

**Water Resources Center  
Annual Technical Report  
FY 2014**

# 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), University of Minnesota Extension, and Minnesota Agricultural Experiment Station (MAES). 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 and includes faculty and students across the Twin Cities campus as well as the University of Minnesota - Duluth. 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

In previous years, the Water Resources Center conducted a grants competition and selected awardees using a rigorous external review process. Due to the reduced funding in FY2013 caused by sequestration, the Water Resources Center took a different approach with its grants competition in FY2014 (it was burdensome to request proposal submissions when only one could be funded; the tremendous uncertainty in funding this year led us to award our funds in a more efficient and targeted manner.). We dedicated the 104B funds to student research training since training future water scientists is a top priority for USGS, the state of Minnesota, and the University of Minnesota. Support was offered in the form of Graduate Assistant Research grants of \$22,500 (the cost of one year salary for a graduate student). Grants requests were solicited from faculty to enhance ongoing or follow-on research related to current or past 104B funding. Successful applicants needed to provide evidence of one year of tuition benefits for the Research Assistant, how the student would enhance the research, and how this work fit with the USGS priorities for the WRRI program.

We received eight requests for funding, and selected three based on the criteria described above. An abstract of the research, the student, publications, and presentations related to the student's participation in the research are provided below. Also, any follow-on funding awarded to the PI is listed.

Building a Sustainable Governance Framework to Sustainably Manage Minnesota's Water Resources. Mae Davenport, P.I., Department of Forest Resources, University of Minnesota.

Research Assistant: Amanda Sames. She received her M.S. in Natural Resources Science and Management in 2014 as a result of this project.

Research Abstract: A study of key decision makers in the Cannon River Watershed was conducted by the Department of Forest Resources at the University of Minnesota. The study goal was to provide a deeper understanding of water governance and how governance regimes affect users, stakeholders and Minnesota's water resource from the perspectives of government officials and staff. Study data were gathered through key informant interviews with a sample of decision makers in two subwatersheds of the Cannon River Watershed intersecting six different counties. Fourteen interviews were conducted in 2013 and 2014. Study findings reveal diverse perceptions of a watershed scale approach to planning and managing resources. Several participants described using a watershed approach as a "complex issue" and one that is controversial among local governmental units (LGUs). Uncertainty was expressed around what a watershed approach would entail as a planning tool or a management and enforcement regime. One participant explained, "Politically I think keywords pop up and then things change, and I don't think people fully understand the complexity of it, to be quite honest. So shifting it again and again- I guess it maybe can't hurt to try, but I think there's very large issues that ultimately don't get addressed." Analysis revealed several perceived advantages and disadvantages of a watershed approach to water resource planning and management. Though a watershed approach would compel LGUs to work together to address problems and may increase opportunities for resource pooling, many decision makers we interviewed feared that centralization of power would result in inequalities in terms of relevance and value of decisions and actions to small communities or individuals within those communities.

Presentations: None.

Publications: Sames, A. (2014). The foundations of community capacity: An exploration of the role of fairness, trust and legitimacy in sustainable watershed management. M.S. Thesis. Natural Resources Science and Management, University of Minnesota, St. Paul, MN

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Related Funding Minnesota State Colleges and Universities (Minnesota Pollution Control Agency).  
Community readiness and engagement in the Watonwan Watershed. M. Davenport. \$14,736. 1/2/15-6/30/17.

Cannon River Watershed Partnership (Minnesota Pollution Control Agency 319). Building a culture of citizen engagement. M. Davenport, \$24,000 (UMN subcontract). 6/1/15-6/30/17.

Minnesota Sea Grant. Integrative social and hydrologic models for enhanced resiliency of coastal communities under extreme weather events. G. Host, Davenport, M., Enzler, S., Johnson, L. \$239,465, 9/1/14-8/31/16.

McKnight Foundation. Inspiring conservation action for nonpoint source pollution control: A guidebook. M. Davenport, Nelson, P., Kuphal, T. \$25,000, 9/15/14-9/14/15.

Minnesota Pollution Control Agency. Clean Water Performance Report: Social measures monitoring system. M. Davenport, \$35,000.

Ramsey-Washington Metro Watershed District, Capitol Region Watershed District, & Mississippi Watershed Management Organization. A Community Capacity Assessment for Stormwater Management in the Twin Cities Metro Area. M. Davenport, \$153,440, 8/15/13-8/14/15.

Geological Settings and Geochemical Processes that Release Arsenic to Glacial Aquifers in Minnesota. Brandy M. Toner, P.I., Department of Soil, Water, and Climate, University of Minnesota.

Research Assistant: Sarah Nicholas, Ph.D. candidate, Land and Atmospheric Science, Department of Soil, Water, and Climate. The project described is Sarah's dissertation project. Sarah collected cores, processed samples for wet-chemistry and X-ray absorption spectroscopy (XAS), and conducted XAS analysis of samples. Sarah presented data at state, national and international meetings, and is currently writing up two papers.

Research Abstract: West central Minnesota is a geographic nexus of drinking-water wells with arsenic (As) concentrations above the EPA maximum contaminant level (MCL) of  $10\mu\text{gL}^{-1}$ . Distribution of As-affected wells is heterogeneous with respect to location and well depth. The affected wells are constructed in glacial aquifers in the footprint of the Des Moines Lobe Glacial advance. Previous work comparing well construction with well water As concentrations found that wells with short screens set close to the aquitard (glacial till) were more likely to have elevated As concentrations. This suggested that the tills may be the source of As to the aquifers. We examined aquifer solids from four rotary-sonic cores collected in the area of the As affected wells, to compare As speciation in 1) the mid-aquitard till (away from the aquifer), 2) the contact till near the aquifer, and 3) the aquifer itself. Arsenic speciation in the solid phase is dominated by two end-members, As-bearing iron sulfides (reduced end-member) and As adsorbed to iron oxyhydroxide minerals in the form of arsenate ( $\text{HAsO}_4^{2-}$ ; oxidized end-member). These two species are often found within the same particle, showing that the solids are out of equilibrium with each other, as well as out of equilibrium with the water-chemistry conditions as measured in nearby wells. Lesser amounts of intermediate As(III) in the form of arsenite were also found. These discoveries support two mechanisms for As liberation to waters: incongruent oxidative dissolution of As-bearing sulfide minerals followed by desorption of As from the mineral to water. Dissolution of As-bearing sulfides produces dissolved As (as arsenate in these aquifers), dissolved iron, dissolved sulfate, and solid-phase authigenic iron oxyhydroxides. The sulfate and some of the dissolved As and iron remain in solution while some of the arsenate returns to the solid phase by adsorbing to minerals. The newly formed Fe oxyhydroxides present favorable binding sites for arsenate adsorption, as do other mineral groups present, especially clays. Desorption of arsenic in the pH range of the nearby wells is relatively insensitive to changes in oxidation-reduction potential (Eh), but occurs more rapidly with increasing pH and anion concentration (especially increases in phosphate). Measured Eh and pH, and As, iron, and

## Research Program Introduction

sulfate concentrations for wells close to the rotary sonic cores studied suggest that in at least two of the four cores dissolution and desorption are occurring simultaneously.

