

**South Dakota Water Research Institute  
Annual Technical Report  
FY 2015**

# Introduction

South Dakota Water Resources Institute's (SDWRI) programs are administered through the College of Agricultural and Biological Sciences at South Dakota State University (SDSU). Dr. Van Kelley has served as the Director for the Institute since August 1, 2000. Dr. Kelley is also the head of the Agricultural and Biological Engineering Department. In addition to the Director, the Institute's programs are administered and executed by a staff consisting of an Assistant Professor and an Environmental Research Coordinator. During FY2015, the SDWRI financially supported, through its base funding or through externally funded projects, five MS students and four undergraduate research assistants.

The annual base grant from the United States Geological Survey (USGS) and a South Dakota legislative appropriation form the core of the SDWRI budget. The core budget is supplemented by research grants from a state and federal agencies as well as private organizations and industry interested in specific water-related issues.

The mission of the South Dakota Water Resources Institute is to address the current and future water resource needs of the people, industry, and the environment, through research, education, and service. To accomplish this mission, SDWRI provides leadership by coordinating research and training at South Dakota State University and other public educational institutions and agencies across the state in the broad area of water resources. Graduate research training, technology transfer, and information transfer are services which are provided through the Institute.

This report is a summary of the activities conducted by the SDWRI during the period March 1, 2015 through February 28, 2016.

## Research Program Introduction

Water is one of the most important resources in South Dakota. Together with the state's largest industry, agriculture, it will play an important role in the economic future of the state.

During FY 2015, the South Dakota Water Resources Institute (SDWRI) used its 104B Grant Program funds to conduct research of local, state, regional, and national importance addressing a variety of water problems in the state and the upper Midwest region.

The WRI 104B External Review Panel reviewed 11 grant applications, and 3 projects were funded that addressed research priorities that had a good chance of success, and would increase our scientific knowledge. The projects were titled:

- Nutrient Removal from Agricultural Subsurface Drainage Using Denitrification Bioreactors and Phosphate Adsorbents (year 2). PI's: G. Hua, C. Schmit, C. Hay, South Dakota State University.
- Controlling Harmful Algal Blooms in Eutrophic Lakes by Combined Phosphorus Precipitation and Sediment Capping. PI's: K. Min, G. Hua, South Dakota State University.
- Establishing Gene Fingerprints of Pathogenic Bacteria Along Selected Reaches of Rapid Creek. PI's: L. DeVeaux, L. Kunza. South Dakota School of Mines and Technology.

In addition, the following projects selected for funding during FY2013 and FY2014 were previously granted no-cost project extensions:

- Evaluating Nutrient Best Management Practices to Conserve Water Quality. PI's: L. Ahiablame, S. Kumar, South Dakota State University.
- Source water implications associated with the current Black Hills Mountain Pine-Beetle Infestation. PI's: J. Stone, J. Stamm, South Dakota School of Mines and Technology
- Evaluating the Nitrate-Removal Effectiveness of Denitrifying Bioreactors. PI's: D. Kringen, J. Kjaersgaard, C. Hay, T. Trooien, South Dakota State University.

Furthermore, the project listed below was funded through a USGS 104G grant:

- Hydrologic Life Cycle Impact of Mountain Pine Bark Beetle Infestations. PI: J. Stone. South Dakota School of Mines and Technology.

Progress and completion reports for these projects are enclosed on the following pages.

# Evaluating the Nitrate-Removal Effectiveness of Denitrifying Bioreactors (part 2)

## Basic Information

<b>Title:</b>	Evaluating the Nitrate-Removal Effectiveness of Denitrifying Bioreactors (part 2)
<b>Project Number:</b>	2013SD226B
<b>Start Date:</b>	3/1/2015
<b>End Date:</b>	2/29/2016
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	South Dakota First
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Agriculture, Non Point Pollution, None
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	David Kringen, Christopher Hay, Todd P. Trooien, Jeppe H Kjaersgaard

