



**North Dakota  
Water Resources Research Institute**

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

**ANNUAL REPORT**

March 1, 2009 to February 28, 2010

**Fiscal Year 2009 Report to the U.S. Geological Survey**

June 2010

# **Annual Report**

## **Fiscal Year 2009 Report to the U.S. Geological Survey**

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

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June 2010

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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, 2009 to February 28, 2010.

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

## **Program Management**

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

## **State Appropriation**

The State Water Commission continued its support to the 2009 – 2010 federal 104(B) funding for the Graduate Research Fellowship program of NDWRRI. This is sixth 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 2009-2010 Graduate Research Fellowship competition were posted on the Institute website in September 2008, 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 WRRRI invites applications for 2009 graduate research fellowships**

The North Dakota Water Resources Research Institute (ND WRRRI) has announced its 2009 Graduate Research Fellowship program.

NDSU and University of North Dakota graduate students who are conducting or planning research in water resources areas may apply for fellowships varying from three summer months to a full year in duration. Typically in the past fellowship awards for master's degree students have been in the range \$800-\$1,000 and for doctoral students it has been \$1,000-\$1,400 per month. The fellowship funds must be applied between March 1, 2009, and Feb. 28, 2010.

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

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

Applications are due in the office of the director by 5 p.m., Nov. 14. The proposals will be reviewed by a panel of faculty members and state water resources research professionals. Announcement of awards will be made by early January.

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

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



## **NDWRRI GRADUATE RESEARCH FELLOWSHIPS**

Fellowships ranging from \$4000 to \$12,000 were awarded to graduate students from UND (one) and NDSU (six) conducting research in water resources areas. Selection of student Fellows and the award amounts were based on competitive proposals prepared by the students with the guidance of their advisers. Projects proposed for fellowship support should relate to water resources research issues in the state or region. Regional, state, or local collaboration or co-funding is encouraged. Fellowships have a matching requirement of two non-federal dollars to one federal dollar. A panel of state water resource professionals reviews the proposals and selects the Fellows and award amounts based on the quality of proposals and the priority of the proposed projects for the state and region. The general criteria used for proposal evaluation include: scientific merit, originality of research, research related to state and/or region, and extent of regional, state or local collaboration and/or co-funding.

This year, eleven applications were received: six Ph.D. and five MS students. Not all applications could be funded. Highly competitive proposals and limited availability of funds restricted the number and the amount of awards. Nine Fellowships (6 Ph. D. and 3 M.S.) were awarded. Five of the Fellowships were renewals, one M.S. and four Ph.D. The renewals are Sita Krajangpan (Ph. D), Qigang Chang (Ph. D), Dimuthu Wijeyaratne (Ph.D), Harjyoti Kalita (Ph. D) and Rabiya Shabnam (M. S.).

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

## **2009-10 Fellows and their projects**

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

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

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

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

Rabiya Shabnam, environmental and conservation Sciences, Achintya Bezbaruah and John McEvoy, “Interactions between Microorganisms and Metal Nanoparticles: A New Approach for Groundwater Remediation”

Sita Krajangpan, civil engineering, Achintya Bezbaruah and Bret Chisholm, “Modification of Iron Nanoparticles by Amphiphilic Polysiloxane Graft Co-Polymer for Arsenic, TCE, and RDX Remediation”

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

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

Chase Christenson, geology and geological Engineering, Scott Korom, “Effects of Iron Bacteria on Subsurface Tile Drains: Influence on Nutrient Transport”

Joseph Vistad, civil engineering, Howe Lim, “Regional Flood Frequency Analysis in the Missouri River Basin Based on L-moments and GLS Regression”

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

**Project Number:** 2009ND189B

**Fellow:** Dimuthu Wijeyaratne

**Adviser:** Marinus L. Otte

**Start Date:** 3/1/2009

**End Date:** 2/28/2010

## **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:**

In August 2008 and 2009 sediment samples from the top layer of the riverbed were collected from tributaries along the Souris River. Chemical fingerprints were developed for each site using the element concentrations. Based on the results a simple equation was developed to find the contribution of the tributary to the sediments assuming a linear mixing between tributary and upstream sediments. The assumptions concerning sediment mixing and effects on element concentrations, and the explanations for depletion/enrichment will be further investigated with controlled laboratory experiments. It is also proposed to determine the chemical fingerprints of sediments of the Turtle River in greater detail than done so far for the Souris River in order to assess the spatial variation along the river.