Publications: Nicholas, S.L., A.R. Knaeble, M.A. Marcus, L.G. Woodruff, M.E. Erickson, J.K. Lynch and B.M. Toner (in prep) Micro XAS as a quantitative tool to study the speciation of Arsenic in glacial aquifer samples. In preparation for submission to *Geochimica et Cosmochimica Acta* (pdf on request).

Nicholas, S.L., A.S. Gowan, A.R. Knaeble, L.G. Woodruff, M.L. Erickson, M.A. Marcus, J.K. Lynch and B.M. Toner (in prep) Arsenic speciation in Minnesota aquifer samples: the importance of sample preservation for environmental arsenic speciation. In preparation for *Environmental Science and Technology* (pdf on request).

Toner, B. M., S.L. Nicholas, and J.K. Coleman Wasik, 2014. Scaling up: Fulfilling the promise of X-ray microprobe for biogeochemical research. *Environmental Chemistry* 11, 4-9.

Toner, B.M., S.L. Nicholas, L.J. Briscoe, A.R. Knaeble, J.A. Berg, and M. L. Erickson (2011) Natural Sources of Arsenic in Minnesota Groundwater, *CURA Reporter* 41 (3-4) 3-10

Presentations: Nicholas, S.L., A.S. Gowan, A.R. Knaeble, L.G. Woodruff, M.L. Erickson, M.A. Marcus, and B.M. Toner. (2014). Solid-Phase Speciation of Arsenic as the Primary Control on Dissolved As Concentrations in a Glacial Aquifer System: Quantifying Speciation of Arsenic in Glacial Aquifer Solids with  $\mu$ XAS Mapping. H23E-0919. Annual Meeting of the American Geophysical Union, San Francisco, California, USA. <https://agu.confex.com/agu/fm14/meetingapp.cgi#Paper/11532>

Nicholas S.L., A. R. Knaeble, M.A. Marcus, L.G. Woodruff, M.L. Erickson and B.M. Toner. (2014). Quantification of Arsenic Species in Aquifer Solids using micro-XAS. *Goldschmidt Abstracts 2014* <http://goldschmidt.info/2014/abstracts/abstractView?abstractId=1783>

Nicholas, S.L., B.M. Toner, M.A. Marcus. (2012). Arsenic speciation in glacial aquifer sediments. Invited contribution to *Advanced Light Source, Experimental Systems Group "Research Highlights 10.3.2* (invited)

Nicholas, S.L., B.M. Toner, M.L. Erickson, A.R. Knaeble. (2012). Identifying the arsenic source in glacial aquifer sediments, west-central Minnesota, USA. *N – Goldschmidt Abstracts 2012 Mineralogical Magazine*, November 2012, v. 76, p. 2151-2178, published online 19 November 2012. <http://events.jpdl.com/pdf/e120624aAbstract01706.pdf>

Nicholas, S.L., B.M. Toner, M. L. Erickson, A. R. Knaeble, L. G. Woodruff, and G.N. Meyer. (2011). Speciation and mineralogy of arsenic in glacial sediments and their effect on arsenic concentration in groundwater, Minnesota, USA. *Geological Society of America Abstracts with Programs*, Vol. 43, No. 5, p. 673.

Nicholas, S.L., B.M. Toner, M.L. Erickson, L.G. Woodruff, A.R. Knaeble, and G.N. Meyer. (2011). Sources of arsenic from glacial aquifer sediments to well water in Minnesota, USA. *N – Goldschmidt Abstracts 2011 Mineralogical Magazine*, June 2011, v. 75, p. 1537. <http://minmag.geoscienceworld.org/content/75/3/1521.full.pdf+html?sid=ce8c61d6-0efa-4b0e-bb6e-494d28274188>

Nicholas, S.L. (2011). "Identifying Mineral Sources of Arsenic to Affecting West-Central Minnesota Well Water." 95th Annual Meeting of the Minnesota American Water Works Association, Duluth, MN, USA (invited)

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Nicholas, S.L. (2011). "Identifying mineral sources of arsenic affecting west-central Minnesota well-water: X-ray absorption spectroscopy sheds light on the mystery" North Dakota State University, Environmental and Conservation Sciences Seminar Series (invited)

Nicholas, S.L., M.L. Erickson, A.R. Knaeble, and B.M. Toner. (2010). Identifying mineral sources of arsenic affecting west-central Minnesota well-water: X-ray absorption spectroscopy sheds light on the mystery. Minnesota Water Resources Conference 2010 Final Program and Book of Abstracts, p.33.

Nicholas, S.L., L.J. Briscoe, M.L. Erickson, C.E. Jennings, B.A. Lusardi, A.R. Knable, and B.M. Toner. (2009). Molecular environmental science at the landscape scale: X-ray absorption spectroscopy studies of arsenic geochemistry in glacial tills. Geological Society of America Abstracts with Programs, Vol. 41, No. 7, p. 461.

Predicting Erosional Hotspots in North Shore Streams from High-resolution Datasets. K. Gran, P.I., Department of Geological Sciences, University of Minnesota – Duluth.

Research Assistant: Tiffany Sprague, M.S., Water Resources Science, University of Minnesota. Tiffany assisted with expanding the scope of the original 104B project to additional streams up the North Shore of Lake Superior. She also developed a methodology for calculating stream power as a continuous running variable along the main stem channels (rather than just every 25 meters). The hot spot model was applied with a higher threshold than previously used, and applied to areas near high bluffs. Tiffany is also monitoring discharge in Duluth-area streams to investigate the role of upland land use on hydrologic response. She expects to defend her thesis in 2016.