## Publications

1. Kjaersgaard, J., 2013. Denitrifying Bioreactors for N Removal from Tile Drainage Water. NDCDEA, ND/SD 319 Coordinators Meeting, Bismarck, ND, March 20-21 2013.
2. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors for Improved Drainage Water Management. Eastern South Dakota Water Conference, Brookings, SD. October 30 2013.
3. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors for Improved Drainage Water Management. Eastern South Dakota Water Conference, Brookings, SD. October 30 2013.
4. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors in South Dakota for Improved Drainage Water Management. ASA, CSSA, and SSSA International Annual Meeting, Tampa, FL, November 3-6 2013.
5. Kjaersgaard, J., 2013. Denitrifying Bioreactors for N Removal from Tile Drainage Water. NDCDEA, ND/SD 319 Coordinators Meeting, Bismarck, ND, March 20-21 2013.
6. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors for Improved Drainage Water Management. Eastern South Dakota Water Conference, Brookings, SD. October 30 2013.
7. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors for Improved Drainage Water Management. Eastern South Dakota Water Conference, Brookings, SD. October 30 2013.
8. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors in South Dakota for Improved Drainage Water Management. ASA, CSSA, and SSSA International Annual Meeting, Tampa, FL, November 3-6 2013.
9. Partheeban, C., Kjaersgaard, J., Hay., C., Trooien, T., 2014. A Review of the factors controlling the performance of denitrifying woodchip bioreactors. 2014 ASABE Intersectional Meeting, Brookings, SD, March 28-29 2014. 10 p.
10. Partheeban, C., Kjaersgaard, J., Hay., C., Trooien, T., 2014. Demonstrating the nitrogen removal effectiveness of denitrifying bioreactors for improved drainage water management in South Dakota. 2014 ASABE and CSBE/SCGAB Annual International Meeting, Montreal, Quebec, Canada, July

## Evaluating the Nitrate-Removal Effectiveness of Denitrifying Bioreactors (part 2)

- 13-16 2014. 11 p.
11. Partheeban, C., Karki, G., Khand, K., Cortus, S., Kjaersgaard, J., Hay, C., Trooien, T. 2014. Calibration of an AgriDrain Control Structure by using Generalized “V” Notch Weir Equation for Flow Measurement. Western South Dakota Hydrology Conference, Rapid City, SD, April 9 2014.
  12. Partheeban, C., Kjaersgaard, J., Hay., C., Trooien, T., 2014. A review of agricultural practices and technologies to reduce the nitrate nitrogen load in tile drainage water. The 8th International Student Prairie Conference on Environmental Issues. Fargo, ND, August 6-8 2014.
  13. Partheeban, C., Karki, G., Khand, K., Cortus, S., Kjaersgaard, J., Hay, C., Trooien, T. 2014. Calibration of an AgriDrain Control Structure by using Generalized “V” Notch Weir Equation for Flow Measurement. Western South Dakota Hydrology Conference, Rapid City, SD, April 9, 2014.
  14. Partheeban, C., Kjaersgaard, J., Hay., C., Trooien, T., 2014. A review of agricultural practices and technologies to reduce the nitrate nitrogen load in tile drainage water. The 8th International Student Prairie Conference on Environmental Issues. Fargo, ND, August 6-8 2014.
  15. Kjaersgaard, J., 2013. Denitrifying Bioreactors for N Removal from Tile Drainage Water. NDCDEA, ND/SD 319 Coordinators Meeting, Bismarck, ND, March 20-21 2013.
  16. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors for Improved Drainage Water Management. Eastern South Dakota Water Conference, Brookings, SD. October 30 2013.
  17. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors for Improved Drainage Water Management. Eastern South Dakota Water Conference, Brookings, SD. October 30 2013.
  18. Partheeban, C., Kjaersgaard, J., Hay, C., Trooien, T., 2013. Demonstrating the Nitrogen-removal Effectiveness of Denitrifying Bioreactors in South Dakota for Improved Drainage Water Management. ASA, CSSA, and SSSA International Annual Meeting, Tampa, FL, November 3-6 2013.
  19. Partheeban, C., Kjaersgaard, J., Hay., C., Trooien, T., 2014. A Review of the factors controlling the performance of denitrifying woodchip bioreactors. 2014 ASABE Intersectional Meeting, Brookings, SD, March 28-29 2014. 10 p.
  20. Partheeban, C., Kjaersgaard, J., Hay., C., Trooien, T., 2014. Demonstrating the nitrogen removal effectiveness of denitrifying bioreactors for improved drainage water management in South Dakota. 2014 ASABE and CSBE/SCGAB Annual International Meeting, Montreal, Quebec, Canada, July 13-16 2014. 11 p.
  21. Partheeban, C., Karki, G., Khand, K., Cortus, S., Kjaersgaard, J., Hay, C., Trooien, T. 2014. Calibration of an AgriDrain Control Structure by using Generalized “V” Notch Weir Equation for Flow Measurement. Western South Dakota Hydrology Conference, Rapid City, SD, April 9 2014.
  22. Partheeban, C., Kjaersgaard, J., Hay., C., Trooien, T., 2014. A review of agricultural practices and technologies to reduce the nitrate nitrogen load in tile drainage water. The 8th International Student Prairie Conference on Environmental Issues. Fargo, ND, August 6-8 2014.
  23. Partheeban, C., Karki, G., Khand, K., Cortus, S., Kjaersgaard, J., Hay, C., Trooien, T. 2014. Calibration of an AgriDrain Control Structure by using Generalized “V” Notch Weir Equation for Flow Measurement. Western South Dakota Hydrology Conference, Rapid City, SD, April 9, 2014.
  24. Partheeban, C., Kjaersgaard, J., Hay., C., Trooien, T., 2014. A review of agricultural practices and technologies to reduce the nitrate nitrogen load in tile drainage water. The 8th International Student Prairie Conference on Environmental Issues. Fargo, ND, August 6-8 2014.