# **Ion Imprinted Polymer for Removal and Monitoring of Arsenic (Phase II)**

**Project Number:** 2009ND188B

**Fellow:** Harjyoti Kalita

**Adviser:** Achintya Nayan Bezbaruah, Bret Chisholm

**Start Date:** 3/1/2009

**End Date:** 2/28/2010

## **Publications:**

Krajangpan, S., Chisholm, B. J., Kalita, H., and Bezbaruah, A. N. Challenges in Groundwater Remediation with Iron Nanoparticles: Enhancement Colloidal Stability (Chapter 8) in Nanotechnologies for Water Environment Applications (Eds: Zhang, T., Surampalli, R.; Lai, K.; Hu, Z.; Tyagi, R.; Lo, I.), Environmental and Water Resources Institute/American Society for Civil Engineers, 2009, 191-212. (Book Chapter)

Kalita, H., Chisholm, B. J., Bezbaruah, A. N. Effects of different graft copolymer constituent groups on sedimentation characteristics of coated iron nanoparticles, PMSE Preprints, 2009, 100, 683-685.

Kalita, H., Chisholm, B. J., Bezbaruah, A. N. Synthesis of Ion Imprinted Polymer to Remove Arsenic from Water, ND EPSCoR State Conference, September 2009, Fargo, North Dakota. (Poster Presentation)

## **Progress:**

The progress is summarized below:

**Task I-** Thiol- arsenic complex was synthesized and solid white colored thiol- arsenic complex compound was found

**Task II-** The complex formed in Task I was imprinted in styrene-divinyl benzene copolymer. FT-IR was taken for the polymer which again illustrated that arsenic is still bound to the polymer.

**Task III-** The dried polymer (from Task II) was mixed with 6 M HCl for 6 hr to leach the arsenic from the polymer. Arsenic came out from the polymer leaving the As imprints (i.e., void spaces of the As ions). Such spaces are specific to arsenic only.

**Task IV-** 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. Sorption and elution of arsenic was optimized from ICP-OES analysis. All these analysis were carried out in ppm level. Now our target is to analyze in ppb level.

# Development of GAC-NZVI Adsorbent for Arsenic Removal

**Project Number:** 2009ND186B

**Fellow:** Qigang Chang

**Adviser:** Wei Lin

**Start Date:** 3/1/2009

**End Date:** 2/1/2010

## Publications:

Chang, Q.G. and Lin, W. (2009) Development of GAC-Fe to remove arsenic from water. Proc. of the 82nd WEFTEC, Orlando, USA, 1552-1571.

Chang Q. G. (2009) ND EPSCoR 2009 State Conference. .Preparation of iron impregnated granular activated carbon for removing of arsenic from groundwater, NDSU, Fargo, September 24, 2009

## Progress:

### *Synthesis of GAC-Fe*

In 2008, a new iron impregnation method was developed and GAC-Fe adsorbents with different iron contents were synthesized. Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Scope (EDS), and X-Ray Diffraction (XRD) were used to characterize GAC-Fe adsorbents in terms of distribution, morphology, and species of iron. Three different methods were compared as to measure the iron contents of GAC-Fe adsorbents. In 2009, this impregnation method was modified to improve the impregnating efficiency, the stability of iron, and the arsenic adsorption capacity of GAC-Fe adsorbent. The synthesis of GAC-Fe adsorbents using the modified method was finished in the summer 2009 and 11 different GAC-Fe adsorbents were obtained. With a stabilizing step included in each repetition of the synthesizing process rather than at the end of the entire synthesis, iron is more stable in GAC-Fe and iron impregnation efficiency is improved. The results demonstrated that the modified method is about 2 times efficient in terms of the amount of iron impregnated in GAC than the original one. More than 28% of iron was impregnated inside GAC Darco 20×50.

### *Analytical methods for arsenic*

In 2008, the arsenic analytical method was established using Inductively Coupled Plasma (ICP) at the Department of Biological Sciences, NDSU. ICP has the advantage to analyze multi-elements simultaneously; however, the detection limit (30 ppb) of ICP is too higher to conduct research close to the arsenic standard (10 ppb) for drinking water. Alternative analytical method is needed to carry experiments out at low arsenic concentration range (<10 ppb). In 2009, Fargo Water Treatment Plant donated a Graphite Furnace Atomic Absorption Spectrometer (GFAAS) to the Environmental Engineering Lab at Department of Civil Engineering, NDSU. I spent three months on setting up and making the instrument functional. Currently, this GFAAS is updated with new part, calibrated and working well. It has a detection limit of 1ppb on arsenic.

