* 184, 515-522.
2. **Chang, Q.G.;** Lin, W. (2010) Impacts of amount of impregnated iron in granular activated carbon on arsenic adsorption capacities and kinetics. Proc. of 83rd WEFTEC, New Orleans, Louisiana, U.S.A., 282-299.

Presentations:

1. **Chang, Q.G.** and Lin, W. Arsenic Adsorption on Iron Impregnated Granular Activated Carbon: Isotherm and Breakthrough. Presented at the 81st ND WPCC, Fargo, ND, Oct 12th, 2010;
2. **Chang, Q.G.** and Lin, W. Impacts of the Amount of Impregnated Iron in GAC on Arsenic Adsorption Capacities and Kinetics. Presented at the 83rd WEFTEC, New Orleans, LA, Oct 4th, 2010;
3. **Chang, Q.G.** and Lin, W. pH impact on As(III) and As(V) Adsorption Using Fe-GACs. Presented at the 3rd International Student Prairie Conference-Environmental Issue. University of Manitoba, Winnipeg, CA, June 8th, 2010;
4. **Chang, Q.G.** and Lin, W. As(III) and As(V) adsorption on iron impregnated granular activated carbon. Green Bag Lunch seminar, Environmental & Conservation Sciences Program, North Dakota State University. Fargo, ND, April 14th, 2010.

Progress:

Modification of Fe-GAC synthesis method and adsorption studies

The multi-step iron impregnation method was further modified to improve the impregnation efficiency and the arsenic adsorption properties. Using GAC Darco 20×50, iron content 28.90% (by weight) of iron was successfully impregnated inside GAC stably and evenly. This modification improved the impregnation efficiency approximately 100%.

Arsenic adsorption isotherm tests were conducted using Fe-GACs with iron content of 4.56-28.90% at low arsenic concentration ($<250\mu\text{g/L}$). Langmuir model fits arsenic adsorption very well. The maximum arsenic adsorption capacity increased with impregnation iron up to 13.59% and then slowly decreased with further increase of iron content. BET analysis found that both surface area and pore volume of Fe-GACs decreased with impregnated iron. It was found that the BET surface area of impregnated iron reaches the maximum at the iron content of 13.59%. Unlike the arsenic maximum adsorption capacity that was affected significantly by iron content, the affinity of Fe-GAC for arsenic was not affected by the iron content, which is $0.0223\text{ L}/\mu\text{g}$ for As(V) and $0.0170\text{ L}/\mu\text{g}$ for As(III).

Arsenic adsorption kinetics

A new second-order kinetics model was developed to investigate the impact of the amounts of impregnated iron on arsenic adsorption kinetics. This new kinetics model can well fit arsenic adsorption kinetics. With iron content increase from 1.64% to 28.90%, the intrinsic adsorption rate constants kept reducing from $4.6\times 10^{-2}\text{ 1/hr}$ to $1.18\times 10^{-3}\text{ 1/hr}$, which indicates that impregnated iron slows arsenic intraparticle diffusion rate in Fe-GAC. Decreased arsenic intraparticle diffusion rate was most likely caused by reduced pore size of Fe-GACs. The intrinsic adsorption rate constant is independent on initial arsenic loading in kinetics tests, which eases the comparison of the arsenic adsorption kinetics of Fe-GACs.

Environmental implementations

The groundwater sample was taken from the former Arsenic Trioxide Superfund site (Site ID #0800522) in southeastern North Dakota for evaluation of the potential implementations of Fe-GACs. The average arsenic concentration in the groundwater sample is $205\mu\text{g/L}$ and the groundwater was spiked with As(V) to obtain an initial arsenic concentration of $3000\mu\text{g/L}$ for isotherm tests. No other modification to the groundwater sample was made. Fe-GACs can effectively remove arsenic from the groundwater to meet $10\mu\text{g/L}$ regulation and the arsenic adsorption capacity was enhanced greatly with impregnated iron. Compared with As(III) and As(V) synthetic water, Fe-GACs exhibited the approximately same maximum adsorption capacity for groundwater, which is reasonable because the maximum adsorption capacity is determined by the density of adsorption sites of Fe-GACs. However, the affinity of Fe-GACs for groundwater ($0.0073\text{ L}/\mu\text{g}$) is much less than these for As(III) and As(V) synthetic water. The presence of a large amount of phosphate in groundwater probably explains the lower affinity for arsenic. Due to the similar molecular structure with arsenic, phosphate is the most competing anion with arsenic on iron-based adsorbents.

Information Transfer Program Introduction

Information dissemination is done through an annual newsletter, and presentations and publications by grant and fellowship recipients. A web site also helps disseminating institute research information. The institute's website address is <http://www.ndsu.edu/wrri>.