**Progress report for: *Demonstrating the Nitrate Removal Effectiveness of Bioreactors for Improved Drainage Water Management in Eastern South Dakota***

Covering the period March 1, 2015 – February 29, 2016

Submitted By: D. Kringen, SDSU Extension

**Introduction**

This report summarizes the project activities during March 1, 2015 – February 29, 2016 for the project titled *Demonstrating the Nitrate Removal Effectiveness of Bioreactors for Improved Drainage Water Management in Eastern South Dakota*. The project is a collaborative effort between South Dakota State University and partner organizations, industry, government agencies and landowners. A list of project sponsors is available at <http://www.sdstate.edu/abe/wri/research-projects/upload/Project-Sponsors.pdf>.

More information about the project, including background information about denitrifying bioreactors, is available at <http://www.sdstate.edu/abe/wri/research-projects/bioreactors.cfm>.

**Bioreactor Installations**

At this time, the team has installed four woodchip bioreactors: the first near Baltic SD, the second near Montrose SD, the third near Arlington SD, and the newest near Hartford SD. A fifth bioreactor site within the Vermillion River watershed was planned for installation in the spring of 2014, but the combination of an appropriate site and willing landowner was never found. A description of the Hartford bioreactor site and installation can be seen below. Installation information of the Baltic, Montrose, and Arlington sites can be seen in previous progress reports.

Table 1. Approximate location, county, watershed and installation dates for bioreactor installation.

Location	County	Watershed	Installation Dates
Baltic	Minnehaha	Silver Creek	July 23-24, 2012
Montrose	McCook	Skunk Creek	December 5-6, 2012
Arlington	Brookings	Lake Sinai	July 23-24, 2013
Hartford	Minnehaha	Wall Lake	November 14, 2014

*Hartford Bioreactor Location*

The Hartford bioreactor site is located in the SE<sup>1/4</sup> of Section 20 T101 R51, Wall Lake Township, Minnehaha County, SD. Drainage water from the bioreactor outlets into the Dewey C. Gevik Outdoor Conservation Learning Area pond and eventually Wall Lake (Figure 1).