### *Arsenic adsorption study*

Since 2008, arsenic adsorption tests were carried out to measure adsorption capacity of the GAC-Fe. To keep conditions close to the drinking water treatment, the pH of adsorption tests was controlled around neutral using 0.05N bicarbonate buffer solution. It was found that GAC-Fe adsorbents have high affinity to arsenate and GAC-Fe adsorbent with 4.22% performed the best among 5 GAC-Fe adsorbents. In 2009, more arsenic adsorption tests were conducted to identify the relationships among iron content, arsenic adsorption capacity, and iron efficiency of GAC-Fe adsorbents. In addition, the impacts of pH and reaction time on adsorption capacity were investigated. GAC-Fe adsorbents exhibit high level removal rate of arsenic at pH range 5-7.5 and low removal rate at pH above 8. Langmuir Model was used to interpret the arsenic adsorption behavior of GAC-Fe adsorbents in this research. Different from the conventional way to estimate parameters in Langmuir model, nonlinear regression (rather than linear regression) was employed to estimate these parameters. The nonlinear regression procedure was coded using Statistical Analysis System (SAS). Results indicated that nonlinear regression fits isotherm curves much better than linear regression, because there is a serious transformation bias in the linearization of Langmuir model. Currently, with the aid of GFAAS, a series of isotherm tests is in the process to determine the arsenic adsorption capacity of the 11 new GAC-Fe adsorbents, synthesized using the modified impregnation method, at a low arsenic concentration window (1-200ppb). The results will discover the new relationship relationships among iron content, arsenic adsorption capacity, and iron efficiency of GAC-Fe adsorbents. Available data showed a promising sign that the new GAC-Fe adsorbents exhibit enhanced arsenic adsorption capacity.

# Interactions between Microorganisms and Metal Nanoparticles: A New Approach for Groundwater Remediation (Final Phase)

**Project Number:** 2009ND187B

**Fellow:** Rabiya Shabnam

**Adviser:** Achintya Nayan Bezbaruah, John McEvoy

**Start Date:** 3/1/2009

**End Date:** 2/28/2010

## Publications:

Rabiya Shabnam, John McEvoy, Eakalak Khan, Senay Simsek and Achintya Bezbaruah.(2009) Interactions between Iron Nanoparticles and Microorganisms: Environmental Significance, NDEPSCOR, September 2009, NDSU, Fargo, ND. (Poster)

Rabiya Shabnam, Achintya Bezbaruah, Senay Simsek, Eakalak Khan.(2009) Evaluation of exposure and growth of gram-negative bacteria with zero-valent iron nanoparticles, Annual Joint Student Environmental Conference, July 2009, SDSU, SD. (Podium Presentation)

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

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

## Progress:

The specific objective was to study iron nanoparticle-microorganism interactions in terms of microbial growth and their behavioral changes. The results obtained so far demonstrate that nanoscale zero-valent iron (NZVI) particles can be effectively introduced along with microorganisms without significant damage to the microorganisms. Gram negative bacteria were used to evaluate growth activity and viability of microorganisms in the presence of NZVI. The specific microorganisms like *Escherichia coli* (ATCC 8739 and JM109) and *Pseudomonas putida F1* were used in the presence of nutrients and without them. Compatibility of the microorganism with NZVI has been observed. Growth and inactivation studies in the presence of nutrients with *Pseudomonas putida F1*, *E.coli* JM 109 and 8739 carried out with different NZVI concentrations (1, 2, 5, 10 mg/mL). *Pseudomonas putida F1* demonstrated no effect at low (1, 2 mg/mL) NZVI concentrations. Studies with *E. coli* 8739 showed that actively growing bacteria are not affected by NZVI but non-dividing cells/ bacteria are susceptible to NZVI toxicity at higher concentrations (5, 10 mg/mL). Again there was no effect of NZVI on the bacteria when nutrient broth was used and *E. coli* 8739 showed a remarkable growth in the presence of NZVI. During inactivation studies without nutrients at different NZVI concentrations, the non-dividing cells were wiped out and the extent of killing was observed to be NZVI concentrations specific.

# Polymer Modified Zero-valent Iron Nanoparticles for Arsenic Remediation: Longevity and Ionic

**Project Number:** 2009ND184B

**Fellow:** Sita Krajangpan

**Advisers:** Achintya Nayan Bezbaruah, Bret Chisholm

**Start Date:** 3/1/2009

**End Date:** 2/28/2010

## Publications:

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

Krajangpan, S., Chisholm, B.J., Kalita, H., Bezbaruah, A.N. (2009). Challenges in Groundwater Remediation with Iron Nanoparticles: Enhancement Colloidal Stability (Chapter 8) in *Nanotechnologies for Water Environment Applications* (Eds: Zhang, T.C., Surampalli, R.Y., Lai, K.C.K., Hu, Z., Tyagi, R.D., Lo, I.M.C.), American Society for Civil Engineers, pp 191-212. (Book Chapter)

Krajangpan, S., Jarabek, L., Jepperson, J., Chisholm, B., Bezbaruah, A. (2008). Polymer Modified Iron Nanoparticles for Environmental Remediation, *Polymer Preprint*, 49, 921-922.