Research Abstract: Streams along the North Shore of Lake Superior in Minnesota meander across low-gradient uplands increasing in slope as they approach the lake downstream. The increase in slope with distance downstream drives a sharp increase in stream power and thus in fluvial erosion. Where rivers cut through glacial tills and glaciolacustrine deposits, there is a high potential for fine sediment erosion as stream power increases. By using high-resolution lidar topographic data coupled with soils and bedrock maps, we have developed a predictive model to delineate where along the channel is the highest risk for erosion. We coupled calculations of topographic and geometric drivers (stream power, high bend curvature) with data on sediment availability and erodibility (high bluff locations, bedrock outcrop maps) to develop a threshold-based erosional hot spot model. The model was developed in Amity Creek in east Duluth, and expanded to other streams in the Duluth area and up the North Shore. The individual predictor variables were compared to field maps of erosion that occurred during a 500-year flood event in June 2012 to determine which variables correlated with magnitude of erosion in the flood. The resulting model achieved an accuracy of over 80% in most watersheds when compared to erosion from the high-magnitude 2012 event. Lower thresholds may be more appropriate for predicting reaches susceptible to erosion in typical bankfull events.

Publications: Host, G., T. Sprague, P. Meysembourg and K. Gran. 2015. LiDAR-based bluff assessment for coastal land use planning. NRRRI Technical Report: NRRRI/TR-2015/17. 17 p.

Presentations: Sprague, T., K. Gran, T. Hollenhorst, and G. Host. Oct 2014. Hydrologic Conditioning of Urban Watersheds: How Much is Enough? Poster Presentation, MN GIS/LIS Annual Conference. Rochester, MN.

# Understanding Pesticide Photolysis in Prairie Potholes for Water Management Strategies

## Basic Information

<b>Title:</b>	Understanding Pesticide Photolysis in Prairie Potholes for Water Management Strategies
<b>Project Number:</b>	2012MN344G
<b>USGS Grant Number:</b>	G12AP20153
<b>Start Date:</b>	9/1/2012
<b>End Date:</b>	8/31/2014
<b>Funding Source:</b>	104G
<b>Congressional District:</b>	MN05
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Surface Water, Non Point Pollution, Hydrology
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	William Alan Arnold

## Publications

1. Sleighter, R. L., Y-P. Chin, W.A. Arnold, P.G. Hatcher, A.J. McCabe, B.C. McAdams and G.C. Wallace. 2014. Evidence of Incorporation of Abiotic S and N into Prairie Wetland Dissolved Organic Matter. *Environmental Science & Technology Letters*. 2014, 1, 345-350.
2. Arnold, W.A. 2014. One Electron Oxidation Potential as a Predictor of Rate Constants of N-containing Compounds with Carbonate Radical and Triplet Excited State Organic Matter. *Environmental Science Processes & Impacts*, 16, 832-838.
3. Karpuzcu, M. E. and W.A. Arnold. 2014. Phototransformation of Pesticides in Prairie Potholes: Effect of Dissolved Organic Matter in Triplet-induced Oxidation. 248th ACS National Meeting and Exposition, San Francisco, CA, United States, August 10-14. ENVR-337.
4. McCabe, A. J. and W.A. Arnold. 2014. Exploring Seasonal Dynamics Between Water Chemistry and Photochemical Transformations of Pesticides in Natural and Reconstructed Wetlands. 248th ACS National Meeting & Exposition, San Francisco, CA, United States, August 10-14, 2014. ENVR-516.
5. Invited Seminar: Arnold, W.A. 2015. Pesticide Processing and Organic Matter Composition in Prairie Pothole Wetlands, University of California-Riverside, Department of Chemical and Environmental Engineering, Riverside, CA, February, 2015.
6. Invited Seminar: Arnold, W.A. 2014. Pesticide Processing and Organic Matter Composition in Prairie Pothole Wetlands. University of Wisconsin-Madison, Department of Civil & Environmental Engineering, Madison, WI, October.
7. Invited Seminar: Arnold, W.A. 2014. Abiotic Transformation of Pesticides in Prairie Potholes, Woods Hole Oceanographic Institution, Marine Chemistry & Geochemistry, Woods Hole, MA, January, 2014.
8. Invited Seminar: Arnold, W.A. 2013. Abiotic Transformation of Pesticides in Prairie Potholes, Minnesota State University-Mankato, October, 2013.
9. Invited Seminar: Arnold, W.A. 2012. Abiotic Transformation of Pesticides in Prairie Potholes, University of Colorado-Boulder, November 30, 2012.

# 2012MN344G Understanding Pesticide Photolysis in Prairie Potholes for Water Management Strategies

## 1) Research Synopsis:

### Background

Prairie potholes are severely and detrimentally impacted by farming, climate change, and oil exploration. In considering responsible water resource management in the prairie pothole region, a foremost concern is pesticide contamination of drinking water reservoirs and groundwater wells. The primary goal of this research is to quantify relative importance of pesticide photolysis processes in prairie pothole wetlands such that appropriate, adaptive water management strategies can be developed to handle agricultural runoff and drainage. This includes both the design of constructed wetlands and the optimization of transient drainage features. Prairie potholes have unique water chemistry (e.g., up to 2 g  $\text{SO}_4^{2-}/\text{L}$ ; up to 2 mg  $\text{NO}_3^-/\text{L}$ ; and 20 – 40 mg C/L). They are also shallow, typically less than 2 m deep. Taken together, these characteristics suggest that direct and indirect photochemical processes may be active in transforming pesticides in prairie potholes. The desired outcomes of this study are models that predict observed photochemical rates of pesticide loss based on simple water quality measurements (e.g., absorbance spectra, dissolved organic carbon and nutrient concentrations, pH, and alkalinity).