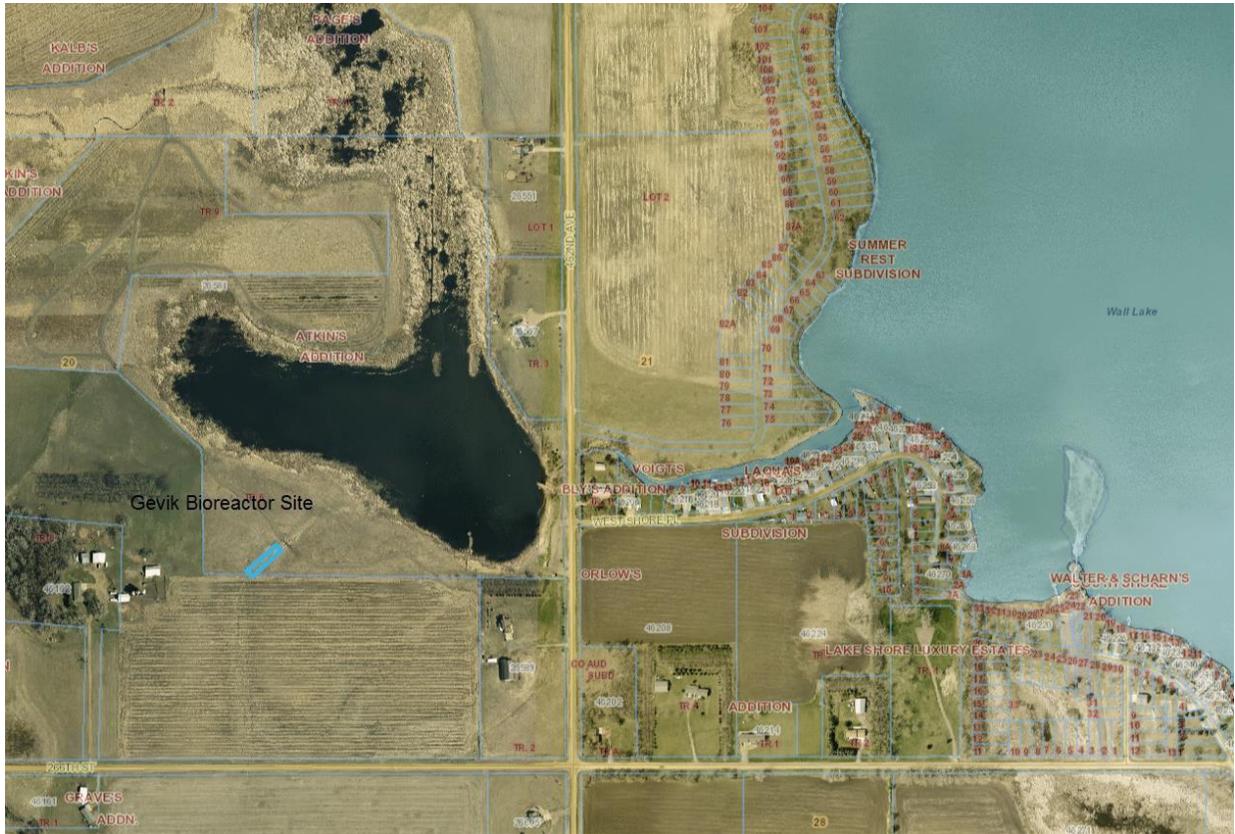


Figure 1. Location of bioreactor site near Hartford, SD.

### *Bioreactor Design*

The Hartford bioreactor was installed on a tile drainage system that was installed in November of 2013. The main line is 6 inches in diameter and has a grade of approximately 0.4%. The bioreactor trench is 125 feet L x 10 feet W x 4 feet D. Volume of woodchips is 5,000 cubic feet. The reactor is designed to keep a head of up to 2 feet above the bottom at the inlet and outlet height of 0.46 feet above the bottom. The estimated hydraulic retention time (HRT) is 6.3 hours at design capacity. Percentage of peak flow that can be passed through the bioreactor is estimated to be 17.7%.

