

**Water Resources Center  
Annual Technical Report  
FY 2009**

# Introduction

The Minnesota WRI program is a component of the University of Minnesota's Water Resources Center (WRC). The WRC is a collaborative enterprise involving several colleges across the University, including the College of Food, Agriculture and Natural Resource Sciences (CFANS), the University of Minnesota Extension, Minnesota Agricultural Experiment Station (MAES) and the University of Minnesota Graduate School. The WRC reports to the Dean of CFANS. In addition to its research and outreach programs, the WRC is also home to the Water Resources Sciences graduate major which offers both MS and PhD degrees. The WRC has two co-directors, Professor Deborah Swackhamer and Faye Sleeper, who share the activities and responsibilities of administering its programs.

# Research Program Introduction

The WRC funds 3-4 research projects each year, and the summaries of the current projects are found in the rest of this report.

# Application of Wireless and Sensor Technologies for Urban Water Quality Management

## Basic Information

<b>Title:</b>	Application of Wireless and Sensor Technologies for Urban Water Quality Management
<b>Project Number:</b>	2006MN187G
<b>Start Date:</b>	9/1/2006
<b>End Date:</b>	8/31/2009
<b>Funding Source:</b>	104G
<b>Congressional District:</b>	MN 5
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Nutrients, Surface Water, Non Point Pollution
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	William Alan Arnold, Miki Hondzo, Raymond M Hozalski, Paige J Novak

## Publications

1. Jazdzewski, J. 2007. Stream Water Quality Monitoring using Wireless Embedded Sensor Networks. M.S. Dissertation. Department of Civil Engineering, University of Minnesota – Twin Cities, MN. 44 pp.
2. Henjum, M.B., C. Wennen, M. Hondzo, R.M. Hozalski, P.J. Novak, W.A. Arnold, 2009. Linking Near Real-Time Water Quality Measurements to Fecal Coliforms and Trace Organic Pollutants in Urban Streams, 2009 Joint Assembly (AGU), Toronto, CA.
3. Kang, J.M., S. Shekhar, M. Henjum, P.J. Novak, W.A. Arnold, 2009. Discovering Teleconnected Flow Anomalies: a Relationship Analysis of Dynamic Neighborhoods (RAD) Approach. Lecture Notes in Computer Science, vol. 5644. 11th International Symposium on Spatial and Temporal Databases, Aalborg, Denmark, Springer-Verlag, 44-61. (peer-reviewed)
4. Kang, J.M., S. Shekhar, C. Wennen, P.J. Novak, 2008. Discovering Flow Anomalies: A SWEET Approach. In: IEEE International Conference on Data Mining. 851-856. (peer-reviewed)
5. Arnold, W.A. The WATERS Project: Wireless Sensor Technologies for Urban Water Quality Management, Urban Ecosystems Seminar Series, University of Minnesota, St. Paul, MN, 2009
6. Novak, P.J. Sensor Networks for Urban Water Quality Monitoring. Environmental Sciences: Water Gordon Research Conference, Plymouth, NH, 2009.
7. Wennen, C.R., M.B. Henjum, R.M. Hozalski, P.J. Novak, W.A. Arnold, 2008. Application of Wireless and Sensor Technologies for Urban Water Quality Management: Pollutant Loading in Stormwater Ponds. Minnesota Water Conference, October 27-28, St. Paul, MN.
8. Henjum, M., C. Wennen, M. Hondzo, R.M. Hozalski, P.J. Novak, W.A. Arnold, 2008. Application of Wireless and Sensor Technologies for Urban Water Quality Management: Pollutant Detection in Urban Streams. Minnesota Water Conference, October 27-28, St. Paul, MN.
9. Novak, P., J. Jazdzewski, S. Kim, W.A. Arnold, R. Hozalski, and M. Hondzo, 2007. Wireless Technologies and Embedded Networked Sensing for Urban Water Quality Management. Presentation at the Association of Environmental Engineering and Science Professors Education and Research Conference, Blacksburg, Virginia, July 2007.
10. Hozalski, K., J. Jazdzewski, M. Hondzo, P.J. Novak, W.A. Arnold, 2007. Wireless Technologies and Embedded Networked Sensing: Application to Integrated Urban Water Quality Management, World

## Application of Wireless and Sensor Technologies for Urban Water Quality Management

Environmental and Water Resources Congress, May 15-18, Tampa, FL.

11. Hondzo, M., W.A. Arnold, R.M. Hozalski, P.J. Novak, P.D. Capel, 2006. Wireless Technologies and Embedded Network Sensing: Options for Environmental Field Facilities. Presented at International Research and Education Planning Visit: Cyberinfrastructure based water research: towards the next generation of environmental observatories. August 31-September 1, Delft, The Netherlands and Sept. 2-3, Newcastle upon Tyne, UK.
12. Arnold, W.A., R.M. Hozalski, M. Hondzo, P.J. Novak, P.D. Capel, 2006. Wireless Technologies and Embedded Network Sensing: Options for Environmental Field Facilities.. Presented at CLEANER Planning Grant PI meeting, March, Arlington, VA.
13. Kim, S.C., M. Hondzo, R.M. Hozalski, P.J. Novak, W.A. Arnold, J.D. Jazdzewski, N. Jindal, P.D. Capel, 2006. Integrated urban water quality management: wireless technologies and embedded networked sensing. Poster presented at the American Geophysical Union National Meeting, San Francisco, CA. December.
14. Jazdzewski, J.D., M. Hondzo, W.A. Arnold, 2006. Stream water quality monitoring using wireless embedded sensor networks. Poster presented at the Minnesota Water 2006 and Annual Water Resources Joint Conference, October 24-25, Brooklyn Center, MN.
15. Jeremiah, J. 2007. Stream Water Quality Monitoring Using Wireless embedded Sensor Networks. M. S. project, University of Minnesota, Department of Civil Engineering.
16. Wennen, C.R. 2009. Application of Wireless and Sensor Technologies for Urban Water Quality Management: Pollutant Loading in a Stormwater Pond. M. S. thesis, University of Minnesota, Water Resources Science.
17. Henjum, M.B. 2009. Application of a Near Real-Time Wireless Sensor Network: Pollutant Load Estimation and Surrogate Relationships between Water Quality Parameter and Organic Contaminants. M. S. thesis, University of Minnesota , Department of Civil Engineering.

# **Application of wireless and sensor technologies for urban water quality management**

## **Principal Investigators**

**W.A. Arnold**, Associate Professor and PI, Department of Civil Engineering

**M. Hondzo**, Professor and co-PI, Department of Civil Engineering

**R.M. Hozalski**, Associate Professor and co-PI, Department of Civil Engineering

**P.J. Novak**, Associate Professor and co-PI, Department of Civil Engineering

**Funding Source:** USGS-WRRI 104G National Grants Competition

**Project Duration:** 9/01/2006-8/31/2009

**Report Duration:** 3/01/2009-2/28/2010

## **1) Research**

### **Abstract**

The water quality of streams draining watersheds has been degraded by increasing urbanization. The general symptoms of this degradation include more frequent large flow events, reduction in channel complexity, reduced retention of natural organic matter, and elevated concentrations of nutrients. Newly emerging urban water quality threats, including insecticides, herbicides, pharmaceuticals, and estrogens, are known or suspected to damage the health of humans and ecosystems. The restoration and management of streams have traditionally attempted to improve the hydrological and water quality conditions in-stream or in riparian zones. Recent studies have indicated the portion of a watershed covered by impervious surfaces and connected to the stream by stormwater drainage is the primary degrading process of stream ecology and health. These findings suggest that the sustainable restoration and management of stream water quality require quantification of hydrological, chemical, biological, and geomorphological processes, and that these processes must be assessed across a range of scales. Furthermore, interactions among biogeochemical processes across watersheds are either non-linear processes or linear processes dependent on non-linear drivers. The monitoring of such a system inherently requires a change in traditional field sampling strategies. We propose to transform traditional and very limited (in terms of spatial and temporal resolution) field measurements through the integration of multi-scale, spatially-dense, high frequency, real-time, and event-driven observations by a wireless network with embedded networked sensing.

The goals of the proposed research are to assess the benefits of stormwater best management practices in mitigating the pollutant loads from urban and peri-urban sources, to evaluate the effectiveness of traditional grab sampling in calculating pollutant loads, and to develop correlations to predict the concentrations of non-sensed chemical or biological pollutants. These goals will be achieved by establishing a wireless sensor network capable of monitoring fundamental water quality parameters at high spatial and temporal resolution. It is hypothesized that sensed fundamental water quality parameters can be used for predicting the presence of emerging chemical contaminants in urban streams. It is also hypothesized that the water quality in streams draining similar impervious urban areas is controlled by the mean and variance of effective stormwater residence time. The mean and variance of water residence time, the time it takes urban runoff to travel between the impervious urban land and a receiving aquatic body,

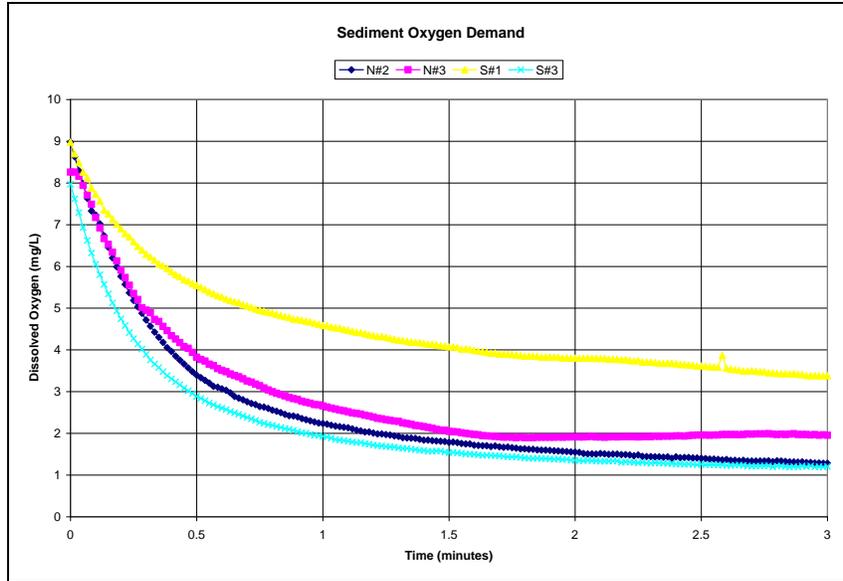
will be characterized by radio frequency identification technology (RFID), which will augment the proposed wireless network. Ultimately, data generated from such a monitoring network will enable mechanistically-based scaling and forecasting of water quality in urban streams and rivers. This will transform urban planning practices and management of water quality in streams draining urban land.

## **Progress**

In the spring through summer of 2008 and 2009, the network was deployed in Shingle Creek to allow continuous monitoring of water quality and BMP performance. An additional six week deployment in Minnehaha creek was done in the fall. The network consists of 5 stations, each equipped with a datalogger and water quality sensors. The sensors measure temperature, depth (used to calculate flow), pH, specific conductance, dissolved oxygen, and turbidity every minute. Nitrate is measured at either 30 minute or 2 hour intervals. All stations are equipped with radios and antennae. One station (the base station) also has a wireless cellular modem, which is used to communicate remotely with the entire network. The data collected is uploaded via the cell phone modem to our server every night. Data is available using the Hydrologic Information System (HIS) at <http://his.saf1.umn.edu/dash3>. Grab samples for the target pesticides and fecal coliforms were also taken during dry periods and during rainfall events.

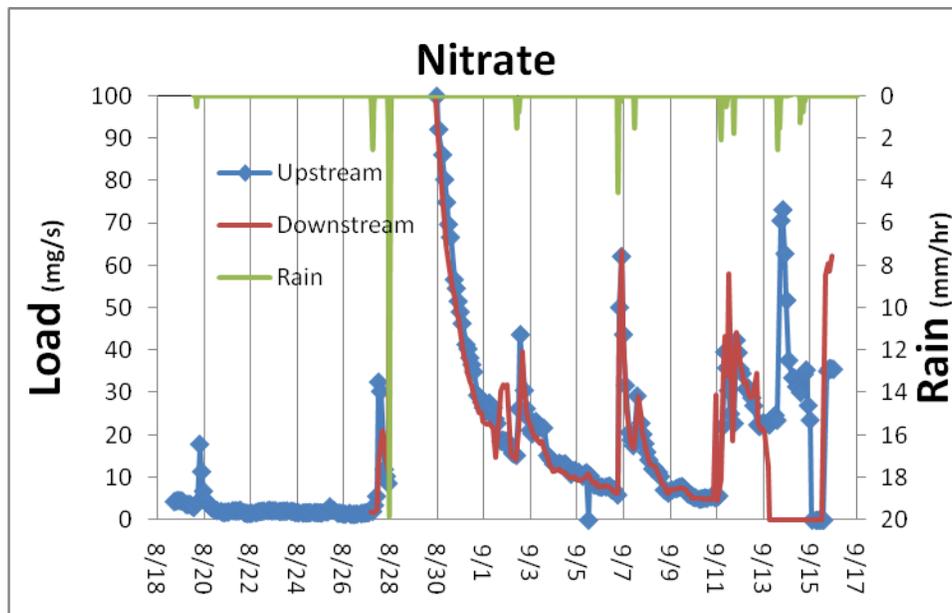
At the Shingle Creek site, we investigated the performance of ponds used as stormwater on the removal of nitrate and total suspended solids (TSS). TSS is effectively removed by the ponds. We have found that the ponds effectively removed nitrate and TSS during rain events but that the ponds may serve as a source of nitrate during dry period. The mechanism of removal appears to be denitrification in the sediments. A comparison of real-time data collection versus limited grab sampling was also made for the rainfall event and the dry period. The percentage removals calculated for limited grab sampling were within 8% of the removal calculated for continuous data collection. The actual mass loading, however, was twice as high for a grab sample collected during peak discharge versus the continuous data. During the dry period, the different sample collection times produced similar removal efficiencies and mass loading.