## Progress:

Arsenic in groundwater is a major concern in not only in North Dakota world. The threat of arsenic pollution in drinking water is a serious environmental problem because of the toxicity of arsenic on human and on other living organisms. The effectiveness of nanoparticles for groundwater remediation depend on the contaminants. Another important characteristic needed in remediation is their ability to individually disperse and suspend in water. In aqueous environment they tend to agglomerate due to interparticle magnetic and van Amphiphilic polysiloxanes hydrophobic/hydrophilic nature. A carboxylic acid anchoring group and polyethylene glycol (PEG) is also used in the present design. The carboxylic acid anchoring group in conjunction with the polysiloxane polymer backbone allowed for efficient absorption of polymer mol particles while the water-soluble grafts, such as poly ethylene glycol (PE and colloidal stability in an aqueous medium. successfully synthesized by hydrosilylation The colloidal stability of APGC sedimentation rates of the CNZVI suspension using UV spectrophotometer (wavelength 508 nm). CNZVI resulted in higher dispersibility than bare of carboxylic acid (anchoring group) provided the highest colloidal stability. Studies indicate that the As reduction rates ( $k_{SA} = 0.16-0.46 \text{ L m}^{-2}\text{h}^{-1}$ ) as well as than the As reduction with bare nZVI (k colloidal stability and contaminant degradation by CN sedimentation studies for CNZVI were conducted in salt (Na mM of NaCl). There was no significant difference in Kinetics studies for As, with different ionic strength. Change in ionic strength did not make significant difference in the As(V). Further to be commercially viable Effects of aging of CNZVI were studied through colloidal stability and a 12-month and 6-month periods, respectively. CNZVI remained unchanged after 12 months. The efficiency of NZVI in contaminant degradation did not change.



# Fate of Biodegradable Dissolved Organic Nitrogen in Fargo Wastewater

**Project Number:** 2009ND191B

**Fellow:** Halis Simsek

**Adviser:** Khan Eakalak

**Start Date:** 3/1/2009

**End Date:** 2/28/2010

## Progress:

From March 1, 2009 to August 9, 2009, efforts were put on analytical procedure trainings and practices. The BDON determination is based on DON reduction during a 28 day incubation period. Four measurements of different dissolved nitrogen species including total dissolved nitrogen (TDN), dissolved NH<sub>3</sub>-N (DNH 3-N), dissolved nitrite nitrogen, and dissolved DNO 3-N (DNO 3-N) are required to determine DON. The first set of samples from the Fargo WWTP was collected on August 10, 2009. Since then, the samples have been collected weekly as opposed to bi-weekly as originally proposed in order to obtain more data and to see whether there is a weekly variation in the sample characteristics. TDN was reduced by the BOD and nitrification trickling filters because of biological nitrogen uptake for cell synthesis. The reduction in DNH 3-N by the trickling filters was also observed. As expected, the trickling nitrified DNH 3-N to DNO 3-N almost completely. The DON profile along the treatment train exhibits the same general trend as the TDN profile. The effluent DON concentration was in a medium to high range before dechlorination. In several occasions, DON increase after dechlorination was observed. This interesting phenomenon has not been observed in previous studies. Sulfur dioxide used for dechlorination could be the cause of the DON increase. More data collection and a further investigation on this matter will be performed. Unlike the other nitrogen species profiles, BDON fluctuated tremendously along the treatment train. Effluent BDON was lower or comparable to influent BDON. To explain the fluctuation of BDON, more data collection is needed. For future work, more samples will be collected from the Fargo WWTP until August 2010 to obtain the nitrogen species profiles particularly for BDON all year round. This will elucidate the effect of season on the nitrogen species profiles. Seasonal changes of the nitrogen species profiles are expected because of high variations in temperature among different seasons in Fargo. From September 2010 to December 2010, effect of light on BDON experiment will be conducted to evaluate the eutrophication and oxygen depletion potentials of effluent BDON from the Fargo WWTP. Also, this time frame will be used for data analysis and to prepare a final report and publications which will include recommendations to the Fargo WWTP on how to reduce effluent DON and BDON concentrations and their eutrophication and oxygen depletion potentials which in turn would benefit the quality of the Red River. A good working relationship including data sharing with the Fargo WWTP treatment has been established and the plant highly values the proposed research

# Source tracking of *Cryptosporidium* in rural watersheds

**Project Number:** 2009ND183B

**Fellow:** Brianna Schneck

**Advisers:** John McEvoy, Mark Clark

**Start Date:** 3/1/2009

**End Date:** 2/28/2010

## Publications:

Schneck, B.L., Pennil, C.C., Lanctot, V.T., Giddings, C.W., Clark, M.E., and McEvoy, J.M. 2009. *Cryptosporidium* genotypes in Midwestern mammals. Poster presented at III International Giardia and *Cryptosporidium* Conference, Orvieto, Italy, Oct.11-15, 2009.