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.

Information Dissemination and Communication

Project Number: 2009ND175B

Start Date: 3/1/2010

End Date: 2/28/2011

Principal Investigator: G. Padmanabhan

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

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

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

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

The Institute continued its efforts to enhance communication between the State and Federal agency personnel and university faculty and students. Advisors and fellows presented their research results to State and Federal professionals in Bismarck. The Institute also encouraged its Fellows and faculty to attend seminars and conferences held in the region. Modest support for travel was provided by the institute whenever appropriate.

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

WRRRI sponsored seminars:

1. Dr. Ed Dickey, former acting assistant secretary of the army for civil works, Washington, D.C., shared his insights on federal water projects on Wednesday, Jan. 12, at 11 a.m. in the Memorial Union Century Theater. Dr. Dickey focused on the Washington perspective on Fargo-Moorhead diversion project.

While working for the federal government, Dr. Dickey was responsible for a variety of policies and programs related to federal water management activities, including new water resource investments for navigation, flood damage reduction and ecosystem restoration. Two Presidential Rank Awards, including Meritorious Executive in 1988 and Distinguished Executive in 1993, acknowledged his successes as a member of the federal Senior Executive Service.

NDSU's School of Natural Resources, Department of Agribusiness and Applied Economics, Environmental and Conservation Sciences Graduate Program and the North Dakota Water Resources Research Institute sponsored Dr. Dickey's presentation.

2. An annual seminar series "ND WRRRI Annual Distinguished Water Seminar Series" was instituted.

The first of this series took place on October 7, 2010 at NDSU. The talk was co-sponsored by the Agricultural and Biosystems Engineering department and the Environmental and Conservation Sciences program of North Dakota State University.

Dr. Vijay Singh, a leading hydrologist and Caroline and William N. Lehrer Distinguished Chair in Water Engineering and Professor, Texas A&M University, spoke on "Challenges, Opportunities, and Research Directions in Hydrology and Water Resources."

Dr. Singh also had a talk "Water Resources and Climate Change" at University of North Dakota. This talk was also sponsored by the ND WRRRI and co-sponsored by the Department of Civil Engineering and Department Earth Systems Science and Policy of University of North Dakota.

NATIONAL COMPETITIVE PROGRAM (104-G)

Two proposals were submitted; but were not funded:

“Quaternary Ammonium-Functional Porous Polymers for the Removal and Recovery of Phosphates” by Achintya Bezbaruah, Department of Civil Engineering, North Dakota State University

“Evaluation of Potential Climate Change Effects on Future Flood Risk for the Northern Great Plains” by Howe Lim, Department of Civil Engineering, University of North Dakota

Institute Publications

None

THESES AND DISSERTATIONS

The following Fellows successfully defended their theses and graduated:

Adam Guy (MS)
Dimuthu Wijeyaratne (Ph. D)
Qigang Chang (Ph. D)
Rabiya Shabnam (MS)

Abstracts of their theses follow:

ABSTRACT

Guy, Adam Christopher, M.S., Department of Soil Science, College of Agriculture, Food Systems, and Natural Resources, North Dakota State University, May 2011. Effects of Major Flooding on Water and Sediment Characteristics in an Urban Environment. Major Professor: Dr. Thomas DeSutter.

Spring flooding of the Red River of the North is a common phenomenon, but no information exists on how these flooding events impact both water and sediment quality within an urban area. The objectives of this study were to assess if urban environments affect floodwater quality and to determine the quality of sediment deposited in an urban environment after floodwaters recede. Water samples were taken on 12 dates from two locations before and after the city limits of Fargo, North Dakota and Moorhead, Minnesota (F-M), and were measured for 12 variables including total sediment, PO₄, and 17β-estradiol. Sediment and underlying soil samples were collected from three locations within F-M where at each location there were three equidistant transects parallel to the river channel, and analyzed for 40 variables including dry sediment mass, carbon, nitrogen, diesel and gasoline range organics, and trace elements. Considering river discharge, and total sediment and PO₄ concentrations at each sampling date, about 4500 Mg of sediment and 30 Mg of PO₄ were estimated to have been deposited within F-M. 17β-estradiol was detected in 9 of 24 water samples with an average concentration of 0.61 ng L⁻¹ and diesel range organics were detected in 8 of 24 samples with an average concentration of 80.0 μg L⁻¹. Average mass of sediment across locations and transects ranged from about 2 to 10 kg m⁻² where transects closest to the river channel had the higher mass deposits of sediment. Total carbon and nitrogen within the sediment was determined to be mostly organic and ranged from about 40 to 59 g kg⁻¹ and about 2,100 to 4,200 mg kg⁻¹, respectively, with the highest concentrations occurring at the transect furthest from the river channel. No gasoline range organics were detected, but diesel range organics were detected in 26 of the 27 sediment samples analyzed with a maximum concentration of 49.2 μg g⁻¹. Total Hg concentrations in the sediment and soil averaged about 55 and 61 ng g⁻¹, respectively, and all trace elements detected in the sediments were within ranges for non-contaminated sites. Although sediments remaining after floodwaters recede can be unsightly and cleanup efforts can be labor intensive, these sediments can also provide essential plant nutrients for urban riverine ecosystems, which may include turf grass, fruits and vegetables, and horticultural plants.