### Materials and Methods

#### *Sampling Sites*

Prairie pothole surface waters were collected from 6 sites beginning in July 2012. Four sites were located in the Cottonwood Lake study area (CLSA) near Jamestown, ND, and two sites were located in Glacial Ridge Wildlife Refuge (GRWR) near Crookston, MN. Additionally, three agricultural drainage samples were collected from a single site near Tracy, MN. The CLSA sites included a groundwater recharge wetland, a flow-through wetland (with direct cropland runoff input), and two groundwater discharge wetlands. The GRWR sites have been restored since 2007 and do not have defined hydrologic regimes. Sites were selected to allow comparisons between restored and native wetlands as well as between wetlands receiving and not receiving direct agricultural runoff. Samples were collected on a seasonal basis throughout the growing season because prairie wetland water chemistry (e.g., dissolved organic matter, DOM, quality) is known to vary on a seasonal basis. Table 1 contains sampling location descriptions and the dates of sample collection.

#### *Sample Collection and Characterization*

Samples were collected as grab samples in 4-L glass bottles, filtered through 0.22  $\mu\text{m}$  mixed cellulose membrane filters (Millipore), and stored at 4 °C until use. Samples collected in July and November 2012 were stored frozen. Before use, these samples were thawed and noticeable precipitate was dissolved by raising the pH with solid NaOH and subsequently readjusting to the original pH with 0.5 N  $\text{H}_2\text{SO}_4$ .

Sample collection bottles, filtration apparatuses and experimental glassware were cleaned with Alconox (except for glass frits), rinsed with Milli-Q water (18 M $\Omega$ , Millipore), and either combusted at 550°C for >4 hours or autoclaved.

Anions were measured using a Metrohm 761 Compact IC. Dissolved organic carbon (DOC) was measured using a Shimadzu TOC-L Total Organic Carbon Analyzer. Alkalinity was measured by bromocresol titration, pH was measured using a WTW 340i meter with a Senorex combination pH electrode, conductivity was measured with an Engineered Systems and Design conductivity/TDS meter, and dissolved oxygen was measured with a YSI DO200 meter.

**Table 1.** Sampling site descriptions, locations, and sampling dates

Site I.D.	Description	Location (coordinates)	Sampling Dates
P1	Permanent emergent wetland, groundwater discharge	Cottonwood Lakes Study Area (47°5'51"N, 99°5'58"W)	July-2012, Nov-2012, May-2013, July-2013, Nov-2013, May-2014, Aug-2014, Nov-2014
P7	Permanent emergent wetland, groundwater flow-through, cropland runoff (corn/soybean)	Cottonwood Lakes Study Area (47°5'43"N, 99°5'57"W)	July-2012, Nov-2012, May-2013, July-2013, Nov-2013, May-2014, Aug-2014, Nov-2014
P8	Permanent emergent wetland, groundwater discharge	Cottonwood Lakes Study Area (47°5'56"N, 99°6'16"W)	July-2012, Nov-2012, May-2013, July-2013, Nov-2013, May-2014, Aug-2014, Nov-2014
T9	Temporary emergent wetland, groundwater recharge, pastureland influence (cattle)	Cottonwood Lakes Study Area (47°5'47"N, 99°5'28"W)	July-2012, May-2013, July-2013, Nov-2013, May-2014, Aug-2014, Nov-2014
R1	Restored emergent wetland	Glacial Ridge Wildlife Refuge (47°42'2"N, 96°18'48"W)	May-2013, July-2013, Nov-2013, May-2014, Aug-2014, Nov-2014
R2	Restored emergent wetland, cropland runoff (corn/soybean)	Glacial Ridge Wildlife Refuge (47°44'2"N, 96°20'7"W)	May-2013, July-2013, Nov-2013, May-2014, Aug-2014, Nov-2014
D1	Drain tile inlet (corn/soybean)	Tracy, MN (44°9'22"N, 95°38'3"W)	Mar-2013, June-2014(2)

### *Photochemical Experiments*

All photochemical experiments were performed using an Atlas Suntest CPS+ solar simulator with an arc xenon lamp and a 290-nm wavelength cutoff filter. The intensity was set to 350 W/m<sup>2</sup>. This value was chosen because it closely matches the average summer daily irradiance, approximately 400 W/m<sup>2</sup>, in Jamestown, ND (this average was calculated from modeled data for months June, July, and August in 2005 from the National Solar Radiation Database, National Renewable Energy Laboratory, 2012). Consistency in light intensity was assessed using p-nitroacetophenone and p-nitroanisole actinometry as well as by conducting repeated experiments. All reactions were conducted in 13×100 mm quartz test tubes (Ace Glass) covered with combusted aluminum foil sealed with rubber septa (Suba Seal). Test tubes were held at a 30° angle from horizontal (Leifer, 1988). Sub-samples were removed from test tubes at selected time points and analyzed with either an Agilent 1100 high pressure liquid chromatograph (HPLC) with a multiwave and fluorescence detector or with an Agilent 1200 HPLC with a diode array detector. Additional experimental details are provided below with the results.

## **Results**

### *Water Chemistry Parameters*

Water chemistry parameters of collected prairie pothole surface waters are summarized in tables 2 and 3. Table 2 shows a times series to demonstrate how parameters change throughout the 2013 growing season. Table 3 shows average values for all surface waters collected.

**Table 2.** Water chemistry parameters throughout the 2013 growing season

<i>Sample I.D.</i>	<i>pH</i>	<i>DOC (mg C/L)</i>	<i>Conductivity (<math>\mu</math>S/cm)</i>	<i>TDS (mg/L)</i>	<i>DO (ppm)*</i>
<b>R1</b>					
May 2013	7.5	21.6	577	402	3.8 (15)
July 2013	7.5	29.7	847	591	7.1 (20)
Nov. 2013	8.1	25.4	816	570	14.5 (2)
<b>R2</b>					
May 2013	7.3	19.9	300	204	4.7 (18)
July 2013	8.0	32.6	524	366	13.3 (24)
Nov. 2013	7.1	33.2	738	513	10.1 (10)
<b>P7</b>					
May 2013	8.3	30.1	910	636	8.3 (15)
July 2013	9.2	30.7	1030	718	16.1 (22)
Nov. 2013	8.9	31.5	1390	794	19.4 (2)
<b>T9</b>					
May 2013	7.8	19.4	270	230	8.5 (22)
July 2013	9.6	39.1	335	237	12.9 (20)
Nov. 2013	8.1	22.4	328	230	—

\*Measured only at the time of collection; number in parentheses indicates water temperature in °Celsius.