Pennil, C. C., Clark, M.E., Schneck, B.L., Giddings, C.W., and McEvoy, J.M. 2009. High prevalence of *Cryptosporidium andersoni* in surface water during a major spring flooding event. Poster presented at III International Giardia and *Cryptosporidium* Conference, Orvieto, Italy, Oct.11-15, 2009.

Pennil, C.C., Clark M.E., Giddings C.W., Schneck B.L., and McEvoy J.M. 2009. Determining sources of *Cryptosporidium* in a rural watershed. Master.s Thesis (Chapter 2), North Dakota State University, Fargo, North Dakota, Chapter 2.

## Progress:

Empirical evidence supports host adaptation and a limited host range for most *Cryptosporidium* species and genotypes. This knowledge has been used to track sources of water contamination and characterize human health risk; however, the factors affecting host range remain unclear. We are using small mammals (mainly rodent species) as a model to study the effect of factors such as host population density, diversity and behavior on the host range of *Cryptosporidium* genotypes. Over 250 wildlife fecal samples (from rodent species) have been collected and analyzed over the past year. Trapping grids were set up in various locations near water sources including rivers, streams, and drainage ditches. *Cryptosporidium* species/genotypes were found in over 40% of the samples. We found that red squirrels, grey squirrels, fox squirrels, and deer mice can carry *Cryptosporidium corvine* genotype which has been known to affect humans. Deer mice were also found to carry *C. parvum*, a known human pathogen. Rodents may be a significant source of *Cryptosporidium* in watersheds. We found a high prevalence of *Cryptosporidium* species in water samples collected during the major flooding event that affected the Red River Valley in 2009. Nine out of thirteen water samples tested positive for *Cryptosporidium*. A cattle adapted species, *Cryptosporidium andersoni*, was found in seven of the nine samples. *Cryptosporidium* deer mouse III genotype was found in a sample taken from a drainage ditch. We also found DM III in grey squirrels and deer mice. *Cryptosporidium suis*, a pig adapted species, was also found in a water sample. Livestock contributed significantly to *Cryptosporidium* contamination in the Red River during a major spring flood.

# Effects of Iron Bacteria on Subsurface Tile Drains: Influence on Nutrient Transport

**Project Number:** 2009ND177B

**Fellow:** Chase Christenson

**Adviser:** Scott F Korom

**Start Date:** 3/1/2009

**End Date:** 2/28/2010

**Funding Source:** 104B

## Project Background:

Subsurface agricultural drainage, a growing practice, has allowed the reclamation of unproductive land since the earliest of settlements. Despite its agricultural benefits, agricultural drainage bypasses the reduced zones where denitrification is likely to occur, contributing to higher nitrate yields as it is discharged directly to surface water. It is estimated that principal contributor of nitrogen inputs in the Gulf of Mexico and the North Atlantic Ocean are agricultural in origin. Remediation of nitrate contamination may occur through denitrification. This naturally occurring process reduces nitrate (NO<sub>3</sub><sup>-</sup>) to harmless nitrogen gas. Denitrification through natural attenuation requires the following: the availability of electron donors, an oxygen limited environment and the presence of nitrogen digesting bacteria. The availability of suitable electron donors within aquifer sediments has been shown to be the controlling factor in this reaction. The three most common electron donors are organic carbon, sulfide, and ferrous iron minerals. Anaerobic groundwater draining into subsurface tile drains forms an ecological niche for iron oxidizing bacteria. These bacteria obtain energy for growth from the reaction converting ferrous iron and oxygen into ferric iron and water. With respect to hydraulic efficiency, ferric iron forms highly insoluble ferric oxyhydroxides and some iron bacteria produce a sheath of slimy material, both of which tend to plug the tile drain system. However, with respect to nutrient transport, ferric oxyhydroxides may adsorb phosphorus (P) and iron bacteria denitrify nitrate concentrations in the tile effluent.

## Project Objectives:

The Oakes Test Area (OTA) is a 64-hectare tile-drained agricultural site within the USBR Best Management Practices study area. Denitrification research performed at the site will include the following:

1. Determine denitrification rates in aquifer sediments and around gravel drain envelopes at the OTA.
2. Determine sediment properties that relate to NO<sub>3</sub><sup>-</sup> reduction.
3. Correlate NO<sub>3</sub><sup>-</sup> reduction potential with sedimentary facies present at the OTA.

## Progress:

1. Collected Oakes aquifer core samples from 10 boreholes using a drill rig provided by the USBR.
2. Installed two in situ mesocosms (ISMs) in the Oakes aquifer and completed a pair tracer tests in each of them. At the G1 ISM, which was in the finer-grained sediments, the zero order

denitrification rate for the first test was 0.59 mg/L/day and for the second test it was 0.28 mg/L/day. At the C1 ISM, which was in the coarser-grained sediments, the zero order denitrification rate for the first test was 0.061 mg/L/day and for the second test it was 0.033 mg/L/day.