Sediment cores were taken from the stormwater pond, and sediment oxygen demand tests were performed on the cores. Oxygen-saturated pond water was applied to the sediment core, and dissolved oxygen levels were recorded continuously (every second). The sediment oxygen demand tests showed that the pond sediments consumed most of the oxygen in the overlying water within 1-3 minutes (Figure 1). On average, 67% of the oxygen was depleted within the first minute.



**Figure 1:** Sediment oxygen demand of stormwater pond sediment.

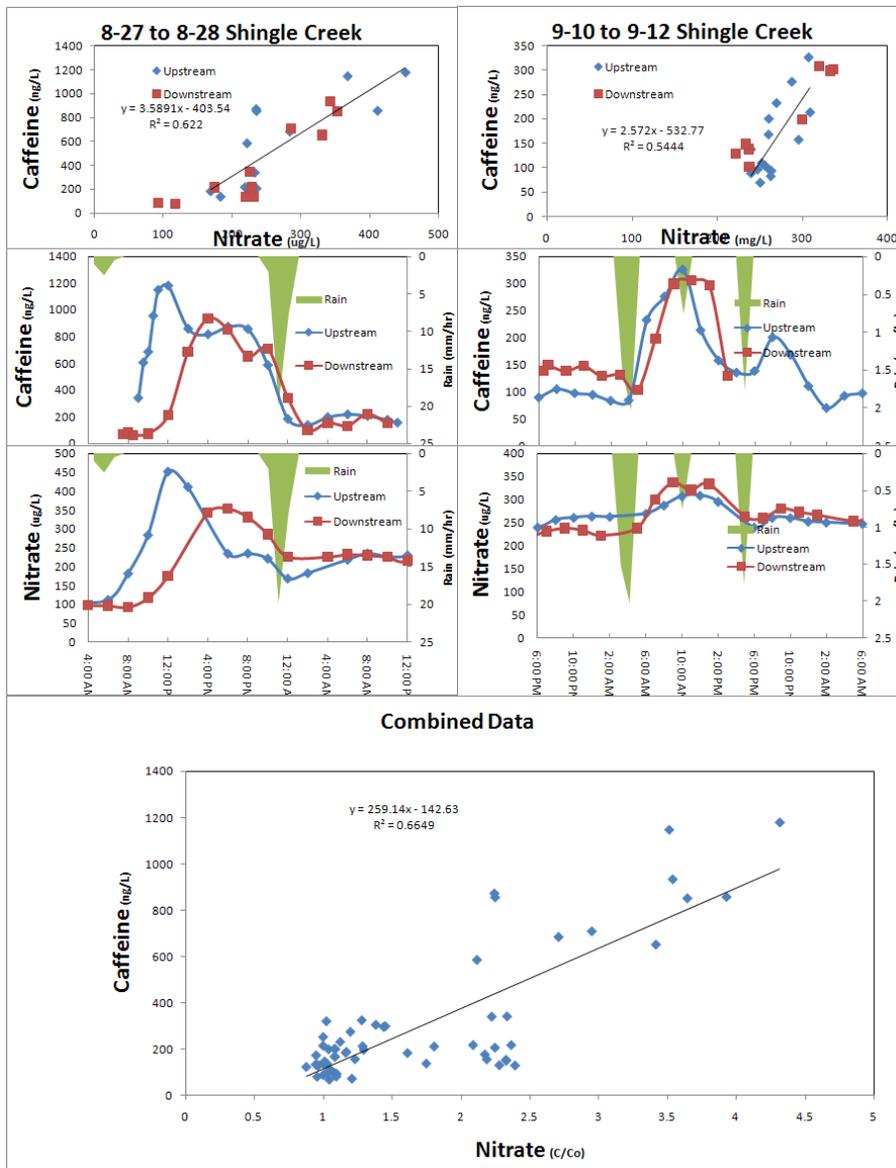
We have also used the continuous sensor data to evaluate the practice of using grab samples to determine total maximum daily loads of pollutants. It was concluded that the most effective way to determine pollutant loading rates is through continuous monitoring. Alternative methods either are too labor intensive (daily sampling) or result in significant (> 50%) error (monthly and bi-weekly sampling) relative to continuous monitoring. As a partial result of urbanization and increased watershed imperviousness, pollutant fluxes within urban streams are highly variable. The majority (>90%) of pollutant loading rate occurs during the minority of the time (<20%). Additionally, over half of the 28-day load was discharged within a 4-day period beginning on August 28<sup>th</sup>. It is therefore probable that discrete sampling will under predict annual fluxes.



**Figure 2:** Nitrate loading results within Shingle Creek in Brooklyn Center, MN. Although, the range of load data fluctuated as high as 800-mg/s the displayed axis was limited to 100-mg/s.

Upstream and downstream stations are relative to a stormwater input discharged from a series of retention ponds.

It was hypothesized that consistent relationships exist between easy-to-measure fundamental water quality parameters and difficult-to-measure organic and bacterial pollutants within urban streams. This was tested by collecting and analyzing grab samples for four-target analytes (atrazine, prometon, caffeine, and fecal coliforms) concurrently with seven-high frequency, near-real-time sensed water quality parameters. Within Shingle Creek, surrogate relationships were developed between nitrate and caffeine (C.D.= 0.68), turbidity and prometon (C.D.=0.91), and discharge and prometon (C.D.=0.92) and at the Minnehaha Creek location a relationship between caffeine and specific conductivity (C.D.=0.64) was developed. In turn, observations of bacterial and organic pollutants concentrations in near real-time can forecast potential human or ecological health hazards, give suppliers and municipalities timely information to adjust water treatment strategies, and can enhance pollutant loading calculations.



We have also had productive meetings with local watershed district and USGS personnel which have been helpful in interpreting data and planning future deployments.

## 2) Publications

1. Henjum, M.B.; Hozalski, R.M.; Wennen, C.R.; Arnold, W.A.; Novak, P.J. 2010. Correlations between in situ sensor measurements and trace organic pollutants in urban streams. *J. Environ. Monit.*, 12, 225-233.
2. Henjum, M.B.; Hozalski, R.M.; Wennen, C.R.; Novak, P.J.; Arnold, W.A. 2010. A Comparison of Total Maximum Daily Load (TMDL) Calculations In Urban Streams Using Near Real-Time and Periodic Sampling Data. *J. Environ. Monit.*, 12, 234-241.
3. Jeremiah, J. M.S. Project, University of Minnesota, Department of Civil Engineering. Stream Water Quality Monitoring using Wireless Embedded Sensor Networks. 2007.
4. Christine Wennen M.S. Thesis *Application of Wireless and Sensor Technologies for Urban Water Quality Management: Pollutant Loading in a Stormwater Pond*, 2009.
5. Michael Henjum. M.S. Thesis. *Application of a Near Real-Time Wireless Sensor Network: Pollutant Load Estimation and Surrogate Relationships between Water Quality Parameters and Organic Contaminants*, 2009.

## 3) Student Support

Jeremiah Jazdzewski, M.S. Civil Engineering, awarded 2007.  
Christine Wennen, M.S. Water Resources Science, awarded June 2009.  
Michael Henjum, M.S. Civil Engineering, awarded June 2009.  
Kevin Erickson, M.S. Civil Engineering, anticipated Fall 2010.

## 4) Presentations

Henjum, M.B., Wennen, C.R., Hondzo, M., Hozalski, R.M., Novak, P.J., Arnold, W.A. Linking Near Real-Time Water Quality Measurements to Fecal Coliforms and Trace Organic Pollutants in Urban Streams, *2009 Joint Assembly (AGU)*, Toronto, CA, 2009.

Kang, J.M., S. Shekhar, M. Henjum, P. Novak, W.A. Arnold, 2009. Discovering teleconnected flow anomalies: a relationship analysis of dynamic neighborhoods (RAD) approach. Lecture Notes in Computer Science, vol. 5644. 11th International Symposium on Spatial and Temporal Databases, Aalborg, Denmark, Springer-Verlag, 44-61. (**peer-reviewed**)

Kang, J.M., S. Shekhar, Wennen, C., Novak, P.: Discovering Flow Anomalies: A SWEET Approach. In: IEEE International Conference on Data Mining. (2008) 851–856. (**peer-reviewed**)

Arnold, W.A. *The WATERS Project: Wireless Sensor Technologies for Urban Water Quality Management*, Urban Ecosystems Seminar Series, University of Minnesota, St. Paul, MN, 2009

Novak, P.J. Sensor Networks for Urban Water Quality Monitoring. *Environmental Sciences: Water Gordon Research Conference*, Plymouth, NH, 2009.

Wennen, C.R., Henjum, M.B, Hozalski, R.M., Novak, P.J., Arnold, W.A. Application of Wireless and Sensor Technologies for Urban Water Quality Management: Pollutant Loading in Stormwater Ponds. *Minnesota Water Conference*, 2008, St. Paul, MN.

Henjum, M., Wennen, C., Hondzo, M., Hozalski, R.M., Novak, P.J., Arnold, W.A.. Application of Wireless and Sensor Technologies for Urban Water Quality Management: Pollutant Detection in Urban Streams. *Minnesota Water Conference*, 2008, St. Paul, MN.

Novak, P., J. Jazdzewski, S. Kim, W. Arnold, R. Hozalski, and M. Hondzo (2007). Wireless Technologies and Embedded Networked Sensing for Urban Water Quality Management. Presentation at the Association of Environmental Engineering and Science Professors Education and Research Conference, Blacksburg, Virginia, July 2007.

Hozalski, Kim, Jazdzewski, Hondzo, Novak, and Arnold. (2007). 'Wireless Technologies and Embedded Networked Sensing: Application to Integrated Urban Water Quality Management', World Environmental and Water Resources Congress 2007, May 15-18, Tampa, FL.

Hondzo, M., Arnold, W.A.,Hozalski, R.M., Novak, P.J., Capel, P.D., 2006. Wireless Technologies and Embedded Network Sensing: Options for Environmental Field Facilities. Presented at International Research and Education Planning Visit: Cyberinfrastructure based water research: towards the next generation of environmental observatories. August 31-Sept 1 Delft, The Netherlands and Sept. 2-3, Newcastle upon Tyne (UK), 2006.

Arnold, W.A.,Hozalski, R.M., Hondzo, M., Novak, P.J., Capel, P.D., 2006. Wireless Technologies and Embedded Network Sensing: Options for Environmental Field Facilities.. Presented at CLEANER Planning Grant PI meeting, March 2006, Arlington, VA

Kim, S.-C.; Hondzo, M.; Hozalski, R.M.; Novak, P.; Arnold, W.; Jazdzewski, J.D.; Jindal, N.; Capel, P.D., 2006. Integrated urban water quality management: wireless technologies and embedded networked sensing. Poster presented at the American Geophysical Union National Meeting, San Francisco, CA. December 2006.

Jazdzewski, J.D.; Hondzo M.; Arnold, W.A., 2006. Stream water quality monitoring using wireless embedded sensor networks. Poster presented at the Minnesota Water 2006 and Annual Water Resources Joint Conference, Brooklyn Center, MN, October 24-25, 2006.

## **5) Awards**

None to date.

## **6) Additional Funding**

The project led to funding of the following project:

*Evaluating and monitoring BMPs with networked wireless sensors*

Mississippi Watershed Management Organization and Minnehaha Creek Watershed District

PI: W.A. Arnold, co-PIs: R.M. Hozalski, P.J. Novak

\$167,460

January 2009-December 2011

# Triclosan and Triclosan-derived Dioxins in the Mississippi River Sediment Record

## Basic Information

<b>Title:</b>	Triclosan and Triclosan-derived Dioxins in the Mississippi River Sediment Record
<b>Project Number:</b>	2007MN203B
<b>Start Date:</b>	3/1/2007
<b>End Date:</b>	2/28/2010
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	MN 05
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Toxic Substances, Sediments, Acid Deposition
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Kristopher McNeill, William Alan Arnold

## Publications

1. Arnold, W.A., K. McNeill. 2007. Transformation of Pharmaceuticals in the Environment: Photolysis and Other Processes. M. Petrovic and D. Barcelo (eds). A Analysis, Fate and Removal of Pharmaceuticals in the Water Cycle. Elsevier Science, Amsterdam, The Netherlands. pp. 361 383.
2. Steen, P.O., M. Grandbois, K. McNeill, W.A. Arnold. 2009. Photochemical Formation of Halogenated Dioxins from Hydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) and Chlorinated Derivatives (OH-PBCDEs), Environmental Science and Technology.43,4405-4411.
3. Buth, J.M., M. Grandbois, P.J. Vikesland, K. McNeill, W.A. Arnold. 2009. Aquatic Photochemistry of Chlorinated Triclosan Derivatives: Potential Source of Polychlorodibenzo-p-dioxins. Environmental Toxicology and Chemistry., 28 (12), 2555-2563.
4. Arnold, W. A., K McNeill, 2007. Abiotic Degradation of Pharmaceuticals: Photolysis and Other Processes, to appear in Analysis, Fate and Removal of Pharmaceuticals in the Water Cycle, Eds. M. Petrovic and D. Barcelo, 2007.
5. Buth, J.M., W.A Arnold, K. McNeill, 2008. Photochemical Fate of Chlorinated Triclosan Derivatives. Poster. Gordon Research Conference, Environmental Sciences: Water, June 22-27, Holderness, NH.
6. Steen, P.O., M. Grandbois, W.A. Arnold, K. McNeill, 2008. Hydroxylated polybrominated diphenyl ether photolysis quantum yields and product identification. Environ. Chem. Div., American Chemical Society National Meeting, Philadelphia, PA, 48(2), 608-611.
7. Steen, P.O., M. Grandbois, W.A. Arnold, K. McNeill, 2008. Hydroxylated Polybrominated Diphenyl Ether Photolysis: Quantum Yields and Product Identification. Minnesota Water Conference, October 27-28, St. Paul, MN.
8. Steen, P.O., M. Grandbois, K. McNeill, W.A. Arnold, 2009. Photolysis of Hydroxylated Polybrominated Diphenyl Ethers. Micropol & Ecohazard 2009. 6th IWA/GRA Specialized Conference on Assessment and Control of Micropollutants/Hazardous Substances in Water, June 8-10, San Francisco, CA.
9. Buth, J.M., W.A. Arnold, K. McNeill, 2009. Formation and Occurrence of Chlorinated Triclosan Derivatives (CTDs) and their Dioxin Photoproducts. Micropol & Ecohazard 2009. 6th IWA/GRA Specialized Conference on Assessment and Control of Micropollutants/Hazardous Substances in Water, June 8-10, San Francisco, CA.