### **Downstream Control Structure Weir Replacements**

In the absence of oxygen, anaerobic microbes are capable of respiration through the reduction of nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) to nitrogen gas ( $\text{N}^2$ ). This is commonly referred to as denitrification. In severely anaerobic environments when nitrate-nitrogen approaches complete removal, sulfate-reducing bacteria can become active and create a “rotten egg” smell. This situation may occur when water movement through the bioreactor is very slow or stagnant, such as when water flow through the subsurface drainage system ceases. In order to prevent this kind of condition, all downstream stop logs were replaced in the spring of 2015 with weirs that included a lower V-notch (Figure 2). The lower V-notch is meant to end prolonged hydraulic retention times and allow for complete drainage of water during low flow periods, as is now recommended by Illinois NRCS.



Figure 2. Downstream control structure weirs with Upper and Lower V-notches.

*Calibration of Lower V-notch Flow*

On December 2, 2015 a benchtop experiment was performed to determine flow through the lower V-notch. The procedure was similar to the technique used to calibrate the larger, upper V-notch in 2014. Water was run through the lower V-notch for 10 minutes at various depths between 30 mm (above lower V-notch) and 144 mm (bottom of upper V-notch), and an average flow rate was calculated over the 10 minutes using an inline Dynasonics TFXL Transit Time Flowmeter. Based on the flow data, the following constant was derived for the lower V-notch:

$$Q = 27.0 \text{ liters/min}$$

Dimensions for the lower V-notch can be seen in Figure 3.

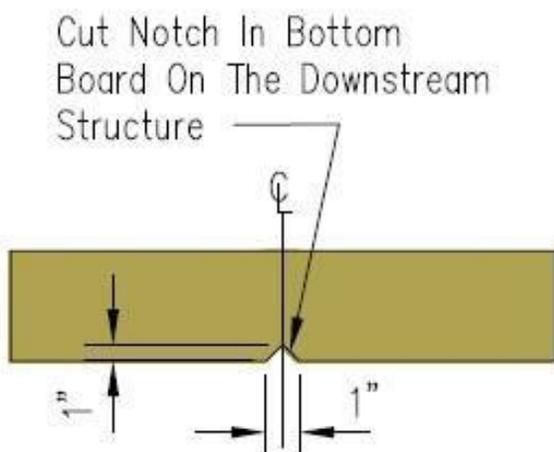


Figure 3. Lower V-notch dimensions for bottom board in downstream control structure.

## Bioreactor Performance

We have installed monitoring equipment to continuously monitor the flow rates, the electrical conductivity of the water and the water temperature at the inlet and the outlets of all bioreactors. Sites are visited when water is flowing in the tiles, during which time we do site maintenance, download the monitored data from the data loggers, collect water samples and make notes of bioreactor and field conditions. Water samples are packed with ice, placed in a cooler, and brought back to SDSU for nitrate-nitrogen analysis.

### *Flow Measurements*

Pressure transducers used to measure water depth in bioreactor control structures do not ordinarily sit at the bottom of the control structure they are located in. Each transducer has a metal or plastic casing which protects the tiny pressure-sensitive sensor. Even if the casing were to touch the bottom of the control structure, the sensor itself would be  $\frac{1}{4}$  to  $\frac{1}{2}$  inch above the bottom (Figure 4). Casings are additionally elevated above the bottom of a structure to keep the



Figure 4. Example of pressure transducer casing and sensor location.

sensor out of any sediment that may settle out. Therefore, water depth readings are relative to the pressure transducer location and not necessarily the bottom of the structure.

In downstream control structures, flow through the smaller, lower V-notch would not necessarily be measured directly by the transducer due to sensor location above the V-notch. Any positive depth reading however, would suggest that the lower V-notch is flowing at capacity (27.0 liters/min).

Converting this constant to liters/day, it is assumed that at a minimum, water flow

through the downstream control structure equals 38,880 liters/day during site visits when water samples are taken. This amount is added to any flow that may be occurring over the upper V-notch at time of sample.

### Water Quality

For 2015, the water quality samples collected at the inlets and outlets of the bioreactors have been analyzed for nitrate-nitrogen concentrations using a Dionex Ion Chromatography (IC) system in the Water & Environmental Engineering Research Center (WEERC) Laboratory in the SDSU Civil and Environmental Engineering Department. The concentration-based  $\text{NO}_3\text{-N}$  reductions in the water samples collected in the upstream and downstream control structures at the four bioreactor sites for 2015 can be seen in Figures 5 – 8.