**Table 4.** Average water quality parameters of collected samples from each site

<i>Sample I.D.</i>	<i>pH</i>	<i>Conductivity (<math>\mu</math>S/cm)</i>	<i>TDS (mg/L)</i>	<i>DO (ppm)*</i>
<b>P1</b>	8.5	3512	2248	12
<b>P7</b>	8.7	1070	713	12
<b>P8</b>	8.1	1522	1067	11
<b>T9</b>	8.3	374	266	8
<b>R1</b>	7.6	764	533	8
<b>R2</b>	7.4	760	530	9
<b>D1</b>	7.7	2037	1398	—

\*Measured only at the time of collection

*Rates of herbicide phototransformation: Estimated half-lives in wetlands*

Herbicide photolysis rates were measured in four prairie potholes collected during two seasons, July and November 2013 (P1 from July 2012). Herbicide loss was monitored over 4 hours of irradiation using simulated sunlight. The data were fit according to pseudo-first order kinetics and half-lives were computed according to equations 1 and 2. Experimental half-lives were transformed to half-lives that are more applicable to conditions in a wetland by first multiplying

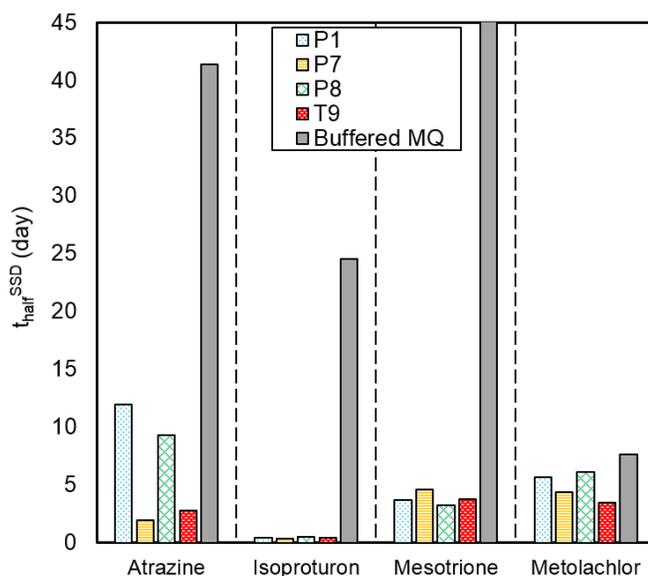
the half-lives by a constant of 2.2 to account for the difference in rates of photolysis between test tubes and flat dishes (Leifer, 1988 and references therein). Second, half-lives were divided by 11, assuming 11 hours of sunlight during a typical summer sunny day ( $t_{half}^{SSD}$ ; equation 3).

$$\frac{d[P]}{dt} = -k_{obs}[P] \quad (1)$$

$$t_{half} = \frac{\ln 2}{k_{obs}} \text{ in hours} \quad (2)$$

$$t_{half}^{SSD} = \left( \frac{2.2}{11 \frac{hrs}{day}} \right) t_{half} \quad (3)$$

The results are summarized in Figure 1. All photochemical half-lives were determined under the same 350 W/m<sup>2</sup> simulated sunlight. Consequently, half-lives do not account for changes in sunlight intensity with season.



**Figure 1.** Estimated photochemical half-lives of atrazine, isoproturon, mesotrione, and metolachlor in field waters collected from CLSA. The bars represent an average half-life of the herbicide as measured in field waters collected during the July and November 2013 (P1 from July 2012).

Key points:

- Average photochemical half-lives on summer sunny days in field waters (according to equation 3):
  - Atrazine: 6.5 days (1.4 – 17 days)
  - Isoproturon: 4.8 hours (3.2 – 6 hours)
  - Mesotrione: 3.8 days (3.2 – 5.8 days)
  - Metolachlor: 4.9 days (3.2 – 7.6 days)

- Atrazine, isoproturon, and mesotrione are photochemically transformed more quickly in field water than buffered Milli-Q water, suggesting that indirect photochemical reactions are important for their observed loss.
- Metolachlor is photochemically transformed at approximately the same rate in field water as in buffered Milli-Q water, suggesting direct photochemical reactions are primarily responsible for the observed loss of metolachlor.

#### *Atrazine direct and indirect photolysis*

To investigate the indirect photochemical processes responsible for the observed acceleration of atrazine in field water as compared to buffered Milli-Q water, a series of quencher experiments were performed in 0.22  $\mu\text{m}$  filtered field waters collected during the 2013 growing season from wetlands P7, T9, R1, and R2. Atrazine was spiked into field waters to a concentration of 10  $\mu\text{M}$  and its photochemical loss was monitored under simulated sunlight for at least 20 hours. One of four quenchers or scavengers was added to the field waters to assess the importance of triplet excited state dissolved organic matter ( $^3\text{DOM}^*$ ), hydroxyl radical ( $^{\bullet}\text{OH}$ ), singlet oxygen ( $^1\text{O}_2$ ), and carbonate radical ( $\text{CO}_3^{\bullet-}$ ) on the overall photochemical loss of atrazine. Sorbic acid was used as a quencher of relatively high energy  $^3\text{DOM}^*$  (~250 kJ/mol), isopropanol (IPA) was used as a scavenger of  $^{\bullet}\text{OH}$ , L-histidine was used as a quencher of  $^1\text{O}_2$ , and N,N-dimethylaniline was used as a scavenger of  $\text{CO}_3^{\bullet-}$ . The individual contributions of each photochemically produced reactive species to the overall rate of atrazine loss was determined by subtracting the pseudo-first order reaction rate constant for the loss of atrazine in the presence of the respective quencher or scavenger from the rate constant in the absence of quenchers or scavengers.