## **Triclosan and triclosan-derived dioxins in the Mississippi River sediment record**

### **Principal Investigators**

**Kristopher McNeill**, Associate Professor, Department of Chemistry, University of Minnesota;  
**William A. Arnold**, Associate Professor, Department of Civil Engineering, University of Minnesota

### **Collaborators**

**Dr. Daniel R. Engstrom**, Director, St. Croix Watershed Research Station; **Peter J. Vikesland**, Associate Professor, Virginia Tech, Dept. of Civil and Environmental Engineering; **Charles V. Sueper**, Technical Director, Pace Analytical Services, Inc.

**Funding Source: USGS-WRRI 104B/ CAIWQ Competitive Grants Program**

**Project Duration: 3/1/07 - 2/29/10**

### **Summary**

This project is focused on establishing whether triclosan has been and continues to be a source of dioxins to the aquatic environment. It is hypothesized that triclosan, a widely used antimicrobial found in consumer products, is transformed into toxic dioxin compounds through chlorination of triclosan-containing wastewater and sunlight exposure in rivers that receive chlorinated wastewater. It is further hypothesized that triclosan and its products will associate with the sediment downstream of point of discharge and their release to the environment thus will be recorded in the sediment record. To determine the historical inputs of triclosan and its products in to the Upper Mississippi river from Minnesota's largest wastewater treatment plant, the Metro Plant, in St. Paul, sediment cores from Lake Pepin will be analyzed. It is expected that triclosan and its products will not be found in pre-1960 sediment, it will be at low levels between 1960 and 1990 when its use was limited, and will be at the highest levels after 1990 following its widespread use in liquid handsoap and toothpaste. The results of this study will further our understanding of micropollutants in wastewater and will provide specific information about the appropriateness of chlorination disinfection for triclosan-containing waters.

### **Research**

#### **Methods**

##### *Triclosan analytical method development*

A liquid chromatography (LC) method with triple quadrupole mass spectrometry (MS-Q<sup>3</sup>) detection was developed to determine triclosan and its chlorinated derivatives in extracts of sediment and wastewater samples. An 1100 Series Agilent capillary HPLC coupled with a Finnigan TSQ Quantum Discovery MAX triple quadrupole mass spectrometer was used for this analysis. Electrospray ionization (ESI) was carried out in negative mode. Wastewater samples were collected in pre-washed glass bottles, filtered through 0.2 µm filters to remove particulate matter, adjusted to pH 2 for preservation, and stored at 4 °C in the dark until analysis. 250 mL wastewater samples were solid-phase extracted using Oasis HLB cartridges followed by a washing step with 50:50 water:methanol to remove interfering dissolved organic

matter (DOM). The cartridges were eluted with methanol/methyl-*t*-butyl ether. The extracts were concentrated under nitrogen to a minimal volume (~ 100  $\mu$ L) and analyzed by LC/MS.

#### *Synthesis of chlorinated derivatives of triclosan*

The synthetic approach was inspired by the route taken by Marsh et al. (1) Starting with either commercially available or readily synthesized chlorinated phenols, *ortho*-directed formylation followed by phase-transfer catalyzed methylation of the aromatic hydroxyl group yielded 2-methoxy-chlorinated benzaldehydes. Baeyer-Villiger oxidation of the resulting aldehydes yielded the respective phenols. The chlorinated triclosan precursors underwent basic coupling with 2,2',4,4'-tetrachlorodiphenyliodonium iodide to form the diphenylether backbone, which was then deprotected to yield the target triclosan derivatives. The synthetic scheme for the chlorinated triclosans is shown in Figure 1.

### **Results to date**

#### *Triclosan analytical method development*

A liquid chromatographic method has been developed to effectively separate the triclosan and its chlorinated derivatives, including two mono-chlorinated isomers. The injection volume and mass spectrometer parameters have been optimized to maximize sensitivity while maintaining satisfactory chromatographic resolution. A method detection limit on the order of 1 ng/L has been realized. The recovery of the solid-phase extraction pre-concentration step was maximized by optimizing the cartridge type, sample pH, washing step, and elution volume. The Oasis HLB cartridge was found to provide the greatest recovery. The amount of interfering dissolved organic matter (DOM) was reduced by increasing the pH of the sample. However, to keep the analytes fully protonated to aid in their extraction efficiency, a pH of 4 was chosen to extract the samples. Washing the cartridge with 3-5 mL aliquots of 50:50 methanol:water solution prior to elution was found reduce the amount of interfering DOM in the extract by approximately an order of magnitude. Elution with sequential 5 mL aliquots of methanol and 90:10 methyl-*t*-butyl ether:methanol provided maximum recovery. Greater than 75% recovery was obtained for every analyte. Wastewater samples have been collected quarterly from the Metropolitan Plant in St. Paul, MN for 1.5 years both prior to chlorination and after the chlorination step to determine the extent of formation of chlorinated triclosan derivatives during chlorine disinfection.

#### *Synthesis of chlorinated derivatives of triclosan and HO-BDE-47*

The synthesis of 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol was completed in 5 steps to yield 1.670 g as a white solid. The overall synthetic yield for this derivative was 26%. The synthesis of 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol did not follow the general scheme presented above, due to difficulty purifying several intermediates. An alternative approach utilizing regioselective chlorination of guaiacol followed by basic coupling/deprotection mentioned above yielded 1.051 g as a white solid over 3 steps. The overall synthetic yield for this derivative was 18%. The synthesis of 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol required an additional synthetic step not mentioned in the above scheme. 2,3,4-Trichloroaniline was diazotized and then subjected to water to synthesize the corresponding phenol. This was then subjected to the above-mentioned synthetic scheme to yield 0.107 g as a white solid over 6 steps. The overall synthetic yield for this derivative was 5%.

All synthesized compounds have been characterized and found to match by nuclear magnetic resonance ( $^1\text{H}$  and  $^{13}\text{C}$ ), mass spectrometry, and melting point when literature values have already been reported.

#### *Sediment coring and analysis*

Sediment cores were collected in June 2008. The cores were dated via magnetic profiling and then sectioned. The sections were extracted and have been analyzed using via isotope dilution LC/MS/MS to determine triclosan concentrations as a function of depth. Similar analyses were conducted for polychlorinated dibenzo-p-dioxins and furans. Results have been submitted for publication.

#### **Reference:**

(1) Marsh, G.; Stenutz, R.; Bergman, A. Synthesis of hydroxylated and methoxylated polybrominated diphenyl ethers - natural products and potential polybrominated diphenyl ether metabolites. *European Journal of Organic Chemistry* **2003**, 2566-2576.

#### **List of publications & presentations resulting from this project**

##### Peer Reviewed Publications

1. Steen, P.O.; Grandbois, M., McNeill, K.; Arnold, W.A. 2009. Photochemical formation of halogenated dioxins from hydroxylated polybrominated diphenyl ethers (OH-PBDEs) and chlorinated derivatives (OH-PBCDEs). *Environ. Sci. Technol.* 43, 4405-4411.
2. Buth, J.M., Grandbois, M., Vikesland, P.J., McNeill, K., Arnold, W.A. 2009. Aquatic photochemistry of chlorinated triclosan derivatives: potential source of polychlorodibenzo-p-dioxins. *Environ. Toxicol. Chem.*, 28(12), 2555-2563.
3. J.M. Buth, P.O. Steen, C. Sueper, D. Blumentritt, P.J. Vikesland, W.A. Arnold and K. McNeill, 2010. Dioxin Photoproducts of Triclosan and Its Chlorinated Derivatives in Sediment Cores, *Environ. Sci. Technol.* 44, ASAP.

##### Book Chapters

Arnold, W.A., McNeill, K. "Abiotic Degradation of Pharmaceuticals: Photolysis and Other Processes" to appear in *Analysis, Fate And Removal Of Pharmaceuticals In The Water Cycle* Eds. M. Petrovic and D. Barcelo, 2007.

##### Invited Presentations

1. Arnold, W.A., 2007. Solar photochemistry of pharmaceutical compounds. American Water Works Association Water Quality Technology Conference, Advanced Oxidation Technologies in Water Treatment: Fundamentals and Applications Workshop, November 4, 2007.

2. Arnold, W.A., 2008. *Pharmaceutical Photolysis and imPacts: Tetracycline and Triclosan* ETH-Zurich, Institute of Biogeochemistry and Pollutant Dynamics, Zurich, Switzerland.
3. McNeill, K., 2009. Incineration or liquid handsoap: Which is the larger source of dioxins to the aquatic environment? College of St. Catherine, St. Paul, MN.
4. McNeill, K., 2009. Incineration or liquid handsoap: Which is the larger source of dioxins to the aquatic environment? Gustavus Adolphus College, St. Peter, MN.
5. Arnold, W.A. 2009. Photolysis and Fate of Triclosan (or How your handsoap is destroying the planet), Syracuse University, Syracuse, NY.
6. Arnold, W.A. 2009. Photolysis and Fate of Triclosan (or How your handsoap is destroying the planet), Yale University, New Haven, CT.
7. Arnold, W.A. 2009. Photolysis and Fate of Triclosan (or How your handsoap is destroying the planet), Shanghai Jiaotong University, Shanghai, China.

#### Conference Presentations

1. Buth, J.M., Arnold, W.A., McNeill, K., 2008. Photochemical Fate of Chlorinated Triclosan Derivatives. *Poster*. Gordon Research Conference, Environmental Sciences: Water, Holderness, NH.
2. Steen, P.O., M. Grandbois, W.A. Arnold, K. McNeill, 2008. Hydroxylated polybrominated diphenyl ether photolysis quantum yields and product identification. *Environ. Chem. Div., ACS National Meeting*, Philadelphia, PA, 48(2), 608-611.
3. Steen, P.O., Grandbois, M., Arnold, W.A., McNeill, K., 2008. Hydroxylated Polybrominated Diphenyl Ether Photolysis: Quantum Yields and Product Identification. *Minnesota Water Conference*, St. Paul, MN.
4. Steen, P.O., Grandbois, M., McNeill, K., Arnold, W.A., 2009. Photolysis of Hydroxylated Polybrominated Diphenyl Ethers. *Micropol & Ecohazard 2009. 6<sup>th</sup> IWA/GRA Specialized Conference on Assessment and Control of Micropollutants/Hazardous Substances in Water*, San Francisco, CA.
5. Buth, J.M., Arnold, W.A., K. McNeill, 2009. Formation and Occurrence of Chlorinated Triclosan Derivatives (CTDs) and their Dioxin Photoproducts. *Micropol & Ecohazard 2009. 6<sup>th</sup> IWA/GRA Specialized Conference on Assessment and Control of Micropollutants/Hazardous Substances in Water*, San Francisco, CA.

#### **Statement of related grants submitted or funded as a result of this project**

This project is complemented by a project from the National Science Foundation (2006-2009) to study the photolysis of triclosan and polybrominated diphenyl ethers in both the laboratory and in the field.

In 2010, Arnold (with McNeill as a partner) received a three year National Science Foundation award (\$370,000) to continue work on triclosan and hydroxylated polybrominated diphenyl ethers “*Using triclosan and polyhalogenated dibenzo-p-dioxins to elucidate the importance of natural and anthropogenic sources of OH-PBDEs in fresh and estuarine waters*”

### Description of student training provided by project:

#### Graduate Students

Name: Jeffrey M. Buth

Program: Department of Chemistry, University of Minnesota

Degree earned: Ph.D. (2009)

Name: Peter O. Steen

Program: Civil Engineering, University of Minnesota

Degree earned: M.S. (2009)

Name: Matthew L. Grandbois

Program: Department of Chemistry, University of Minnesota

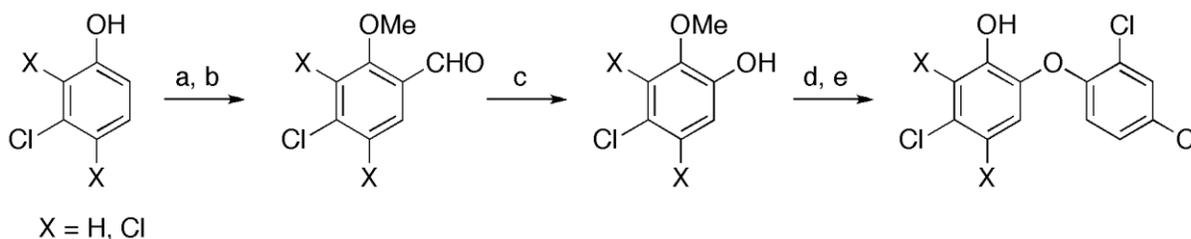
Degree earned: Ph.D. (2010)

#### Awards

Jeff Buth, EPA STAR Fellowship

Jeff Buth, 2008 ACS Graduate Student Award in Environmental Chemistry

#### Figures



**Figure 1. Synthesis of Chlorinated Triclosan Derivatives.** Reaction conditions: a)  $\text{MgCl}_2$ , paraformaldehyde, TEA,  $\text{CH}_3\text{CN}$ ; b)  $(\text{C}_4\text{H}_9)_4\text{NOH}$ , NaOH, MeI,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$ ; c) 1.  $\text{H}_2\text{O}_2$ ,  $(\text{CF}_3\text{CO})_2\text{O}$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{CH}_2\text{Cl}_2$ , 2. MeOH, HCl; d)  $\text{K}_2\text{CO}_3$ , 18-crown-6, 2,2',4,4'-tetrachlorodiphenyliodonium iodide, DMAC; e)  $\text{BBr}_3$ ,  $\text{CH}_2\text{Cl}_2$ .