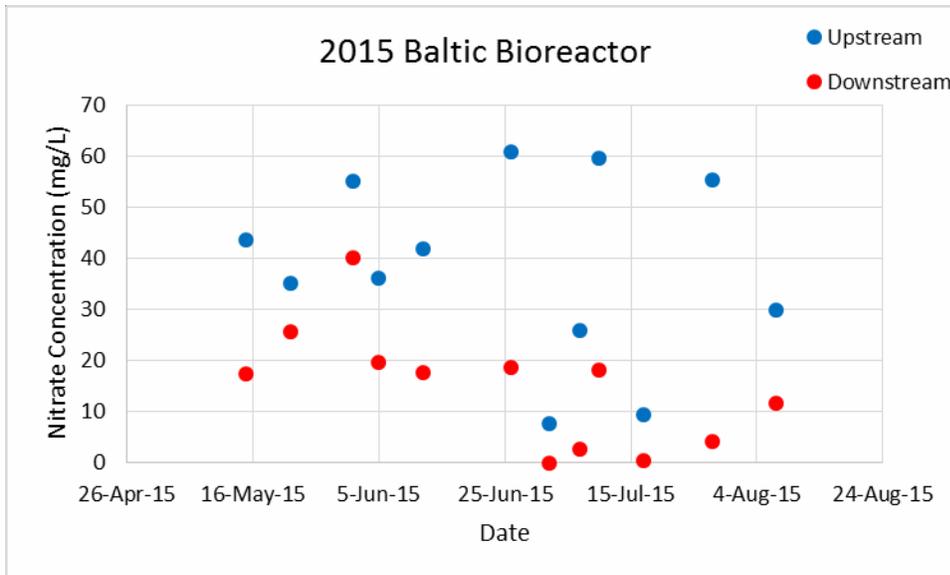


Figure 5. Nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) concentrations in water samples collected upstream and downstream from the Baltic bioreactor during 2015.

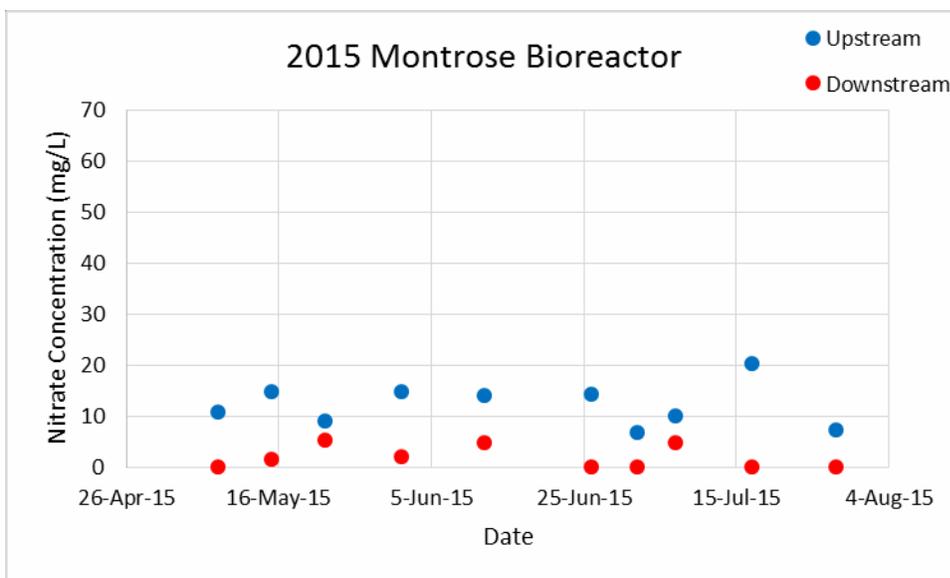


Figure 6. Nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) concentrations in water samples collected upstream and downstream from the Montrose bioreactor during 2015.