3. Installed an in situ microcosm (ISM) in the gravel envelope next to a tile drain. Any denitrification measured here would be expected to be a result of iron bacteria, and not the gravel, because gravel, having a much smaller relative surface area, is much less reactive than finer sediments. At the C3 ISM site, the zero-order denitrification rate was 0.11 mg/L/day.

4. Completed a nutrient tracer test in the tile drain last June. Results showed that NO<sub>3</sub><sup>-</sup> behaved as conservatively as Br<sup>-</sup>, little to no total phosphate was lost, and NH<sub>4</sub><sup>+</sup> was produced, possibly by cation exchange reactions with the Na<sup>+</sup> added in the amended water (as NaNO<sub>3</sub>, NaBr, and NaH<sub>2</sub>PO<sub>4</sub> · H<sub>2</sub>O) knocking off NH<sub>4</sub><sup>+</sup> on exchanger sites associated with the biomass in the tile drain.

5. Recovered sediment samples from tile drain gravel pack and biomass samples from tile drain.

6. Conducted analyses on aquifer sediments to quantify electron donors (organic carbon, pyrite as S, ferrous iron, and manganese) present in aquifer facies. Analysis of the aquifer sediments showed concentrations of organic carbon (0.22% ± 0.22%), inorganic sulfide (0.078% ± 0.067%), ferrous iron (0.43% ± 0.33%), and manganese (0.50% ± 0.35%).

7. Created a cross-section through the Oakes aquifer showing the various sediment textures (from silt to sand).

## **Discussion:**

Our research shows that the denitrification observed at the Oakes aquifer cannot be explained entirely by nitrate reduction associated with the tile drains. To complete my research, I proposed the following tasks:

1. Correlate, using texture, the denitrification rates from the ISM tracer tests with the sediment facies mapped in the cross section of the Oakes aquifer.
2. Using these denitrification rates and the average water table profile for the cross section and hydraulic conductivity values estimated from the sediment textural data, estimate the amount of nitrate lost in the groundwater via denitrification during transport through the aquifer to the tile drains to determine if aquifer denitrification, rather than denitrification in the tile drains, explains the low nitrate concentrations measured in the tile drain effluent.

# **Regional Flood Frequency Analysis in the Missouri River Basin Based on L-moments and GLS Regression**

**Project Number:** 2009ND192B

**Fellow:** Joseph Vistad

**Adviser:** Yeo Howe Lim

**Start Date:** 3/1/2009

**End Date:** 2/28/2010

## **Progress:**

Peak FQ has been run on all sites within the basin. This has resulted in the calculation of Bulletin 17B frequencies at all sites where available throughout the basin. This data is yet to be compiled in the master database but is available at any time. A MatLab procedure was finalized to allow the individual sites to be analyzed using the LMoments method. This program allows the selection of an individual WATSTORE file. Then the file is opened and converted into useable data by recording the peak flow volumes and excluding the subscripts that often follow. The program will then return all relevant L-Moment data. The program has been run as time allows on the collected data for the Missouri River Basin. The results are being compiled in a master Excel file which contains all relevant data about the collection sites including name, river, location, location description, and some include basin characteristics. For the sites which have been run through the MatLab program, L, b,  $\tau$ , and N data is included. This file will include Bulletin 17B frequency flows as well as all L-Moment data when completed. Stationarity study on possible changes in flow regime within the study area due to climate change was also conducted. A two-tail t-test was completed on all gaging stations in the basin that had adequate data. The results have been compiled in a map form. A few sites showed a statistically significant change in mean flows over time.

## 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:** 3/1/2009

**End Date:** 2/28/2010

**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.

## NATIONAL COMPETITIVE PROGRAM (104-G)

A. One proposal was submitted; but was not funded:

“Polymer Modified Zero-valent Iron Nanoparticles for Arsenic Remediation” by Achintya Bezbaruah and Bret Chisholm

B. One project ended by July 31, 2009.

### **Collaborative Research on In Situ Denitrification and Glyphosate Transformation in Ground Water: NAWQA Eastern Iowa Basins Study Unit**

**Project Number:** 2006ND126G

**Start Date:** 8/1/2006

**End Date:** 7/31/2009

**Funding Source:** 104G

**Principal Investigators:** Scott F Korom, and Paul D. Capel

#### **Publications:**

Maharjan, B., and S. F. Korom. (2009) Correlation of electron donor concentrations in sediments with sediment properties: New Providence, Iowa. Technical Report No. ND09-01, North Dakota Water Resources Research Institute, North Dakota State University.