# The Role of Local Stakeholders in Water Resource Management: Characterization and Diffusion of Minnesota Lake Improvement Districts

## Basic Information

<b>Title:</b>	The Role of Local Stakeholders in Water Resource Management: Characterization and Diffusion of Minnesota Lake Improvement Districts
<b>Project Number:</b>	2007MN204B
<b>Start Date:</b>	3/1/2007
<b>End Date:</b>	2/28/2010
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	4
<b>Research Category:</b>	Social Sciences
<b>Focus Category:</b>	Law, Institutions, and Policy, Water Quality, Management and Planning
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Dennis R. R Becker

## Publications

1. Steiger-Meister, K. 2009. The Drama of the Commons and Its Impact on Adaptive Management. American Water Resource Association Specialty Conference: Adaptive Management of Water Resources II, Snowbird, UT. In review
2. Steiger-Meister, K., D. R. Becker. 2009. Connecting Environmental Policy with Citizen Engagement: A Comparative Study Between Minnesota's Lake Improvement Districts and Wisconsin's Lake Districts. Manuscript in preparation for Journal of the American Water Resources Association.
3. Steiger-Meister, K., D. R. Becker. 2009. Citizen Stewardship of Water Resources: A Look at How Water Policy can Create and Coordinate Citizen Action in Minnesota for Environmental Change. Manuscript in preparation for Water Policy.

## **The Annual Program Report 2010**

The role of local stakeholders in water resource management: Characterization and diffusion of Minnesota Lake Improvement Districts

**Principal Investigator:** Dr. Dennis Becker

**Research Assistant:** Kaitlin Steiger-Meister

**Funding Source:** USGS-WRRI 104B Competitive Grants Program

**Project Duration:** 3/1/2007 – 2/28/2010

### **Research:**

According to the Minnesota Pollution Control Agency, as of 2006 there were 1,013 lakes listed as impaired waters, up from 920 in 2004. A large number are impacted by human development, recreation, and pollution leading to unsafe conditions for swimming or fishing, excessive algal blooms, and high levels of mercury transferred throughout the food chain. Despite progress since passage of the Clean Water Act of 1972, more MN lakes are contaminated than at any time in history. Because they are an integral part of community economies and lifestyle of Minnesota's citizens, alternative methods of management solutions are required that capitalize on existing planning efforts and initiatives. The development of policy tools to enable and facilitate management actions at the local level is paramount. The research seeks to assess the effectiveness of existing MN programs that empower citizens to affect water quality solutions in the places they live. In particular, the research will assess use and diffusion of Lake Improvement Districts (LIDs), where local units of government organized to enhance water quality by securing grants and taxing landowners to support mitigation activities within a lake district. Diffusion of the LID program has been slow in MN. Currently, 32 have been created since 1976, compared to more than 200 in Wisconsin.

In order to characterize existing LIDs including funds secured, staff resources, partnerships formed, and accomplishments relative to state priorities, all LIDs in the state were contacted in the summer of 2007. This resulted in in-depth semi-structured interviews with representatives from 14 of the 24 LIDs in the state that existed at the time of research. These interviews were coded to identify barriers to the diffusion of the LID program and then codes were compared across interviews to identify overarching themes. Researchers also met with the LID coordinator from Minnesota's Department of Natural Resources to learn about the agency's role in the program and collect education and outreach materials focused on LIDs. The project's research assistant also attended the annual meetings of three LIDs and through participant observation studied how the public meetings operated. In the fall of 2007 follow-up letters were sent to all the stakeholders involved in the research thanking them for their involvement.

In conjunction with the larger research project, the research assistant received additional competitive funding to carry out a comparative study between Minnesota's LIDs and Wisconsin's Lake Districts (LD) in the summer of 2008. She examined the institutional arrangement surrounding LDs, specifically the Wisconsin Lakes Partnership (WLP), to better

understand their impact on Wisconsin's adoption and diffusion rates of the LD statute. Through targeted in-depth semi-structured interviews with members of the WLP, including representatives from the University of Wisconsin Extensions in Stevens Point, Wisconsin Association of Lakes, and the Wisconsin Department of Natural Resources, the RA identified key institutional differences that are potentially contributing to the two states' differing implementation rates. This research was complemented with a side-by-side comparison of the LID statute and the LD statute to identify major internal policy characteristics that could potentially contribute to implementation rates.

**Research concluded in the summer of 2009** with the release of the project's funders report available at: <http://www.forestry.umn.edu/publications/staffpapers/index.html>

### **Publications:**

Steiger-Meister, K. and Becker, D.R. 2009. The Role of Local Stakeholders in Water Resource Management: Characterization and Diffusion of Minnesota Lake Improvement Districts. University of Minnesota, Department of Forest Resources Staff Paper 202.

Steiger-Meister, K. The drama of the commons and its impact on adaptive management, conference proceeding paper, American Water Resource Association Specialty Conference: Adaptive Management of Water Resources II, Snowbird, UT. (6/09)

### *In Preparation*

Steiger-Meister, K.; Becker, D.R. Connecting Citizens with Water Policy: An Examination of Minnesota's Lake Improvement Districts from the Citizen Perspective. Manuscript in preparation for *National Civic Review*.

Steiger-Meister, K.; Becker, D.R. Exploring the Temporal Dimension of Institutions: A Critique of Minnesota's Lake Improvement District Statute's Diffusion and Implementation. Manuscript in preparation for *Policy Studies Journal*.

### **Student Support:**

These funds supported one full-time Natural Resource Science and Management Ph.D. candidate, Kaitlin Steiger-Meister, in the Department of Forest Resources at the University of Minnesota. The following sections, Presentations, Invited Talks, and Awards catalog Steiger-Meister's activities during the two year funding period. She is on track to graduate in the summer of 2010, with a May 10 final defense date.

### **Additional Funds:**

See "Awards" section.

### **Presentations:**

**Connecting Environmental Policy with Citizen Engagement: A Comparative Study Between Minnesota's Lake Improvement Districts and Wisconsin's Lake Districts**, Minnesota Water Resources Conference, University of Minnesota in Saint Paul, MN. (10/09)

**The Drama of the Commons and its Impact on Adaptive Management: A social science perspective on the slippery nature of water policy**, American Water Resource Association Specialty Conference: Adaptive Management of Water Resources II, Snowbird, UT. (6/09)

**Minnesota's Lake Improvement Districts**, presenter and panelist, Lakes and Rivers Conference hosted by Minnesota Waters, Rochester, MN. (5/09)

**When ripples become waves: building synergy among local stakeholders to affect top-down water policy**, International Symposium on Society and Resource Management, Community Involvement in Resource Planning session, University of Vermont in Burlington, VT. (6/08)

#### **Invited Talks:**

*Minnesota's Lake Improvement District: The Citizen Perspective*. Presenter at Otter Tail's Coalition of Lake Associations meeting, Otter Tail, MN. September 26, 2009

*LID Workshop*. Main speaker for a workshop on Lake Improvement Districts hosted by Minnesota Waters, Ideal Township Hall, Pequot Lakes, MN. September 24, 2009

#### **Awards:**

**Graduate School Block Grant Fellowship**, Natural Resources Science and Management Graduate Program, Department of Forest Resources, University of Minnesota (9/09-12/09)

**Graduate School Block Grant Fellowship**, Natural Resources Science and Management Graduate Program, Department of Forest Resources, University of Minnesota (5/09)

**Consortium Student Scholar Competitive Grant Recipient**, Consortium on Law and Values in Health, Environment, and the Life Sciences, University of Minnesota (5/08)

Upon recommendations from the reviewers of the original Water Resources Research grant to expand the project to include a comparative study of Minnesota's Lake Improvement Districts with Wisconsin's Lake Districts, Steiger-Meister successfully pursued additional funding through competitive internal grant competitions. She is one of the 2008 recipients of the University's Consortium on Law and Values in Health, Environment & the Life Sciences small grants. As a Consortium Student Scholar she received \$5,654 for her project, "Building Clean Water Communities: Understanding How Environmental Policies Can Promote and Coordinate Community Participation in the Long-Term Management of Local Freshwater Resources." This grant was used to fund research occurring in the summer of 2008 that examined Wisconsin Lake Districts and the Wisconsin Lakes Partnership. Additionally, Steiger-Meister was a recipient of the 2008 International Symposium on Society and Resource Management Registration

Scholarship, where she subsequently presented her research. To complete here analysis and write-up of research findings, Steiger-Meister was selected for two Graduate School Block Grant Fellowships for \$1,000 and \$5,000, respectively.

# The Cultivation, Characterization, and Detection of Bacteria that Biodegrade Haloacetic Acids in Drinking Water Distribution Systems

## Basic Information

<b>Title:</b>	The Cultivation, Characterization, and Detection of Bacteria that Biodegrade Haloacetic Acids in Drinking Water Distribution Systems
<b>Project Number:</b>	2008MN233B
<b>Start Date:</b>	3/1/2008
<b>End Date:</b>	2/28/2010
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	5
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Supply, Water Use, Toxic Substances
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Raymond M Hozalski, Timothy Michael LaPara

## Publications

There are no publications.

# **The Cultivation, Characterization, and Detection of Bacteria that Biodegrade Haloacetic Acids in Drinking Water Distribution Systems**

## **Principal Investigators**

Raymond M. Hozalski, Associate Professor, Department of Civil Engineering, University of Minnesota

Timothy M. LaPara, Associate Professor, Department of Civil Engineering, University of Minnesota

## **Research Assistant**

Alina S. Grigorescu, Department of Civil Engineering, University of Minnesota

## **ABSTRACT**

Drinking water distribution systems contain low levels of bacteria that can survive in an environment with very low nutrient concentrations and with a disinfectant residual. These bacteria can catalyze many reactions that impact drinking water quality. In the work discussed here, the diversity of haloacetic acid (HAA)-degrading bacteria and the corresponding metabolic genes were analyzed in drinking water distribution systems and other environmental systems, such as surface waters and soil. The research objectives related to this study were: (1) to isolate and characterize bacteria that can biodegrade haloacetic acids from numerous sources to expand our knowledge of the diversity of HAA-degrading bacteria and (2) to directly characterize the bacterial communities that biodegrade haloacetic acids in drinking water distributions by developing a novel use of terminal restriction fragment length polymorphism (tRFLP) targeting type I and type II dehalogenase genes (i.e. *dehI* and *dehII*).

We have satisfied about 50% of our first objective to date. We have used a filtration and direct plating isolation method and obtained several isolates from the Mississippi River and from agricultural soils. We will continue this work in the next year to obtain additional isolates from other sources. The second objective of this research is also about 50% complete, as we have developed a tRFLP method targeting short fragments (i.e., ~270 to 420 bp) of the *dehI* and *dehII* genes. The method was confirmed with previously obtained bacterial isolates and enrichment cultures and with a sample of granular activated carbon (GAC) from a prechlorinated GAC filter. In the next year, we intended to apply this method to several drinking water distribution system samples to better understand the prevalence and structure of HAA-degrading bacteria in these systems.

## **INTRODUCTION**

The disinfection of drinking water and wastewater is needed for the protection of public health. Typically, chlorine is used to disinfect drinking water and wastewater because of its effectiveness and low cost, but chlorination also leads to the formation of disinfection byproducts (DBPs), the most dominant of which are trihalomethanes (THMs) and haloacetic acids (HAAs) (Krasner et al. 2006). The production of these DBPs is a critical water quality problem because many of these compounds are known or suspected carcinogens and some have suggested other deleterious effects such as increased risk of spontaneous abortion (Swan et al., 1998).

HAAs have been observed to decrease along the distribution systems in some cases (LeBel et al., 1997; Williams et al., 1995; Williams et al., 1997a). Williams et al. (1995) observed that dichloroacetic acid (DCAA) was significantly reduced in concentration in many samples collected from locations of relatively high residence times and this loss was later shown to be due to biodegradation (Williams et al., 1997b). We then demonstrated that bacterial cultures enriched on trichloroacetic acid (TCAA) and monochloroacetic acid (MCAA) could degrade HAAs at very low concentrations similar to those in the drinking water distribution systems (i.e., ~10-100 µg/L) (McRae et al., 2004).

Although there is growing information in the scientific literature about HAA-degrading bacteria, this information mainly comes from studies of soil and wastewater systems at relatively high concentrations of HAAs, such as those found at spill sites (*e.g.*, Olaniran, 2001; Lignell et al., 1984). Moreover, the very few HAA degraders isolated from the drinking water distribution system show that these bacterial isolates are different than those from soil and wastewater (Zhang et al., 2009). Also, the dehalogenase genes responsible for the biodegradation of HAAs are different than those that have been characterized in isolates from soil and activated sludge (Zhang et al., in review). Exploring the diversity of bacterial strains and HAA-dehalogenating genes from drinking water system is therefore important not only for expanding our scientific knowledge on the biodegradation of HAAs but also for being able to predict the fate of HAAs in drinking water distribution systems.