ABSTRACT

Wijeyaratne, Dimuthu Nilmini, Ph.D., Program of Environmental and Conservation Sciences, College of Graduate and Interdisciplinary Studies, North Dakota State University, March 2011. Multi-element Fingerprinting of River Sediments to Identify Diffuse Pollution Sources. Major Professor: Dr. Marinus Otte.

The multi-element fingerprinting technique uses natural tracers in combination with field data collection, laboratory analyses of sediments, and statistical modeling techniques to identify sediment source areas in a watershed. In this technique natural tracers are identified and measured for both sediment sources and sediment mixtures collected at the watershed to identify the potential source areas of sediments.

This study was carried out in two watersheds in North Dakota, the Souris River and the Turtle River. The aim of this study was to develop multi-element fingerprints of the Souris River and Turtle River sediments and to evaluate the suitability of these fingerprints to assess the geographic origin of potential pollutants of the two rivers. In the initial step of this study, existing sediment samples of the Souris River from a previous project were analyzed for multiple elements. This study showed statistically significant variations in element concentrations of surface sediments at different sites and therefore it was confirmed that the multi-element fingerprinting can be used to assess the sediment and contaminant loading patterns.

In the multiple element fingerprinting studies the linear mixing of elements and the absence of enrichments and depletions of elements are assumed. Two laboratory experiments were performed to assess the validity of these assumptions. The results of these experiments verified the assumptions and showed that there is a statistically significant spatial and temporal variation in the element concentrations depending on their mobility and re-deposition.

Field studies were conducted in the Souris River and Turtle River to assess the variation of element concentrations in the top riverbed samples along the main rivers and their tributaries. The sediment contribution from the tributaries and the phosphorus concentrations in the main channel were used to calculate the phosphorus contributions from the tributary sediments to the Souris River. The larger tributaries of the Lower Souris River showed higher phosphorus contribution compared to the smaller tributaries of the Upper Souris River. The differences in phosphorus contributions were related to land use, underlying geology, and the size of the watersheds of the tributaries in the Souris River watershed. Similar analysis was used in the Turtle River to calculate Arsenic, Cadmium and Selenium contribution from the tributaries to the Turtle River. The differences in the contribution of these elements were related to the underlying geology and the size of the watersheds.

This study provides a detailed analysis of element concentrations along the Souris and Turtle Rivers in North Dakota and provides information about relative sediments and element loading rates from the tributaries to the main rivers. Also this study helps to identify the sources and sinks of potentially enriched elements in the two rivers. The multi-element fingerprinting technique can be successfully used as a tool to identify the relative contribution of sediments and assessing and tracing pollution sources in rivers. Multi-element fingerprinting provides a relatively low cost, rapid tool for sediment tracking, without the need for addition of exotic chemicals such radio-tracers or dyes to natural ecosystems.

ABSTRACT

Chang, Qigang, Ph.D., Environmental and Conservation Sciences Program, College of Graduate and Interdisciplinary Studies, North Dakota State University, August 2011. Iron-Impregnated Granular Activated Carbon for Arsenic Removal from Drinking Water. Major Professor: Dr. Wei Lin.

Iron-impregnated granular activated carbon (Fe-GAC) can effectively remove arsenic from water. A new multi-step iron impregnation method was developed in this study to impregnate GAC with high amount of iron that possesses desired characteristics: stable, even distribution, and high arsenic adsorption capacity. Research was carried out to investigate the impact of the amount of impregnated iron on arsenic adsorption properties: capacity, affinity, and kinetics.

Fe-GACs with different iron contents were characterized in terms of the amount, stability, distribution, morphology, and species of impregnated iron. It was found that high amount of iron was stably impregnated in GAC. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis demonstrated that the impregnated iron was evenly distributed on the internal surface of GAC. Impregnated iron formed nano-size particles, and existed in both crystalline (akaganeite) and amorphous iron forms.