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

Korom, S. F., and R. J. S. Klapperich, Why are the sediments of some regional aquifers more reactive than others? 21st Annual Environmental and Ground Water Quality Conference, March 18 . 19, 2009, Fort Pierre, South Dakota.

**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  $^{15}\text{N}$  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 were 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). These data were used 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 edonor supply data at the Iowa site that can be compared to previous ISM studies in the Upper Midwest. Two ISM chambers were installed, purged, and amended with nitrate and bromide, which serves as a tracer for nitrate. The tracer test in the deep ISM (“D-ISM”) went from November, 2007, through September, 2009. Two tracer tests were performed in the shallow ISM (“S-ISM”); the first went from November, 2007, through October, 2008; the second went from October, 2008, through November, 2009, and was amended with nitrate, bromide, and glyphosate. 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 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 and continues to be expanded to other aquifers. This information is vital for the development of tools and quantitative methods to characterize the transport and fate of agricultural chemicals in the Eastern Iowa Basins Study Unit, the Upper Midwest, and beyond.

**2. Progress.** The starting date for the grant was August 1, 2006, and the ending date was July 31, 2009; however, the ISMs were sampled through November, 2009. The previous progress report was written in July, 2009. This is the final progress report.

Denitrification measured in D-ISM had a zero-order rate (that is, independent of concentration) of 0.018 mg/L/day ( $R^2 = 0.98$ ) and a first-order rate (concentration-dependent) of 0.00060/day ( $R^2 = 0.95$ ). Denitrification for the first tracer test in S-ISM had a zero-order rate of (0.0070 mg/L/day ( $R^2 = 0.84$ ) and a first-order rate of 0.00015/day ( $R^2 = 0.72$ ). These rates are at the low end of the range for the ISM network we have in Iowa, Minnesota, and North Dakota. Nitrate concentrations in the second tracer test for the S-ISM increased slightly, which indicates that native groundwater diluting the amended water during the test apparently had nitrate in it. Unfortunately, for this reason, the data from the second tracer test for the S-ISM are not helpful. For the tests that showed denitrification, sulfate concentrations did not increase, which indicates that sulfide (as pyrite) did not serve as an electron donor. Therefore, organic carbon and/or ferrous-iron minerals are the likely source of electrons for the reactions. However, at these low denitrification rates, it is not yet known if there is enough of a denitrification “signature” in the water for geochemical modeling to indicate the likely mix of electron donors contributing to the nitrate reduction. Analysis of the core samples showed low concentrations of organic carbon ( $0.13\% \pm 0.31\%$ ,  $\pm 1$  standard deviation used throughout), inorganic sulfide ( $0.033\% \pm 0.046\%$ ), and ferrous iron ( $0.24\% \pm 0.19\%$ ). A subset of 14 samples measured for organic sulfur were all  $< 0.01\%$ , which was the detection limit. With respect to the electron donor concentrations in the sediments, the nonparametric Spearman rank coefficient test showed the following correlations:

- 1) Organic C was positively correlated to silt and clay (both at  $\alpha = 0.01$ ).



- 2) Inorganic S was positively correlated to clay ( $r = 0.05$ ).
- 3) Fe(II) was positively correlated to silt and clay (both at  $r = 0.05$ ).

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

Incorporation of the results of the two ISMs from the Eastern Iowa Basin Study Unit into the databank of other ISM sites in glacial outwash aquifers in the Upper Midwest is ongoing because more ISM sites continue to be added to the denitrification network. The objective is to correlate denitrification rates with amounts of electron donors in aquifer sediments and to correlate the apparent isotopic enrichment factor for  $^{15}\text{N}$  in nitrate versus denitrification rate among of ISM sites. The goal is to develop a nitrate vulnerability index for the Upper Midwest that may be used to extrapolate the findings to similar, unmonitored agricultural and environmental settings.

#### **Students supported and level of support under the project.**

Bijesh Maharjan completed an M.S. in Environmental Engineering in December, 2008. Currently he is a PhD student in Land and Atmospheric Science at the University of Minnesota.

## **Institute Publications**

[Technical Report No. ND09-01 Brijesh Maharjan](#)

[Technical Report No. ND09-02 Yuhui Jin](#)

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

## ***THESES AND DISSERTATIONS***

Hill, C. (2008). A Comparative Study of Immobilized Nitrifying and Co-immobilized Nitrifying and Denitrifying Bacteria for Ammonia Removal from Sludge Digester Supernatant. M.S. Thesis in Environmental Engineering, North Dakota State University, Fargo, ND.

Ratpukdi, T. (2009). Removal of Natural Organic Matter (NOM) by Ozone and Ultraviolet Based Advanced Oxidation Processes: Development of NOM Fractionation Technique, Process Performances, and Bromate Formation. Ph.D. Dissertation in Civil Engineering, North Dakota State University, Fargo, ND.