## **METHODS**

### *Sample collection and preparation*

Water and soil samples were aseptically collected from five different drinking water distribution systems (Minneapolis, MN (4 locations); St. Paul, MN; Blaine, MN; Bloomington, MN (2 locations); Bucharest, Romania), one source of surface water (Mississippi River) and from agricultural soil. Because tap water typically has relatively few bacteria in it (i.e. < 100 colony forming units per 100 mL), we filtered 10-20 liters of tap water on 0.2 µm sterile membrane filters to obtain useful quantities of bacteria for genomic DNA extractions. A similar filtration was used to concentrate the Mississippi River water, although only 50-100 mL were needed for bacterial strain isolation. In order to isolate HAA degraders from soil, 1 g of soil was placed in 9 mL of autoclaved phosphate-buffered saline (10 mM, pH 7.2) and vortexed for 5 minutes in order to dislodge bacteria. Serial dilutions were then prepared and 100 µL of each dilution were placed on agar plates supplemented with HAAs. Soil samples were obtained from an agricultural field in Blairsburg, Iowa where metolachlor was used in the past as herbicide. Metolachlor is known to photodegrade into MCAA (Wilson and Marbury, 2000).

### *Isolation and characterization of bacterial strains*

Bacterial strains were isolated by directly placing filters or soil solutions on agar plates amended with 100 mg/L of MCAA, DCAA, or TCAA. The plates were incubated at room temperature for 7 to 14 days. A pH indicator (phenol red) was added at 0.03 % (w/v), which yields a yellow color at pH ≤ 6.6 and red at pH ≥ 8 (Kerr and Marchesi, 2006). Strains turning the red color to yellow, due to release of hydrochloric acid during HAA degradation, are presumed to be HAA-degraders. Single colonies were selected and streaked onto fresh plates. The isolates were re-streaked up to 3 times to ensure that the strains were pure.

The phylogeny of unique bacterial isolates was determined by nucleotide sequence analysis of nearly complete 16S rRNA genes. Nearly complete 16S rRNA genes specific to the domain *Bacteria* were amplified by polymerase chain reaction (PCR) using the 338F and 907R primers (Ghosh and LaPara, 2007). PCR products were purified (GeneClean; Qbiogene) and sequenced (BioMedical Genomics Center). Phylogenetic identification of nucleotide sequences was determined by comparison with sequences available in the GenBank database. Individual isolates were also assayed for the presence of group I and group II *deh* gene fragments via PCR using the primers and conditions described by Hill et al. (1999) (see below for more details).

#### Direct characterization of *dehI* and *dehII* genes via tRFLP

We attempted to characterize the HAA-degrading bacteria directly from our samples using a novel method of terminal restriction fragment length polymorphism (tRFLP). This approach was needed because there are numerous examples that have shown that the bacteria that are easy to culture from the environment are not necessarily the environmentally relevant organisms (e.g., Watanabe et al., 1998; McRae et al., 2004). More specifically, Marchesi and Weightman (2003) demonstrated a disconnect between *deh* genes found in pure or enriched cultures with those directly detected from the environment, suggesting that culturing introduces a large bias, not just in the bacteria isolated but also in the degradative genes that they contain (Marchesi and Weightman, 2003). Thus, we compared the dehalogenase gene sequences extracted from the original water samples with those of bacterial isolates previously obtained from the drinking water distribution system.

tRFLP patterns were generated by using PCR to amplify group I and group II *deh* gene fragments using the primers and specific methods described by Hill et al. (1999) (Table 1). The 5'-end of the forward primer was labeled with 6-carboxy-1,4-dichloro-2',4',5',7'-tetrachlorofluorescein (HEX). PCR products were initially resolved by agarose gel electrophoresis to ensure that a PCR product of the correct size was obtained. PCR products were purified using a GeneClean II kit (MPBiomedicals) to remove remaining enzyme, deoxynucleoside triphosphates, etc. The PCR products were then digested with the *MspI* and *BfuCI* restriction enzymes to cut the PCR products at specific sequence locations. The two restriction enzymes were chosen based on a preliminary *in silico* study done with known *deh* sequences that were cut by all the restriction enzymes. The digested PCR products were then resolved on a 3130 XL capillary electrophoresis analyzer at the Biomedical Genomics Center at the University of Minnesota. This provided a sensitive, high-resolution fingerprint of the *deh* genes in our samples.

**Table 1.** Primers used for PCR amplification of Group I and Group II dehalogenase genes

Group I deh genes	
Primer	Sequence
dehI <sub>for</sub> I	5'-ACGYTNSGSGTGCCNTGGGT-3'
dehI <sub>rev</sub> I	5'-AWCARRTAYTTYGGATTRCCRTA-3'
Group II deh genes	
Primer	Sequence
dehII <sub>for</sub> I	5'-TGGCGVCARMRDCARCTBGARTA-3'
dehII <sub>rev</sub> I	5'-TCSMADSBRTTBGASGANACRAA-3'

IUPAC ambiguity code used: B = C, G, or T; D = A, G, or T; K = G or T; M = A or C; N = A, C, G, or T; R = A or G; S = C or G; W = A or T; Y = C or T. *Source*: Hill et al. (1999)

## RESULTS

We previously obtained several HAA-degrading isolates from HAA enrichment cultures (Zhang et al., 2009). It is known, however, that the diversity of isolates is low when using an enrichment culturing technique. On the other hand, Kerr and Marchesi (2006) demonstrated that by improving the enrichment culture technique and by using direct plating as well, they were able to isolate novel bacteria able to degrade  $\alpha$ -halocarboxylic acids. Therefore, our first goal was to use the direct plating isolation method in order to obtain more diverse HAA degraders.

We obtained 11 isolates on MCAA-amended plates and 15 isolates on DCAA-amended plates from Mississippi River water samples. Two of the MCAA-degrading isolates had both *dehI* and *dehII* genes; 3 isolates had only the *dehII* gene; and 6 isolates did not have either of these two genes. One of the DCAA-degrading isolates had both *dehI* and *dehII* genes; 5 isolates had only a *dehII* gene; and 9 isolates did not have either of these two genes. Two of the DCAA-degrading isolates were identified as being *Xanthobacter* spp. We further obtained 8 isolates on MCAA-amended plates and 8 isolates on DCAA-amended plates from agricultural soil samples. Of these, one MCAA-degrading isolate had both *dehI* and *dehII* genes; 4 isolates had only the *dehII* gene; and 3 isolates did not have either of these two genes. Also, 2 DCAA-degrading isolates had both *dehI* and *dehII* genes; 4 isolates had only the *dehII* gene; and 2 isolates did not have either of these two genes. These results show that the *dehII* gene is more prevalent than the *dehI* gene and suggest that novel dehalogenase genes could exist (carried by the isolates that grow on MCAA- or DCAA-amended plates but do not possess either the *dehI* or *dehII* genes). No isolates were obtained on TCAA plates, neither from the Mississippi river water nor from the soil samples. TCAA is a less favorable substrate than the mono- and di-halogenated HAAs because it is so highly oxidized that little energy is gained from aerobic degradation of this compound.

The second goal of our research was to directly characterize the bacterial communities that biodegrade haloacetic acids in drinking water distributions by using the tRFLP method targeting the *dehI* and *dehII* genes. We first did a preliminary theoretical analysis that showed that the tRFLP method can be used with small PCR fragments (~270 bp for *dehI* and ~420 bp for *dehII*) (Table 2). Moreover, the same *in silico* study suggested that the proposed tRFLP method can distinguish between the different phylogenetic *deh* groups and/or bacterial strains carrying *deh* genes. The tRFLP method was then confirmed using *MspI* and *BfuCI* restriction enzymes for the

isolates listed in Table 2 as well as for a small number of other samples (activated sludge and granular activated carbon). The *dehI* gene was found in tap water samples collected from Minneapolis and the *dehII* gene was found in tap water samples collected from Minneapolis, St. Paul and Bucharest. The tRFLP profiles for the drinking water samples from Minneapolis are similar to those of *Afipia* spp. (having a group B *dehI* gene and a group C *dehII* gene), suggesting that this bacterial genus is the predominant HAA degrader in the water distribution system of Minneapolis.

Table 2. Prediction of the size of restriction fragments for several *dehI* (A) and *dehII* (B) sequences cut with *BfuCI* and *MspI*. GTS, GD1, EMD1, EMD2, GM1, GM2, GM3 and P1MI are isolates obtained in a previous study (Zhang et al., in review) from drinking water distribution systems.

A.

isolate or gene	species	<i>dehI</i> PCR fragment	phylogenetic <i>dehI</i> group	<i>BfuCI</i>	<i>MspI</i>
<b>GTS</b>	<i>Afipia broomeae</i>	272	B	123	151
<b>GD1</b>	<i>Afipia felis</i>	272	B	123	152
<b>EMD1</b>	<i>Afipia felis</i>	272	B	123	152
<b>EMD2</b>	<i>Afipia felis</i>	272	B	123	152
<i>dehE</i>	<i>Rhizobium</i> sp.	272	A	272	194
<i>dehIAS1</i>	<i>Xanthobacter</i> sp. AS1	272	B	118	64
<i>dehIDA3</i>	<i>Bradyrhizobium</i> sp. DA3	274	B	123	64
<i>hadD</i>	<i>Pseudomonas putida</i>	280	C	133	51
<i>dehI17a</i>	<i>Pseudomonas</i> sp.	281	C	119	36

B.

isolate or gene	species	<i>dehII</i> PCR fragment	phylogenetic <i>dehII</i> group	<i>BfuCI</i>	<i>MspI</i>
<b>GM1</b>	<i>Burkholderia glathei</i>	422	A	241	74
<b>GM2</b>	<i>Herminiimonas fonticola</i>	422	A	45	422
<b>GM3</b>	<i>Burkholderia glathei</i>	422	A	241	74
<b>GD1</b>	<i>Afipia felis</i>	416	D	104	175
<b>GTS</b>	<i>Afipia broomeae</i>	416	C	165	272
<b>P1MI</b>	<i>Afipia massiliensis</i>	416	C	135	175
<b>EMD1</b>	<i>Afipia felis</i>	415	C	163	173
<b>EMD2</b>	<i>Afipia felis</i>	415	C	164	174
<i>dehH2</i>	<i>Moraxella</i> sp. B plasmid <i>dehH2</i>	422	A	227	175
<i>dehIIPP3</i>	<i>Pseudomonas putida</i> strain PP3	422	A	255	422
<i>dehH109</i>	<i>Pseudomonas putida</i> No.109 plasmid pUOH109	422	A	305	175
<i>L-dex</i>	<i>Pseudomonas</i> , YL	422	A	114	99
<i>dh1B</i>	<i>Xanthobacter autotrophicus</i>	416	D	416	118
<i>dehCI</i>	<i>Pseudomonas</i> sp.	422	B	126	212
<i>hdIIVa</i>	<i>P.cepacia</i>	422	B	117	138

## SUMMARY OF FINDINGS

The first outcome of our research was to establish an efficient bacterial isolation method in order to obtain HAA-degrading bacteria from drinking water distribution systems and environmental samples. We used a filtration and direct plating isolation method and obtained several isolates from the Mississippi River and agricultural soil. The second outcome of this research was to develop and optimize a tRFLP method for the study of the *dehI* and *dehII* gene diversity. We developed a tRFLP method targeting short fragments (i.e., ~270 to 420 bp) of the *dehI* and *dehII* genes. The method was confirmed with previously obtained isolates from drinking water systems as well as samples from an activated sludge bioreactor as well as a granular activated carbon filter treating chlorinated drinking water.

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**PUBLICATIONS**

None

**PRESENTATIONS**

None

**STUDENT SUPPORT**

Name: Alina S. Grigorescu

Program: Civil Engineering, University of Minnesota

Degree being sought: Ph.D. (anticipated May 2010)

**AWARDS**

None

**ADDITIONAL FUNDS**

Hozalski R.M., A. Camper, S. Parsons, and T.M. LaPara. Biodegradation of haloacetic acids in distribution systems. American Water Works Association Research Foundation, January 1, 2006 – June 30, 2008. (\$400,000)

## Reductive degradation of pesticides: Solid-state and solution-phase dynamics

### Basic Information

<b>Title:</b>	Reductive degradation of pesticides: Solid-state and solution-phase dynamics
<b>Project Number:</b>	2009MN246B
<b>Start Date:</b>	3/1/2009
<b>End Date:</b>	2/28/2011
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	MN 05
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Toxic Substances, Geochemical Processes, Non Point Pollution
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	William Alan Arnold, R. Lee Penn

### Publications

There are no publications.

## **Reductive degradation of pesticides: Solid-state and solution-phase dynamics**

### **Principal Investigators**

**William A. Arnold**, Associate Professor, Department of Civil Engineering, University of Minnesota

**R. Lee Penn**, Associate Professor, Department of Chemistry, University of Minnesota;

### **Funding Source: USGS-WRRI 104B/ CAIWQ Competitive Grants Program**

**Project Duration: 3/1/09 - 2/28/11**

**Reporting Period: 3/1/09-2/28/10**

### **Summary**

Every year, thousands of pounds of pesticides are used on Minnesota's farmland. After application these pesticides can leach into groundwater used as drinking water resources. Some of these pesticides can undergo abiotic reductive degradation. Degradation of the pesticides occurs at the mineral-water interface, and over time the reactivity of the mineral surfaces changes. These changes can affect the reactivity of the particles. The project objective is to quantify changes in the mineralogy of iron sediments resulting from abiotic degradation of pesticides and to link these changes with the degradation kinetics of the pesticides. This will make it possible to determine the ability of sediment to degrade pesticides with long term exposure. The pesticides that will be investigated are trifluralin and mesotrione, both of which are nitroaromatic herbicides. Both pesticides also degrade by reductive degradation. Trifluralin is a pre-emergence herbicide, while mesotrione is a pre and post-emergence herbicide. Both pesticides are used for control of grass and broadleaf weeds.

### **Research**

Experiments are carried out under anaerobic conditions. MOPS buffer solutions of pH 7.5 and concentration of 25 mM are prepared using ultrapure water deoxygenated by purging with nitrogen. The buffer solutions are prepared in an anaerobic glovebag. Reactions are carried out in 124 mL serum bottles containing goethite and buffer solution. Enough buffer solution will be added to ensure there is no headspace in the reactors. Ferrous iron is added to the reactors in the form of an acidified ferrous chloride solution at a concentration of 1.0 mM. The reactors sit for a period of time in the glovebag to allow for equilibration.