The pseudo-first order rate constant for the photochemical loss of atrazine can be written as the summation of the pseudo-first order rate constant for direct photochemical loss and second order rate terms for reactions with  $^3\text{DOM}^*$ ,  $^{\bullet}\text{OH}$ ,  $^1\text{O}_2$ , and  $\text{CO}_3^{\bullet-}$  (equation 4). The final pseudo-first order term ( $k'$ ) describes any remaining unquantified photochemical processes.

$$k_{obs} = k_{dir} + k_{\bullet OH}[\bullet OH]_{ss} + k_{CO_3^{\bullet-}}[CO_3^{\bullet-}]_{ss} + k_{^1O_2}[^1O_2]_{ss} + k_{^3DOM^*}[^3DOM^*]_{ss} + k' \quad (4)$$

When the quenchers and scavengers are added, ideally a single reactive species is eliminated. As an example, when isopropanol is added to solution,  $^{\bullet}\text{OH}$  is effectively completely scavenged and is not available to react with atrazine (equation 5).

$$k_{obs,IPA} = k_{dir} + k_{CO_3^{\bullet-}}[CO_3^{\bullet-}]_{ss} + k_{^1O_2}[^1O_2]_{ss} + k_{^3DOM^*}[^3DOM^*]_{ss} + k' \quad (5)$$

The pseudo-first order rate constant for the reaction between atrazine and  $^{\bullet}\text{OH}$  (i.e.,  $k_{\bullet OH}[\bullet OH]_{ss}$ ) is determined from the difference between equations 4 and 5, shown in equation 6.

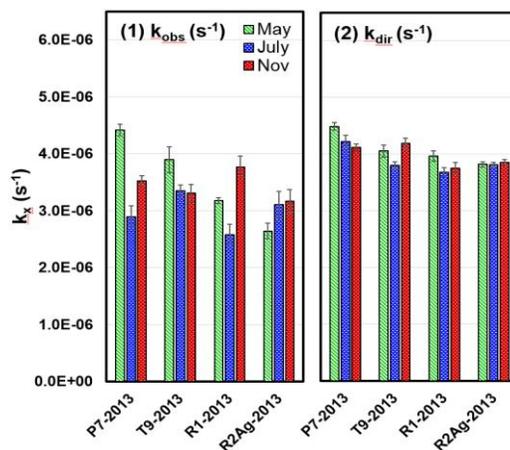
$$k_{obs} - k_{obs,IPA} = k_{\bullet OH}[\bullet OH]_{ss} \quad (6)$$

By completing a similar analysis for the remaining scavengers and quenchers, pseudo-first order rate terms can be computed for each indirect process and determine their overall contribution to  $k_{obs}$ .

The results of these experiments indicate that direct photolysis is the primary transformation pathway of atrazine. Figure 2 shows a comparison between the observed pseudo-first order rate constants ( $k_{\text{obs}}$ ) for atrazine photolysis in field waters and the pseudo-first order rate constants for atrazine's direct photochemical loss ( $k_{\text{dir}}$ ; a product of a screening factor and the pseudo-first order rate constant observed in Milli-Q water). It is important to note that these results do not necessarily exclude the possibility of indirect photochemical reactions. It may be that indirect processes are important, but their entire role cannot be captured with quencher or scavenger experiments due to interferences caused by the nonselectivity of the quenchers and scavengers.

**Key points:**

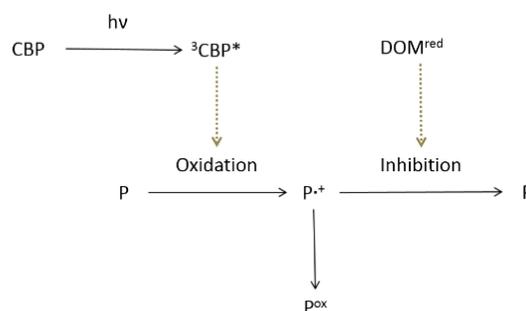
- The observed pseudo-first order rate constant,  $k_{\text{obs}}$ , is comparable to  $k_{\text{dir}}$ , suggesting that atrazine is primarily transformed through direct photolysis. Involvement of indirect processes cannot be eliminated, however.
- Because in most instances  $k_{\text{dir}}$  is greater in magnitude than  $k_{\text{obs}}$ , it is indicative that DOM or another chemical component is inhibiting the photochemical transformation of atrazine.
- These results are consistent with Lam et al. (2003), but contradict results presented above from the 4-hour irradiation experiments. This highlights the necessity of conducting experiments until approximately one half-life.



**Figure 2.** Comparing the observed pseudo-first order rate constant for atrazine photolysis in wetland surface water and the computed first order rate constant for direct photolysis of atrazine.

*Antioxidant properties of DOM in triplet-induced indirect photochemical transformation of herbicide contaminants*

To investigate inhibition of photochemical transformation of herbicides, experiments were conducted to investigate the ability of dissolved natural organic matter to inhibit excited triplet state induced reactions with contaminant herbicides. Canonica and Laubscher (2008) showed that natural dissolved organic carbon could inhibit transformation of organic contaminants by using an excited triplet-state model, 4-carboxybenzophenone (CBP). From their analysis, it is expected that natural DOM could also inhibit transformation of contaminants by  $^3\text{DOM}^*$  (or other photochemically-produced reactive species). A theoretical scheme is shown in Figure 3.



**Figure 3.** Illustration of the theoretical mechanism by which DOM inhibits phototransformation of a contaminant, P.

Following the example of Canonica and Laubscher (2008), the ability of natural organic matter in prairie pothole surface waters to inhibit excited triplet state induced transformation was assessed using the model, CBP. CBP was spiked into 0.22  $\mu\text{m}$  filtered field to a concentration of 40  $\mu\text{M}$  with 10  $\mu\text{M}$  of either atrazine, isoproturon, mesotrione, or metolachlor. Photolysis experiments were conducted as described previously.

Inhibition was quantified with an inhibition factor (I.F.), defined in equations 7 – 9. Where  $k_{\text{CBP,FW}}$  is the pseudo-first order rate constant for loss of herbicide in field water in the presence of CBP;  $k_{\text{FW}}$  is the rate constant for loss of herbicide in field water;  $k_{\text{CBP,FW}}^{\text{corr}}$  is the rate constant for the reaction between CBP and herbicide with dissolved organic carbon present, excluding direct and other indirect photochemical reactions;  $k_{\text{CBP,MQ}}$  is the rate constant for the loss of herbicide in Milli-Q water in the presence of CBP;  $k_{\text{MQ}}$  is the rate constant for the loss of herbicide in Milli-Q water alone; and  $k_{\text{CBP,MQ}}^{\text{corr}}$  is the rate constant for the reaction between CBP and herbicide without dissolved natural organic matter present.

$$k_{\text{CBP,FW}}^{\text{corr}} = k_{\text{CBP,FW}} - k_{\text{FW}} \quad (7)$$

$$k_{\text{CBP,MQ}}^{\text{corr}} = k_{\text{CBP,MQ}} - k_{\text{MQ}} \quad (8)$$

$$IF = \frac{k_{\text{CBP,FW}}^{\text{corr}}}{k_{\text{CBP,MQ}}^{\text{corr}}} \quad (9)$$

An I.F. equal to 1 signifies that dissolved natural organic matter does not affect triplet-induced herbicide photochemical loss, an I.F. greater than 1 indicates that dissolved natural organic matter enhances triplet-induced herbicide photochemical loss, and an I.F. less than 1 indicates that dissolved natural organic matter inhibits triplet-induced herbicide photochemical loss.