# CHRISTOPHER HILL'S THESIS

## ABSTRACT

Hill, Christopher Bruce, M.S., Program of Environmental Engineering, College of Engineering and Architecture, North Dakota State University, May 2008. A Comparative Study of Immobilized Nitrifiers and Co-Immobilized Nitrifiers and Denitrifiers for Nitrification of Sludge Digester Supernatant. Major Professor: Dr. Eakalak Khan.

Bench-scale kinetic experiments were conducted to examine the use of cell immobilization in calcium alginate to remove ammonia in anaerobic sludge digester supernatant. Two systems, immobilized nitrifiers and co-immobilized nitrifiers and denitrifiers, were studied with and without the addition of methanol. Results indicated that partial nitrification (to nitrite) was achieved in both systems. The co-immobilized reactors did not exhibit the extent of nitrite accumulation observed in the solely nitrifying reactors. The nitrifying reactors were unable to buffer the hydrogen ion production during the nitrification process to the level the co-immobilized cell reactors achieved. Both of these differences suggested the occurrence of denitrification in the co-immobilized reactors. Scanning electron microscopic images of bacteria immobilized in the alginate spherical beads support the results of the kinetic experiments. Nitrifiers colonized in the 100-200  $\mu\text{m}$  peripheral layer of the beads. Large voids caused by nitrogen gas due to denitrification were found in a number of co-immobilized bead samples. The gas production and heterotrophic nature of the denitrifying bacteria caused a loss in bead integrity.

# THUNYALUX RATPUKDI'S DISSERTATION

## ABSTRACT

Ratpukdi, Thunyalux, Ph.D., Department of Civil Engineering, College of Engineering and Architecture, North Dakota State University, November 2009. Removal of Natural Organic Matter (NOM) by Ozone and Ultraviolet Based Advanced Oxidation Processes: Development of NOM Fractionation Technique, Process Performances, and Bromate Formation. Major Professor: Dr. Eakalak Khan.

Natural organic matter (NOM) is a complex mixture of organic compounds. The presence of NOM in drinking water is a concern because of aesthetic problems and formation of carcinogenic disinfection byproducts upon reacting with chlorine. In this dissertation, the removal of NOM by advanced oxidation processes (AOPs) including ozone-vacuum ultraviolet (VUV), ozone, VUV, ozone-ultraviolet (UV), and UV was investigated. A new NOM fractionation technique was developed in order to elucidate the change of NOM composition under the treatment processes. NOM was separated into six fractions based on polarity (hydrophobic/hydrophilic) and charge (acid/neutral/base). The new technique provided reliable results within 6 hours compared to 24 hours by traditional procedures.

The process performances on NOM removal was evaluated based on the mineralization of dissolved organic carbon (DOC), reduction of UV absorbance at wavelength 254 nm ( $UV_{254}$ ) (unsaturated and aromatic carbon contents), and biodegradability enhancement. The effects of operating parameters including pH and ozone dose were examined. Results showed that DOC mineralization rate was in the following order: ozone-VUV > VUV > ozone-UV > ozone > UV. Ozone-VUV removed up to 71% of DOC while ozone and ozone-UV mineralized only 7% and 28% of DOC, respectively. Approximately, 90%  $UV_{254}$  reduction and 68% increase of biodegradability were achieved by ozone-VUV process. Among three pH studied (7, 9, and 11), pH 7 provided the highest DOC mineralization rate and biodegradability enhancement. A synergistic effect was observed when combining ozone with UV or VUV at pH 7 and 9 but not at pH 11. The results of NOM fractionation showed that ozone-VUV was effective in mineralizing

hydrophobic neutral and acid fractions. Hydrophilic neutral fraction was a major NOM fraction after oxidation (39-87%) and was contributed by biodegradable DOC produced during the oxidation. High performance size exclusion chromatography results revealed that the combination of UV or VUV with ozone was more effective in breaking down high molecular weight compounds than ozone alone.

The effect of AOPs on bromate formation, a common carcinogenic ozonation byproduct, was also investigated. Bromate formation during the ozone-VUV process was up to 4 and 6 times less than ozone and ozone-UV, respectively. This was because VUV irradiation, which was applied simultaneously with ozone, reduced bromate formation. Ozone dosage was found to have the most effect on bromate formation in the ozone-VUV process. Approximately 64% and 213% increases of bromate concentration were observed when the ozone dosage was increased from 1 to 2 and 4 mg O<sub>3</sub>/mg C with VUV power of 120 W at pH 7. Bromate formation also increased as VUV power and pH increased. Results further indicated that it might be difficult to achieve the drinking water standard for bromate and high DOC removal concurrently.