To initiate reactions methanolic pesticide stock solutions are spiked in at determined concentrations. The reactors are then placed on rotators. Samples are periodically withdrawn and a 1:1 volume extraction with hexane will be performed. The samples are then analyzed using either GC/MS or HPLC. When the pesticide is no longer detected the reactor is respiked with ferrous chloride to return the ferrous iron concentration to 1 mM. The reactor is again allowed to equilibrate and then the pesticide stock solution is respiked to the reactor. This process will be repeated multiple times. The concentration of ferrous chloride in the reactor is measured after each reaction using the ferrozine method. After each spike a sample is withdrawn for TEM analysis of the goethite particles. Particles size, shape and composition will be analyzed. Rate constants will be calculated using the GC/MS and HPLC data for each spike.

Trifluralin has been successfully detected using GC/MS. Reactors have been prepared containing 5 mg of goethite particles. Reactors were spiked with a methanolic stock solution so that the initial reactor concentration was 5  $\mu$ M. Trifluralin was observed to degrade over the course of approximately 3-4 hours. Currently, reactors have been set up and respire experiments are being carried out. It was determined that mesotrione cannot be detected by GC/MS. Mesotrione is a relatively new compound, and there has not been a lot of work done using this compound. Currently an HPLC method to detect the compound is being developed. After this, an appropriate concentration at which to spike the reactor will be determined and reactions with goethite will also be carried out.

**List of publications & presentations resulting from this project**

None to date.

**Statement of related grants submitted or funded as a result of this project**

None to date. An NSF project is pending.

**Description of student training provided by project:**

**Graduate Students**

Name: Kirsten Moore

Program: Department of Civil Engineering, University of Minnesota

Degree: M.S. expected August 2010.

## Fate and bioavailability of litter mercury in Minnesota streams and rivers

### Basic Information

<b>Title:</b>	Fate and bioavailability of litter mercury in Minnesota streams and rivers
<b>Project Number:</b>	2009MN250B
<b>Start Date:</b>	3/1/2009
<b>End Date:</b>	2/28/2011
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	4
<b>Research Category:</b>	Biological Sciences
<b>Focus Category:</b>	Toxic Substances, Water Quality, Ecology
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Jacques C. Finlay, Edward A Nater

### Publications

There are no publications.

## ***Annual Program Report***

**2009MN250B - Fate and bioavailability of litter mercury in Minnesota streams and rivers**

**Principal Investigator: Jacques Finley**

**Funding Sources: USGS-WRRI 104B Competitive Grants Program**

**Project Duration: 3/1/2009 – 2/2/2011**

### **1)RESEARCH**

#### **Introduction and study objectives**

Mercury (Hg) is a global contaminant and elevated Hg levels have been widely found in aquatic food webs which pose serious health concern for human and wildlife through fish consumption (Morel et al., 1998; Wiener et al., 2003). Through atmospheric exchange processes, living trees can take up gaseous Hg through stomatal exchange (Ericksen et al., 2003), and during senescence leaf litter represents a source of Hg to terrestrial and aquatic environments (Grigal, 2002). Streams and rivers receive large amounts of leaf litter, and these inputs are an important energy source for food webs (Wallace et al., 1997; Finlay, 2001). Similarly, leaf litter could also act as a source of inorganic Hg to aquatic food webs, and aggregations of decomposing litter could create conditions that could promote transformation of Hg to methylmercury (MeHg), a highly bioaccumulative form of Hg (Balogh et al., 2002). The processes regulating the fate of Hg associated with litter inputs and decomposition are poorly understood at this time, however.

In this study, we aimed to examine how characteristics in stream environments mediate the speciation and concentration of Hg in leaf litter during decomposition in streams and rivers. Specifically, we are interested in studying whether MeHg is produced during leaf litter decomposition. Once produced, MeHg is readily available to be incorporated into the food webs and biomagnified along the food chains (Chasar et al., 2009). In this work, we examine maple litter decomposition in ten Minnesota streams and rivers across a land cover gradient. Field work associated with the project has been initiated and sample analyses are in progress. We expect the project to be completed by the end of 2010.

#### **Materials and Methods**

##### **Leaf litter collection and processing**

Maple leaf litter was collected in September and October 2009 from the forest floor near Cedar Bog Lake within Cedar Creek Ecosystem Science Reserve (Bethel, MN). Leaf litter was collected using non-powder cleanroom gloves and placed directly into new ziplock bags. Only freshly fallen litter was collected. Upon returning to the laboratory, leaf litter were placed on cleanroom sheet (Kimtech Pure W4 Dry Wipers) and dried with a class 100 laminar clean bench for 2-3 days. Dried litter was stored in clean plastic bags at room temperature before use.

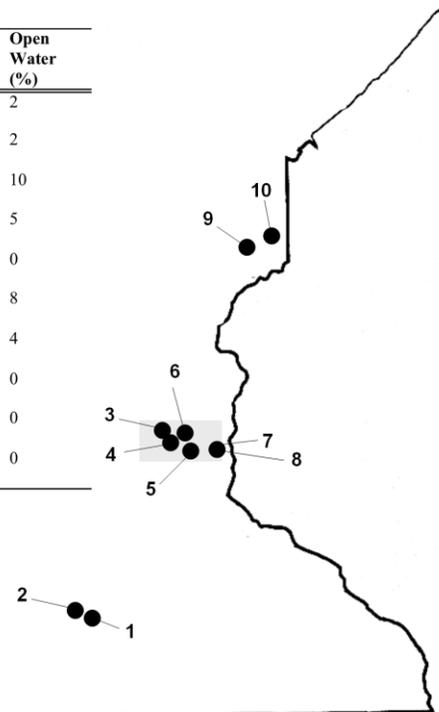
## Litterbag construction and field deployment

Nitex bolting cloth with mesh size of 1 mm (Wildlife Supply Company, Yulee, FL) was used to construct litterbags for this study. Litterbags of approximately 15 cm × 15 cm were sewn with double nylon threads, soaked in 10 % HCl overnight, rinsed thoroughly with ultrapure water, and dried in a clean bench. Dried maple litter was weighed and placed carefully into the litterbags (2.50 ± 0.10 g), and the bag opening was finally closed by sewing an additional nylon thread using a sewing machine in a clean bench. Litterbags were tagged with color cable ties and color label identifier.

The map below shows the site locations of three distinct zones within Minnesota (agricultural 1-2, urban 3-8 and forested/wetland 9-10) and their dominant land cover patterns.

#	Site	City/nearest town	Watershed area (km <sup>2</sup> )	Developed Land (%)	Farmland (%)	Forest (%)	Wetland (%)	Open Water (%)
1	Big Cobb	near Beauford	800	6	86	1	4	2
2	Maple	near Beauford	905	6	86	1	3	2
3	Rice	Fridley	249	46	17	13	10	10
4	Bassett	Minneapolis	113	82	1	10	2	5
5	Battle (sub-catchment)	St. Paul	4.9	96	0	3	0	0
6	Mississippi <sup>a</sup>	Minneapolis	51,500	3	44	33	12	8
7	Valley Branch	Afton	128	20	48	20	2	4
8	Valley Creek	Afton	20	5	64	25	0	0
9	Sand	near Cloverdale	198	2	12	60	19	0
10	Lower Tamarack	near Cloverdale	327	1	1	64	29	0

<sup>a</sup>Data from Balogh *et al.* (1998)



In mid-October 2009, weighed litterbags were secured to a nylon rope which was attached to rebar secured into the streambed. Litter bags were deployed in slowly flowing areas within the streams where litter accumulation occurs. Twenty litterbags were deployed at each site (10 sites total) and four litterbags (i.e. 4 replicates) were retrieved destructively each time (*see below*).

## Water sample collection and *in-situ* measurements

Because our previous study has shown that water characteristics are important in affecting Hg release and methylation in a laboratory-controlled decomposition experiment (Tsui *et al.*, 2008), water samples were collected regularly in this study and measured for different water quality parameters in order to understand if these are related to any observed changes associated

with the leaf litter. Briefly, surface water was collected into two 500 mL of vigorously acid-cleaned Teflon bottles using trace-metal clean techniques. Also, an additional 1 L HDPE bottle was used to collect surface water for analyzing total suspended solids. All water samples were transported on ice to the laboratory for further processing. *In-situ* measurements were performed for water temperature and/or pH by an Orion portable pH meter (Model 250A).

### **Water sample processing and analyses**

Upon return to the laboratory, water samples in one of the Teflon bottles were either subsampled into 125 mL Teflon bottles (unfiltered) or filtered through a 0.45- $\mu\text{m}$  cellulose nitrate membrane housed in a disposable acid-leached filter unit. Samples were analyzed for total-Hg and MeHg, which were preserved by 0.8 to 2 % BrCl (depending on actual organic matter content) and 0.4 % HCl, respectively (Parker and Bloom, 2005). For total-Hg, water samples were digested by BrCl overnight at 60 °C and pre-reduced by hydroxylamine, reduced by SnCl<sub>2</sub> and Hg(0) was quantified by single gold amalgamation technique with cold vapor fluorescence atomic detection (Liang and Bloom, 1993). For MeHg, samples were distilled to remove matrix interferences, ethylated and purged onto Tenax<sup>®</sup> traps using Hg-free N<sub>2</sub> gas, and MeHg was quantified by cold vapor fluorescence atomic spectrometer after GC separation and pyrolysis (Bloom, 1989; Liang et al., 1994). Analysis of MeHg was performed at a cleanroom in Metropolitan Council Environmental Services (St. Paul, MN) managed by Dr. Steven Balogh.

For another Teflon bottle, water was filtered through muffled Whatman GF/F filter (pore size of ~ 0.7- $\mu\text{m}$ ) using an acid-cleaned glass flask, samples were acidified with HCl to < pH 2 for determining dissolved organic carbon and total dissolved nitrogen (by Shimadzu total organic carbon analyzer), unpreserved for analyzing dissolved sulfate and chloride (by Dionex DX120 Ion Chromatograph at Research Analytical Laboratory, University of Minnesota), or treated with 1 % trace-metal grade HNO<sub>3</sub> (J. T. Baker) for quantifying dissolved cations and phosphorus (by Thermo Scientific iCAP 6500 dual view ICP-OES at Department of Geology and Geophysics, University of Minnesota). Known volume of water samples were filtered onto 0.45- $\mu\text{m}$  cellulose nitrate membrane which was then extracted by 90% acetone for analyzing chlorophyll-*a* concentration in the water. Water samples from the HDPE bottle were filtered onto pre-weighed Whatman GF/F filter paper which was then oven-dried and re-weighed again to determine total suspended solids (TSS).

### **Litter processing and analyses**

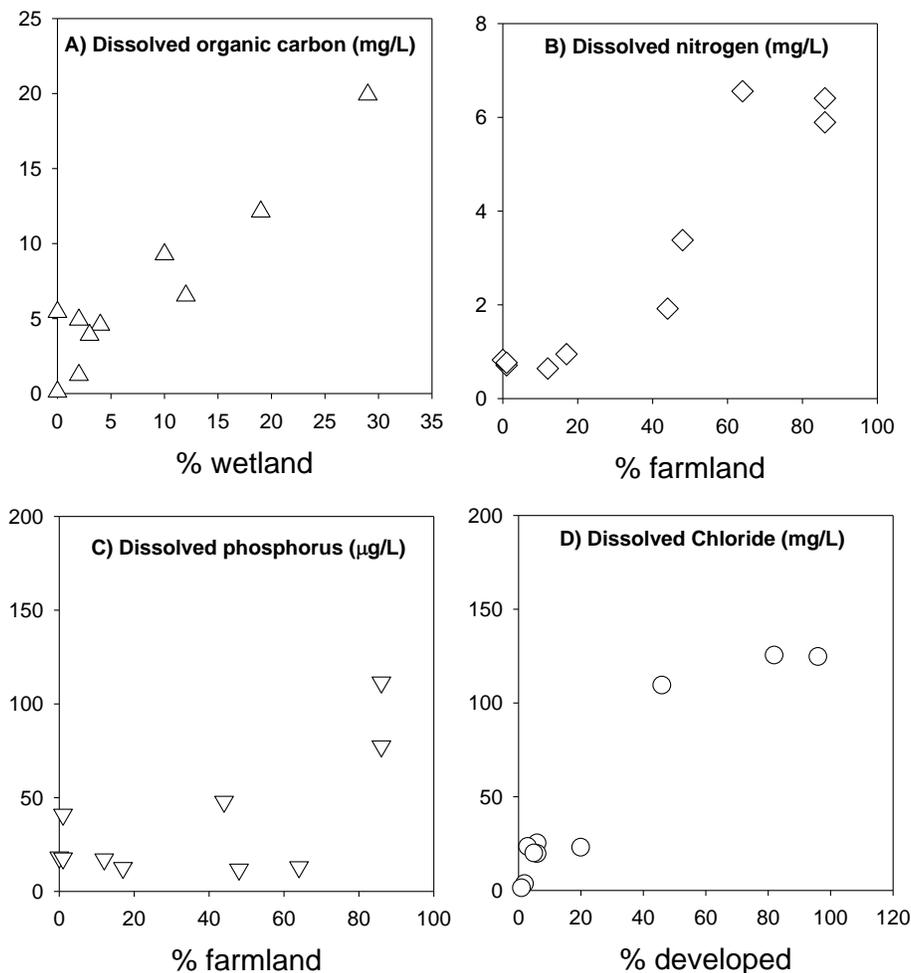
After 1, 3, 5, 10 weeks and the following spring snowmelt period in (i.e., April-May, 2010), litterbags were retrieved from the field. Due periods of limited site accessibility caused by either high flow or frozen surface, some litter samples could not be collected. All litterbags were transferred into clean ziplock bags, transported on ice to the lab. Upon returning the lab, litterbags were immediately frozen at -20 °C. Later, frozen litterbags were freeze-dried (Labconco freezer 4.5) to constant weight, and the litter were carefully transferred to acid-cleaned 50 mL polypropylene vials which were then weighed to determine the mass loss during decomposition in the field. Also, control litterbags without deployment in the field were also included to assess mass loss during litterbag construction and transport.