Key findings:

- The excited triplet state induced loss of atrazine is inhibited by dissolved natural organic matter.
- Inhibition of triplet induced loss of isoproturon is minimal.
- The triplet induced loss of mesotrione is inhibited by DOM, but to a lesser extent as compared to atrazine.
- The triplet induced loss of metolachlor, in general, is enhanced by DOM. This phenomenon does not currently have an explanation, but may be due to a stabilizing interaction between metolachlor's reaction intermediate(s) and DOM.
- The inhibition factors of isoproturon, mesotrione, and metolachlor show more variability than atrazine with season.

*Models for photochemically produced reactive species*

The goal of this portion of the project is to develop kinetic and empirical models that can be used to predict quantum yields and steady-state concentrations of photochemically produced reactive intermediates.

Following the example of Dalrymple et al. (2010), a model was developed to predict the quantum yield of  $^1\text{O}_2$  from the E2/E3 ratio ( $\text{Abs}_{254}/\text{Abs}_{365}$ ). The steady-state concentrations of  $^1\text{O}_2$  were measured using the probe furfuryl alcohol (FFA) (Haag et al., 1984). In solution exposed to light, FFA degrades preferentially by reaction with  $^1\text{O}_2$  with a known second order rate constant (Haag et al., 1984). FFA was spiked into sample water to a concentration of 20  $\mu\text{M}$ . Solutions were irradiated for four hours and subsamples were collected to determine the rate of FFA loss. The steady-state concentration of  $^1\text{O}_2$  is determined with the integrated form of equation 10.

$$\frac{d[\text{FFA}]}{dt} = -k_{\text{FFA}, ^1\text{O}_2} [^1\text{O}_2]_{ss} [\text{FFA}] \quad (10)$$

The quantum yield of  $^1\text{O}_2$  production was computed as the ratio of the rate of formation of singlet oxygen ( $R_f$ ) to the rate of light absorption ( $R_a$ ; equation 11).

$$\Phi = \frac{R_f}{R_a} \quad (11)$$

At steady-state, the rate of singlet oxygen formation and the rate of singlet oxygen deactivation ( $R_d$ ) are equal. The rate of deactivation is primarily controlled by a physical interaction with water and can be readily calculated because the rate constant,  $k_d$ , is well-defined (equation 12).

$$R_f = R_d = \frac{d[^1\text{O}_2]}{dt} = k_d [^1\text{O}_2]_{ss} \quad (12)$$

The rate of light absorption was computed following the example of Sharpless et al. (2014).

Key points:

- The quantum yield of singlet oxygen production appears to increase with E2/E3. Further work is necessary to compare errors associated with predicting steady-state concentrations with the developed model and measuring their concentrations.
- Work is ongoing to develop predictive models for  $\text{CO}_3^{\cdot-}$ ,  $\cdot\text{OH}$ , and  $^3\text{DOM}^*$  quantum yields and steady-state concentrations.

#### *High resolution mass spectrometry of prairie pothole dissolved organic matter*

Because DOM is an integral photosensitizer in prairie pothole surface water photochemistry, its molecular-level character was investigated using Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS). Samples submitted for FTICR MS analysis were collected in May 2013 from the CLSA sites. The DOM was extracted using PPL solid-phase extraction cartridges. Sleighter et al. (2014) contains further details of the analysis.

Key points:

- DOM showed high levels of organic sulfur and nitrogen species as compared to other surface water systems.

- Low FTICR MS signals of autochthonously produced DOM and high concentrations of reduced inorganic sulfur and nitrogen species (e.g., sulfides and ammonium) suggests that organic sulfur and nitrogen species arise from abiotic incorporation.
- This unique incorporation of electron rich species may explain the observed inhibition of herbicide photochemical transformation.

## References

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- Sleighter, R. L., Chin, Y.-P., Arnold, W. a., Hatcher, P. G., McCabe, A. J., McAdams, B. C., & Wallace, G. C. (2014). Evidence of Incorporation of Abiotic S and N into Prairie Wetland Dissolved Organic Matter. *Environmental Science & Technology Letters*, 1(9), 345–350. doi:10.1021/ez500229b

## 2) Publications:

- Sleighter, Rachel L.; Chin, Yu-Ping; **Arnold, William A.**; Hatcher, Patrick G.; **McCabe, Andrew J.**; McAdams, Brandon C.; Wallace, Grant C. Evidence of Incorporation of Abiotic S and N into Prairie Wetland Dissolved Organic Matter. *Environ. Sci. Technol. Lett.* **2014**, 1, 345-350.
- Publication inspired by this work:

Arnold, William A. One electron oxidation potential as a predictor of rate constants of N-containing compounds with carbonate radical and triplet excited state organic matter. *Environ. Sci. Processes Impacts* **2014**, *16*, 832-838.

### 3) Student Support:

- Andrew J. McCabe (Ph.D. candidate, 2012 – present)
- Dr. M. Ekrem Karpuzcu (Post Doc, 2014)

### 4) Presentations:

- Karpuzcu, M. Ekrem; Arnold, William A. Phototransformation of Pesticides in Prairie Potholes: Effect of Dissolved Organic Matter in Triplet-induced Oxidation. 248th ACS National Meeting and Exposition, San Francisco, CA, United States, August 10-14, 2014, ENVR-337.
- McCabe, Andrew J.; Arnold, William A. Exploring seasonal dynamics between water chemistry and photochemical transformations of pesticides in natural and reconstructed wetlands. 248th ACS National Meeting & Exposition, San Francisco, CA, United States, August 10-14, 2014, ENVR-516.
- Invited Seminar: William A. Arnold. *Pesticide processing and organic matter composition in prairie pothole wetlands*, University of California-Riverside, Department of Chemical and Environmental Engineering, Riverside, CA, February 2015.
- Invited Seminar: William A. Arnold. *Pesticide processing and organic matter composition in prairie pothole wetlands*. University of Wisconsin-Madison, Department of Civil & Environmental Engineering, Madison, WI, October, 2014.
- Invited Seminar: William A. Arnold. *Abiotic Transformation of Pesticides in Prairie Potholes*, Woods Hole Oceanographic Institution, Marine Chemistry & Geochemistry, Woods Hole, MA, January 2014.
- Invited Seminar: William A. Arnold. *Abiotic Transformation of Pesticides in Prairie Potholes* Minnesota State University-Mankato, October 2013.
- Invited Seminar: William A. Arnold. *Abiotic Transformations of Pesticides in Prairie Potholes*, University of Colorado-Boulder, November 30, 2012.