Arsenic adsorption tests were conducted using Fe-GACs with iron content of 1.64-28.90% and adsorption isotherms covered the range of arsenic equilibrium concentration that is typical for drinking water treatment. Langmuir model fit both As(III) and As(V) isotherm adsorption well. The amount of impregnated iron affects arsenic maximum adsorption capacity (q_m), but have little impact on the Langmuir constant b (the affinity of adsorbent for adsorbate). The q_m for both As(V) and As(III) adsorptions increased significantly with increase of the amount of impregnated iron up to 13.59%. Further increase of iron amounts caused gradually decrease of q_m for As(V). The q_m for As (III) continued to slightly increase to 2456 $\mu\text{g/g}$ at iron content of 24.73%. BET analysis indicated that the surface area of Fe-GAC decreased with increase of the iron amount. At 13.59%, impregnated iron fully covered the internal surface area of GAC.

A new second-order kinetic model was developed to investigate the impact of the amounts of impregnated iron on arsenic adsorption kinetics. This new kinetic model can well fit arsenic adsorption kinetics. With iron content increase from 1.64% to 28.90%, the intrinsic adsorption rate constants kept reducing from 4.6×10^{-2} 1/hr to 1.18×10^{-3} 1/hr, which indicates that impregnated iron slows arsenic intraparticle diffusion rate in Fe-GAC. Decreased arsenic intraparticle diffusion rate was most likely caused by reduced pore size of Fe-GACs. The intrinsic adsorption rate constant is not dependent on initial concentration in kinetic tests, which eases the comparison of the arsenic adsorption kinetics of Fe-GACs.

Groundwater sample taken from a former superfund site in North Dakota with a total arsenic concentration of 205 $\mu\text{g/L}$ was used in column tests to investigate the effect of the amount of impregnated iron on arsenic breakthroughs. With empty bed contact time (EBCT) of 600 second, the number of bed volume (BV) treated at breakthrough (10 $\mu\text{g/L}$) increased from 140 to 1000 with iron content increasing 4.56-13.59%. Further increase of iron content, BV treated at breakthrough slightly decreased. The slope of breakthrough curves became smaller with increase of iron content, which implies that arsenic intraparticle diffusion rate in Fe-GACs decreased with more impregnated iron. Fe-GACs with high iron content require long EBCT to achieve a better performance. This indicates that Fe-GACs with high iron content require longer EBCT to utilize Fe-GACs in column tests.

ABSTRACT

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Nanoparticles (<100nm) are being used in different applications such as biomedical, personal care, industrial, and environmental remediation. NZVI particles have unique physico-chemical properties like high surface area and high reactivity. High reactivity of nanoparticles is a concern when it comes to various ecosystem components. The impacts of NZVI particles on ecosystem components including endemic microbial community are not well studied. This research is an effort to elucidate the interactions between NZVI and some environmentally significant gram negative bacteria. Experiments were designed to study the interactions of three model gram negative bacterial species (*Escherichia coli* 8739, *E. coli* JM 109, and *Pseudomonas putida* F1). The growth and viability of all bacteria were evaluated in the presence of NZVI particles with nutrients (in nutrient media) and without nutrients (in buffer solution). The bacterial species were exposed to various NZVI concentrations (0.09-10 mg/mL) under stirring (800 rpm) and shaking (150 rpm) conditions at different temperatures (4, 22, and 37°C). Microorganisms exposed to 0.09, 0.2, 0.5, 0.8 and 1.0 mg/mL of NZVI in buffer (stirring condition), showed variable viability. At very low NZVI concentration (0.09 mg/mL) viable cells were seen until 60 min and at higher concentration (0.2-1.0 mg/mL) no viable cells were observed after 5 min. NZVI had no significant effect on the three strains at lower concentrations (1 and 2 mg/mL) in the nutrient media. *E.coli* JM109 and *P.putida* F1 were significantly reduced at environmentally significant NZVI concentrations. However, following an initial reduction *E. coli* 8739 recovered back to the same level as the control. The recovery of *E. coli* 8739 was not due to a reduction in the toxicity of NZVI as redosing with NZVI at 3 and 6 h did not affect the regrowth. Hence it was postulated that the observed regrowth in the presence of NZVI was a result of growth characteristics of the microorganism. Further experiment at suboptimal growth temperatures of 22°C and 4°C resulted in reduction in bacterial viability for both 5 and 10 mg/ml of NZVI. Based on the results obtained from experiments done at suboptimal temperature and comparing them with the results from experiments conducted at optimal temperature of 37°C it can be concluded that NZVI toxicity on microorganisms are microbial species/strain specific and in some cases depends on the growth of the microorganisms. Actively growing *E.coli* 8739 are not affected by NZVI toxicity while non-dividing cells are adversely affected.