Litter were digested by 4.6 M HNO<sub>3</sub> for 12 h and analyzed for MeHg contents by CVAFS according to an established protocol (Tsui et al., 2009). Samples were further oxidized by BrCl at room temperature to analyze total-Hg contents by CVAFS. Moreover, litter was determined for elemental contents of carbon and nitrogen by a Perkin-Elmer elemental CHN analyzer in Department of Ecology, Evolution and Behavior, University of Minnesota. Processing of litter samples is currently in progress.

### **Preliminary Results for Water Characteristics**

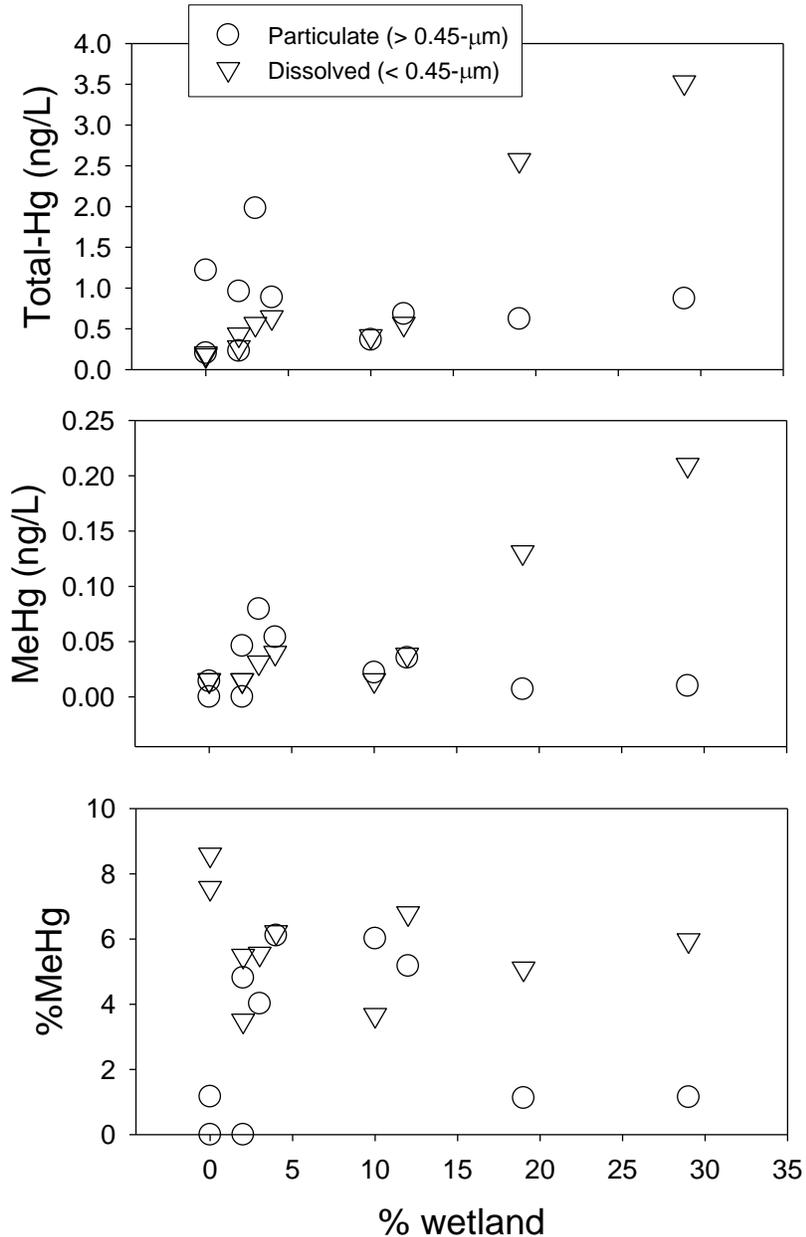
Litter Hg analyses is ongoing. Below we present some preliminary results for water characteristics, data that will be useful for the analyses of variation in MeHg generation in leaf litter. All sample collection will be completed by late spring and remaining sample analyses will be completed during the summer 2010.

Land cover patterns in the study watershed have a strong influence on the chemical constituents in the streamwater. As expected, dissolved organic carbon was positively related to % wetland cover in the watershed, and nitrogen (but not phosphorus) was associated with % agricultural land in the watershed. Chloride was strongly related to % developed land in the watershed (*see* Figure 1).



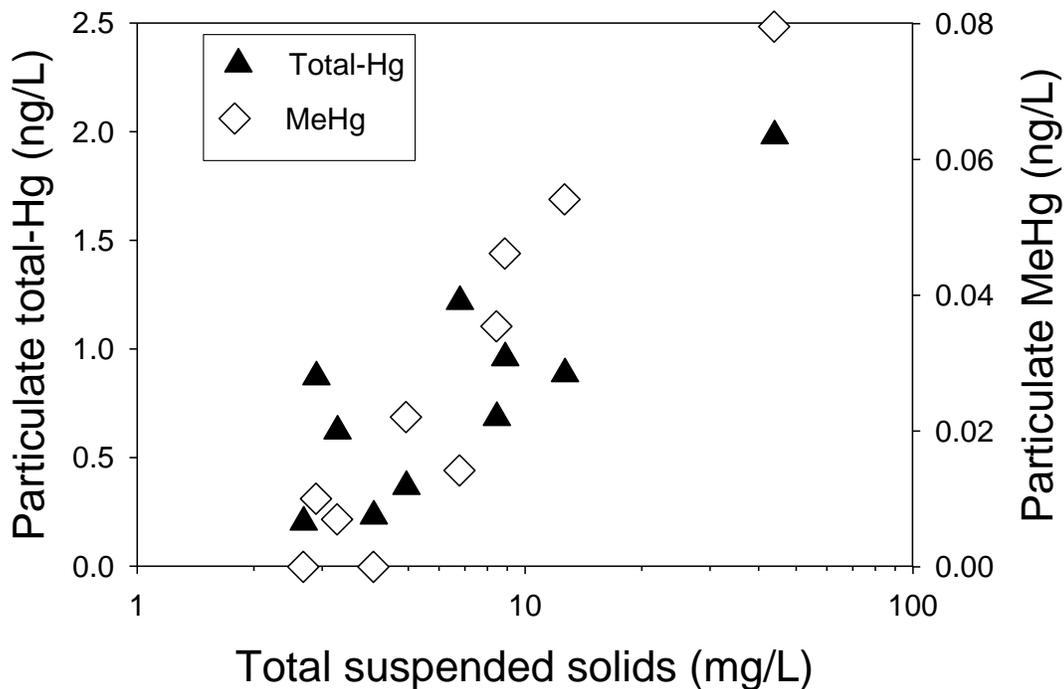
**Fig. 1** Relationships between mean concentrations of dissolved organic carbon, nitrogen, phosphorus and chloride and different land cover attributes in the watershed of the study streams.

Dissolved total-Hg and MeHg concentrations were correlated with % wetland in the watershed, while particulate Hg was not. Fraction of total-Hg as MeHg (i.e. %MeHg) was relatively similar among sites for the dissolved fraction but highly variable for the particulate fraction (*see* Figure 2).



**Fig. 2** Relationships between mean concentrations of particulate and dissolved total-Hg, MeHg and %MeHg and %wetland in the watershed of the study streams.

Particulate total-Hg and MeHg concentrations were highly dependent on the levels of suspended solids in the water column in the study streams (*see* Figure 3).



**Fig. 3** Relationships between mean concentrations of particulate total-Hg and MeHg and total suspended solids in the water column of study streams.

The varying land cover patterns among the study streams generate strong gradients in streamwater chemistry and site characteristics. Differences among sites are expected to drive variation in decomposition of leaf litter, and changes in Hg speciation in the organic material. We will use these site characteristics to help interpret to any observed compositional changes in the litter in this study, in order to better understand the underlying processes in controlling the fate of litter Hg in stream ecosystems.

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## 2) PUBLICATIONS

None

## 3) STUDENT SUPPORT

Martin Tsui – Doctoral Candidate Research Assistant (WRS Program)

Yuntian Gu – Undergraduate Research Assistant I (CFANS major)

Stefanie Wolf – Undergraduate Research Project (UROP) (EEB major)

**4) PRESENTATIONS**

None

**5) AWARDS**

None

**6) RELATED FUNDING**

None

# Urban Stormwater Inputs of Perfluorochemicals

## Basic Information

<b>Title:</b>	Urban Stormwater Inputs of Perfluorochemicals
<b>Project Number:</b>	2009MN253B
<b>Start Date:</b>	3/1/2009
<b>End Date:</b>	2/28/2011
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	5
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Non Point Pollution, Sediments, Solute Transport
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Matt Francis Simcik

## Publications

There are no publications.

## Title: Urban Stormwater Inputs of Perfluorochemicals

**Principal Investigator** – Matt Simcik, Associate Professor, Department of Environmental Health Sciences

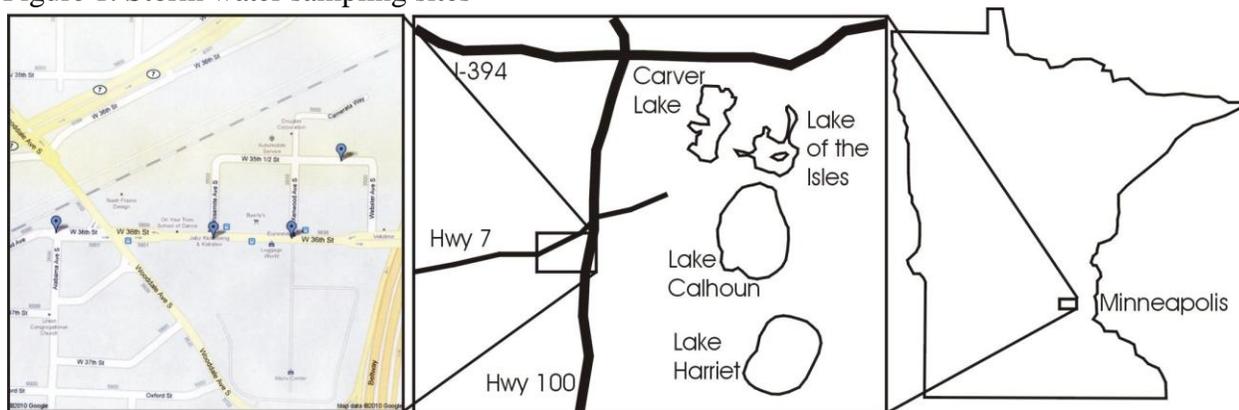
**Funding Source:** USGS WRI 104B Competitive Grant Program

**Project Duration:** 3/1/09-2/28/11

1) Research: A synopsis of your ongoing research project and of any research project completed during this reporting period. This includes projects funded under the base grant and the National Competitive Grants program. These reports are for a technical audience, and are posted and regularly accessed on the main USGS website. We do not do any editing of these, so please take care in their preparation. Somewhere between 5-10 pages including tables and figures is typical.

Five stormwater samples were taken from an area of Minneapolis, MN that was suspected to have an industrial source nearby. This industrial area and the subsequent loadings to storm water are expected to be responsible for contamination of Lake Calhoun nearby. Samples consisted of 4L grab samples taken by lowering 4L HDPE bottles into the storm water flow from street level down drain holes. The five samples were taken at different points along the same storm drain system, and covered an area of only a few city blocks. A map of the sites is given in Figure 1.

Figure 1. Storm water sampling sites



Water samples were filtered to separate the dissolved phase from the particulate phase perfluorochemicals (PFCs). Filters were 47mm polypropylene (Millipore) filters with 2um pore size. Several filters were required per water sample as the particles in the samples clogged the filters and head pressure increased (or flow decreased). The filtrate was then extracted using solid phase extraction cartridges packed in the laboratory with cleaned XAD-7 polymeric resin. The resin and filters were extracted separately with methanol (Optima grade, Fisher Scientific). Internal standards consisting of 13C labeled PFOS and PFOA were added to each extract and a suite of perfluorochemicals (Table 1) quantified by liquid chromatography/mass spectrometry (LC/MS) utilizing electrospray negative ionization (HP 1090 LC and Agilent 1100 MS).

PFC identification was performed by comparing retention times and m/z corresponding to native standards. The LC/MS was operated in the selective ion monitoring mode corresponding to the m/z for each analyte and standard.

Table 1. List of Analytes

Analyte	Abbreviation	CAS #
perfluorobutanoic acid	PFBA	375-22-4
perfluorobutane sulfonate	PFBS	375-73-5
perfluoropentanoic acid	PFPeA	2706-90-3
perfluorohexanoic acid	PFHxA	307-24-4
perfluorohexane sulfonate	PFHxS	355-46-4
perfluoroheptanoic acid	PFHpA	375-85-9
perfluorooctanoic acid	PFOA	335-67-1
perfluorooctane sulfonate	PFOS	1763-23-1
perfluorooctane sulfonamide	PFOSA	754-91-6
perfluorononanoic acid	PFNA	375-95-1
perfluorodecanoic acid	PFDA	335-76-2
perfluoroundecanoic acid	PFUnA	2058-94-8
perfluorododecanoic acid	PFDoA	307-55-1

Perfluorooctane sulfonate (PFOS) was the most frequently detected and highest concentration PFC contaminant measured in the five storm water samples from Minneapolis. Perfluorooctanoic acid (PFOA) was also detected in one dissolved sample. Other PFCs were not detected.

Concentrations of PFOS and PFOA are presented in Table 2. The dissolved phase ranged from 9 to 156 ng/L with no spatial trend among the five sites. Only one storm water sample resulted in PFOA detection and that was 21 ng/L at the 36<sup>th</sup> Street and Yosemite intersection sampling site.