### 5) Awards:

- 2015 Graduate Student Awards in Environmental Chemistry, Awarded to Andrew J. McCabe from the Division of Environmental Chemistry of the American Chemical Society

### 6) Related Funding:

- *Project Title:* Solar Driven Transformation of Pesticides, Pharmaceuticals, Contaminants  
*Sponsor:* Environment and Natural Resources Trust Fund, Legislative-Citizen Commission on Minnesota Resources  
*Amount:* \$291,000  
*P.I.:* Dr. William A. Arnold  
*Project Period:* July 1, 2014 – June 30, 2017

- Moos Graduate Research Fellowship in Aquatic Biology, Summer 2013 fellowship awarded to Andrew J. McCabe from the College of Biological Sciences, University of Minnesota

# Information Transfer Program Introduction

We did not fund any information transfer projects with our WRII funds.

# USGS Summer Intern Program

None.

<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>	1	0	0	0	1
<b>Masters</b>	5	0	0	0	5
<b>Ph.D.</b>	0	1	0	0	1
<b>Post-Doc.</b>	0	1	0	0	1
<b>Total</b>	6	2	0	0	8

## Notable Awards and Achievements

Minnesota Governor's Geospatial Commendation award was presented at the Minnesota Annual GIS/LIS Conference in Rochester, Minnesota, October 2, 2014 to The Minnesota Elevation Mapping Project. Certificates were presented to representatives of the Minnesota Department of Natural Resources, Minnesota Geospatial Information Office, Minnesota Department of Transportation, the University of Minnesota, and United States Geological Service for their contributions to the project.

Les Everett of the Water Resources Center (WRC) accepted the certificate for the UM. Everett led the legislative request to obtain the project funding, and with Ann Lewandowski (WRC), led the training program for local conservation staff on use of the LiDAR derived elevation data for conservation applications.

Larry Baker (WRS faculty, BBE) has been appointed to the Environmental Protection Agency's Board of Scientific Counselors' (BOSC) Safe and Sustainable Water Resources Subcommittee, effective September 4, 2014.

Jake Bailey (WRS faculty, Earth Sciences) received a Sloan Research Fellowship, recognizing his research in geobiology.

Ryan Birkemeier (WRS student) received a travel grant to attend the Upper Midwest Stream Restoration Symposium in LaCrosse, WI, February 23-26, 2014 to present Baseflow Restoration in Minnehaha Creek: Watershed with Stormwater Infiltration.

Brad Gordon (WRS student) was awarded a Graduate Research Fellowship from the MN Drive Initiative for Global Food Supply. His research project is Impact of Vegetative Quality on Stream Bank Erosion and Wetland Storage. The fellowship covers stipend for one year and funds research.

Sergei Katsev (WRS faculty, UMD Physics and LLO) visited the University of Western Australia July-August, 2013 as a Gledden Visiting Fellow.

Lucinda Johnson (WRS faculty, NRRI) was appointed in March 2014 to the International Joint Commission's Science Advisory Board to serve a three year term.

Hongyu Li (WRS student) received a travel grant to attend the Ocean Sciences Meeting in Honolulu, Hawaii, February 23-28, 2014, to present The Complementary Use of Wet Extraction Methods with FTIR to Investigate the Seasonal Changes of Sinking Particulate Organic Matter in Lake Superior.

Jiyong Li (WRS student) received a travel grant to attend the Ocean Sciences Meeting in Honolulu, Hawaii February 23-28, 2014, and presented Large lakes as analogues for sediment cycling of carbon and nitrogen in coastal and deep ocean.

Jane Mazack (WRS student) was awarded a Sawyer Seminar Graduate Fellowship from the Institute for Advanced Study for the 2014-2015 academic year. The Sawyer Seminar (<http://ias.umn.edu/programs/sawyer-seminar/>) is funded through the Andrew W. Mellon Foundation and is entitled: Making the Mississippi: Formulating new water narratives for the twenty-first century and beyond. Mazack also received a travel grant to attend the Joint Aquatic Science Meeting in Portland, Oregon, May 18-23, 2014 where she presented Overwinter emergence dynamics of adult Chironomidae [Insecta: Diptera] in groundwater-fed streams of southeastern Minnesota.

Leah Smith (WRS student) was awarded a 25 percent Research Assistant position as the Assistant for the Graduate Review & Improvement Process (GRIP) in the Department of Organizational Leadership, Policy, and Development.

David Mulla (SWC, WRS faculty) was honored with the Applied Soil Science Research Award at the Annual Meeting of the Soil Science Society of America (SSSA) in Tampa, FL.

Robert Sterner (WRS faculty, UMD Biology, LLO) has joined the University of Minnesota Duluth (UMD) as the new director of the Large Lakes Observatory (LLO) and member of the faculty in the UMD Department of Biology.

Daniel Wheeler (SWC, OSTP staff) received CFANS Distinguished Teaching Award for undergraduate faculty in a non-tenured position.

Mohd-Rozham Zakaria (WRS student) received a travel grant to attend the Ocean Sciences Meeting in Honolulu, Hawaii February 23-28, 2014, to present Sedimentary Fluxes of Great Lakes of Different Latitude Determined Using Moored Sequential Sediment Traps.

Xiaowei Zhao (WRS student) received a travel grant to attend the Joint Aquatic Science Meeting in Portland, Oregon, May 18-23, 2014 to present a poster Relationships between bacterial biodiversity and environmental parameters along an estuarine transect from the lower St Louis River to nearshore Lake Superior.