Table 2. PFOS and PFOA in stormwater runoff (2009, 9, 25)

Sample I.D.	PFOS (ng/L)	PFOA (ng/L)
<b>36 – Yosemite</b>	<i>55.4</i>	<i>21.2</i>
<b>365 Xenwood</b>	<i>155.8</i>	<i>ND</i>
<b>952,9/25,35<sup>th</sup> αβ ---</b>	<i>50.0</i>	<i>ND</i>
<b>10/2, 35 1/2, 10/2, SW, 9/25</b>	<i>59.6</i>	<i>ND</i>
<b>36 A/A 9/25, 945</b>	<i>8.7</i>	<i>ND</i>

Only PFOS was detected in any of the particle phase samples. Three samples resulted in measurable PFOS ranging from 0.12 to 0.59 ng/mg of total suspended solids (TSS; Table 3).

Table 3. PFOS and PFOA on the total suspended solids (TSS) in stormwater runoff (2009, 9, 25)

Sample I.D.	PFOS (ng/mg TSS)	PFOA (ng/mg TSS)	TSS (mg/L)
365 Xenwood	0.12	ND	67.4
952,9/25,35 <sup>th</sup> $\alpha\beta$ ---	0.59	ND	22.2
10/2, 35 1/2, 10/2, SW, 9/25	0.28	ND	133.6

The levels of PFOS on the solids phase in stormwater runoff are surprisingly high based on what is known from previous research on partitioning of PFCs to suspended particles. For example, for the sample (952,9/25,35<sup>th</sup>  $\alpha\beta$  ---), The soli/water partition coefficient,  $K_d$ , is around  $0.28/50 = 5600$  L/kg, which is  $\sim 500$  times higher than reported  $K_d$  values for PFOS. Therefore, we performed a series of laboratory experiments to determine the cause of high partitioning in our field samples. The first set of experiments involved constructing adsorption isotherms for single compound systems as well as multi-compound systems onto clay particles.

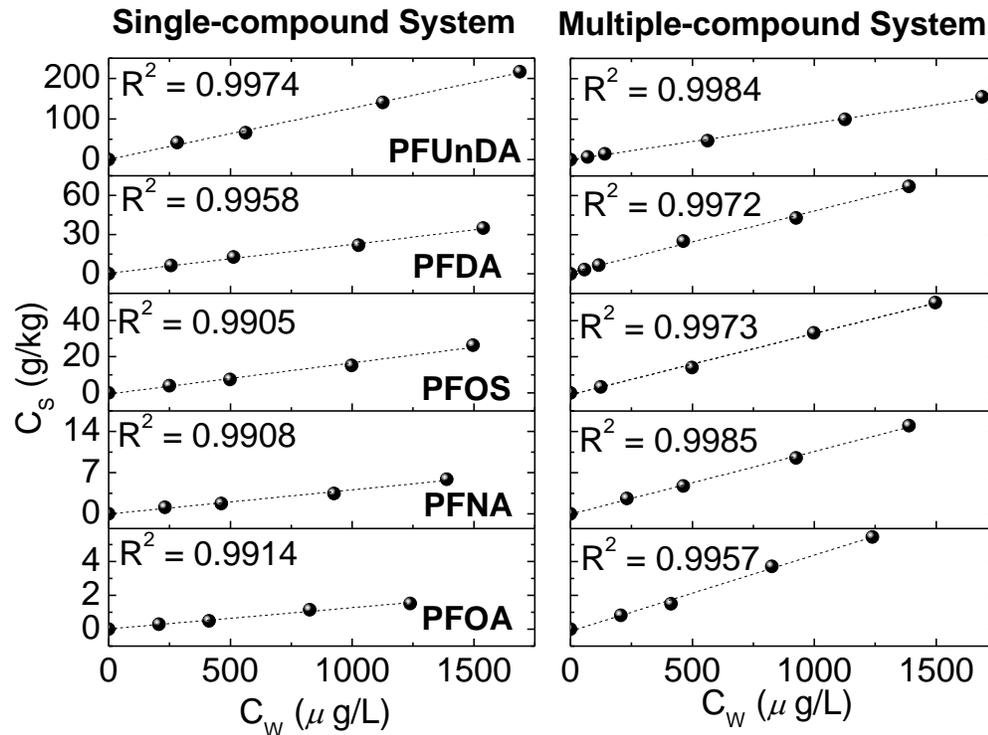


Fig. 2 – Adsorption isotherms

The results of the single/multiple compound adsorption isotherms (Figure 2) indicate that over a small  $C_w$  range upto 1500 ug/L, we often see a linear isotherms. Furthermore, PFCs with longer chains tend to out-compete PFCs with shorter chains. For comparison, we obtained the  $K_d$  values in both a single-compound sorption system and a multiple-compound system containing all PFCs (Table 4). The obtained  $K_d$  values of PFCs with shorter  $-CF_2$  chain in a single-compound system are much larger than the  $K_d$  values in a multiple-compound system. However, the  $K_d$  values of PFCs with longer  $-CF_2$  chains are not significantly different between the single-compound and multipl-compound systems.

Table 4. Solid/water partition coefficient

	$K_d$ (L/kg) (Single-compound System)	$K_d$ (L/kg) (Two-compound System)	$K_d$ (L/kg) (Multi-compound System)
<b>PFOA</b>	$4.12 \pm 0.41$	$1.82 \pm 0.28$	$1.30 \pm 0.11$
<b>PFNA</b>	$10.62 \pm 0.46$		$4.12 \pm 0.49$
<b>PFOS</b>	$30.71 \pm 3.89$	$16.73 \pm 1.56$	$15.80 \pm 1.29$
<b>PFDA</b>	$47.55 \pm 4.12$		$23.38 \pm 1.52$
<b>PFUnDA</b>	$102.60 \pm 8.41$		$110.12 \pm 13.18$

So the competitive adsorption theory will not explain the large amount of PFOS observed on the particles. Therefore, we devised another set of experiments to investigate the role of ionic strength on the adsorption of PFCs to clay particles. These experiments have resulted in some very interesting observations. It appears that what is more important than the overall ionic strength of the solution is the valence of the cation used to alter the ionic strength (Figure 3). This suggests that PFCs may act more like charged particles/colloids in solution than molecules adsorbing to solids. This could have important implications in the environmental partitioning of these chemicals and potentially for their removal from water. The results of this latter experiment is expected to be the rationale for future funding.

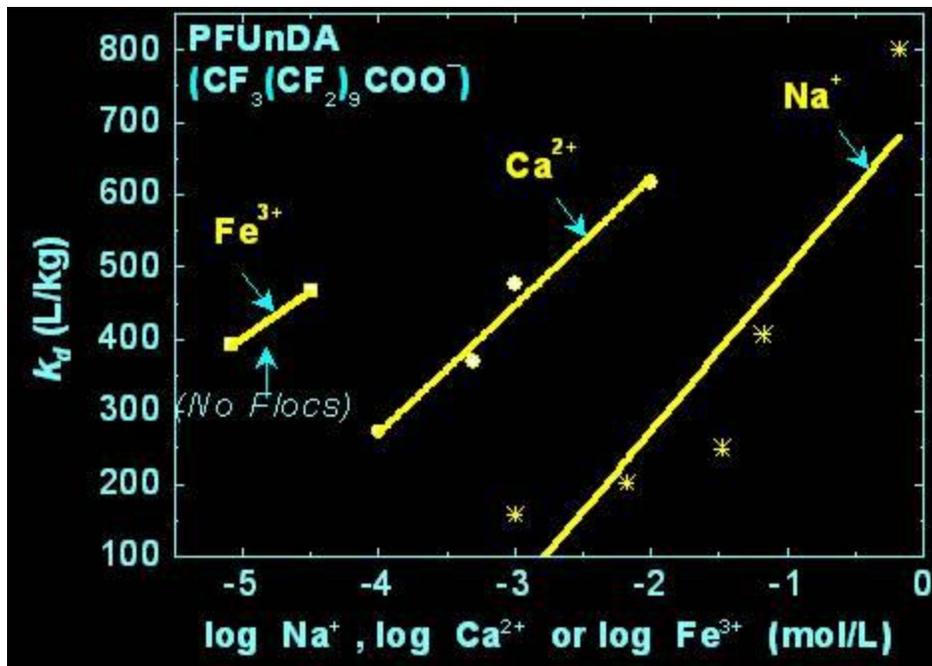


Figure 3. Effect of changing ionic strength and cations on PFC adsorption.

2) Publications: None, yet.

3) Student Support: This project has supported one Ph.D. student, Feng Xiao, in Civil Engineering at the University of Minnesota.

4) Presentations:

Do Perfluorinated Compounds act like a Solid in Competitive Adsorption onto a Solid/Water Interface? Feng Xiao, John Gulliver and Matt Simcik (presented by Feng Xiao) Poster presentation at the Gordon Research Conference on Environmental Sciences: Water in Plymouth New Hampshire June 2010.

5) Awards: Civil Engineering travel award to Feng Xiao.

6) Related Funding: None

## USGS Award No. G10AP00050 Data Management and GIS Analysis for the Ecosystem Technical Work Group

### Basic Information

<b>Title:</b>	USGS Award No. G10AP00050 Data Management and GIS Analysis for the Ecosystem Technical Work Group
<b>Project Number:</b>	2010MN276S
<b>Start Date:</b>	2/1/2010
<b>End Date:</b>	9/30/2010
<b>Funding Source:</b>	Supplemental
<b>Congressional District:</b>	
<b>Research Category:</b>	Biological Sciences
<b>Focus Category:</b>	None, None, None
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	

### Publications

There are no publications.

# Progress report for award G10AP0050, “Data Management and GIS support for the Ecosystem Technical Working group.”

**Author:** Terry Brown  
**Date:** May 7, 2010  
**Email:** [tbrown@nrri.umn.edu](mailto:tbrown@nrri.umn.edu)

Reporting period March 1, 2009 through February 28, 2010.

As the budget for this project became active February 17, 2010, some of the activity discussed occurred after the end of the reporting period.

This progress report follows the structure described on page three (section C.1.b) of the Assistance Award.

1. A comparison of actual accomplishments to the goals established for the period and any significant research findings.

In accordance with the goals listed on page two of the Assistance Award:

- Maps of regional and local areas of apparent vulnerability to water level change were produced.
- Collection and description (metadata generation) of data sets is ongoing as the study site list is finalized.
- Pending final site selection an updated Lake Superior wide bathymetry layer was built from from a newly digitized set of soundings not previously incorporated in bathymetry data sets. Assessment of the shoreline resolution of this data set continues.
- The spatial framework and parameterization necessary for the construction of the Performance Indicators was discussed and refined in large and small group meetings.
- Guidance for field collection of bathymetry data was provided.

2. Reasons why established goals were not met, if applicable.

N/A

3. Other pertinent information including, where appropriate, analysis and explanation of cost overruns or projected changes in the time or funding needed for completion of the project objectives.

N/A

4. One copy of any publication resulting from the USGS-supported project.

N/A

# Information Transfer Program Introduction

We have not funded Information Transfer projects.

<b>Student Support</b>					
<b>Category</b>	<b>Section 104 Base Grant</b>	<b>Section 104 NCGP Award</b>	<b>NIWR-USGS Internship</b>	<b>Supplemental Awards</b>	<b>Total</b>
<b>Undergraduate</b>	2	0	0	0	2
<b>Masters</b>	2	3	5	0	10
<b>Ph.D.</b>	5	0	0	0	5
<b>Post-Doc.</b>	0	0	0	0	0
<b>Total</b>	9	3	5	0	17

## Notable Awards and Achievements

William Arnold and co-PIs Raymond Hozalski and Paige Novak received funding for Evaluating and Monitoring BMPs with Networked Wireless Sensors from the Mississippi Watershed Management Organization and Minnehaha Creek Watershed District in the amount of \$167,460, January 2009-December 2011.

Jeffery M. Buth received an EPA STAR Fellowship.

Jacques Finlay and Martin Tsui received a National Science Foundation Doctoral Dissertation Improvement Grant, "Mercury Bioavailability and its Environmental Controls in a River Network." Finlay is a professor in the college of Environmental Engineering and Biotechnology and a faculty member in the Water Resources Science graduate program. Tsui is a Water Resources Science student.

Kaitlyn Steiger-Meister received \$5,654 through the 2008 University of Minnesota Consortium on Law and Values in Health, Environment & the Life Sciences for her project titled: Building clean water communities: Understanding how environmental policies can promote and coordinate community participation in the long-term management of local freshwater resources. The research will supplement the project by examining Wisconsin Lake Districts and the Wisconsin Lakes Partnership

Kaitlyn Steiger-Meister received \$100 from the International Association for Society and Resource Management for to present a paper on the project at the 14th International Symposium on Society and Resource Management.

Kaitlyn Steiger-Meister received a Graduate School Block Grant Fellowship in the amount of \$1,184 from the University of Minnesota to support her while she continues analysis and final write-up of research findings for publication.

Kaitlyn Steiger-Meister received a Graduate School Block Grant Fellowship in the amount of \$5,000 from the University of Minnesota to support her while she continues analysis and final write-up of research findings for publication.

Triclosan and Triclosan-derived Dioxins in the Mississippi Sediment Record project is complemented by a project from the National Science Foundation (2006-2009) to study the photolysis of triclosan and polybrominated diphenyl ethers in both the laboratory and in the field.

Feng Xiao received an Civil Engineering travel award.

The Role of Local Stakeholders in Water Resource Management: Characterization and diffusion of Minnesota Lake Improvement Districts project was, upon a recommendation from the review panel for this project, expanded to include a comparative analysis of Minnesota's Lake Improvement Districts with Wisconsin's Lake Districts.

Jeffery M. Buth received a 2008 ACS Graduate Student Award in Environmental Chemistry.

# Publications from Prior Years