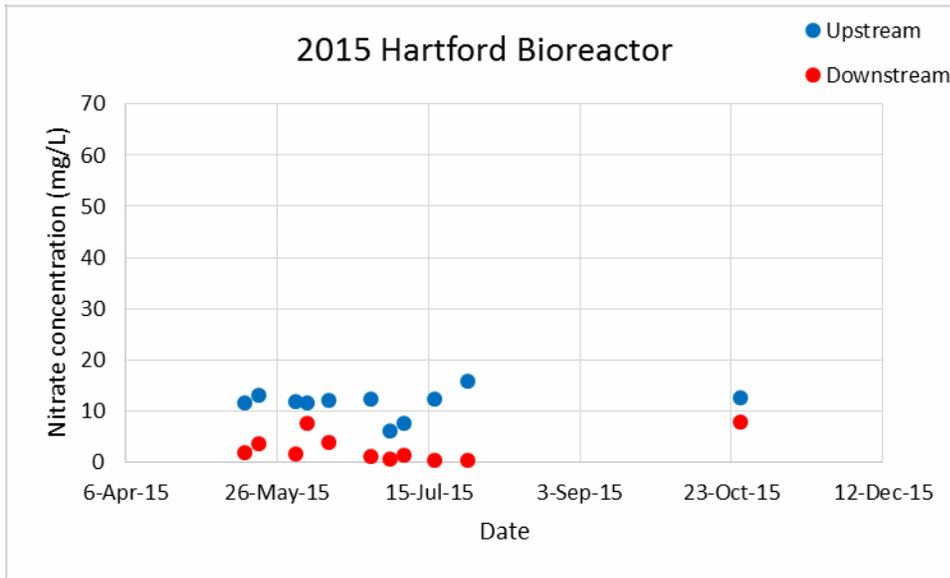


Figure 7. Nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) concentrations in water samples collected upstream and downstream from the Hartford bioreactor during 2015.

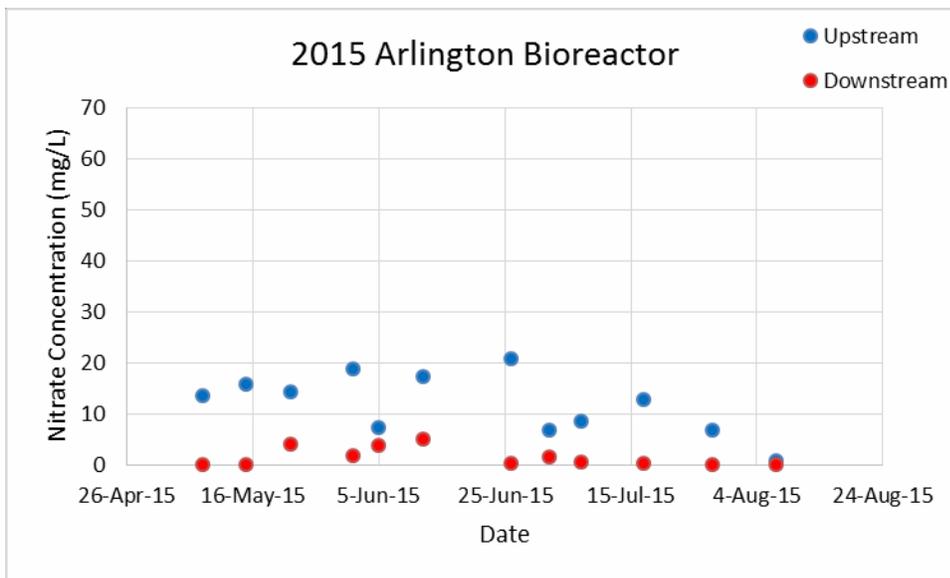


Figure 8. Nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) concentrations in water samples collected upstream and downstream from the Arlington bioreactor during 2015.

The Arlington site uses a single, 4-chamber control structure placed at the upstream end of the bioreactor where both upstream and downstream flow are routed (Figure 9). On occasion, excess upstream drainage water that cannot be processed through the bioreactor is routed over the by-pass and into the downstream control chamber. This by-pass water is mixed with the treated downstream water and will result in an incorrect downstream nitrate concentration when taking samples.

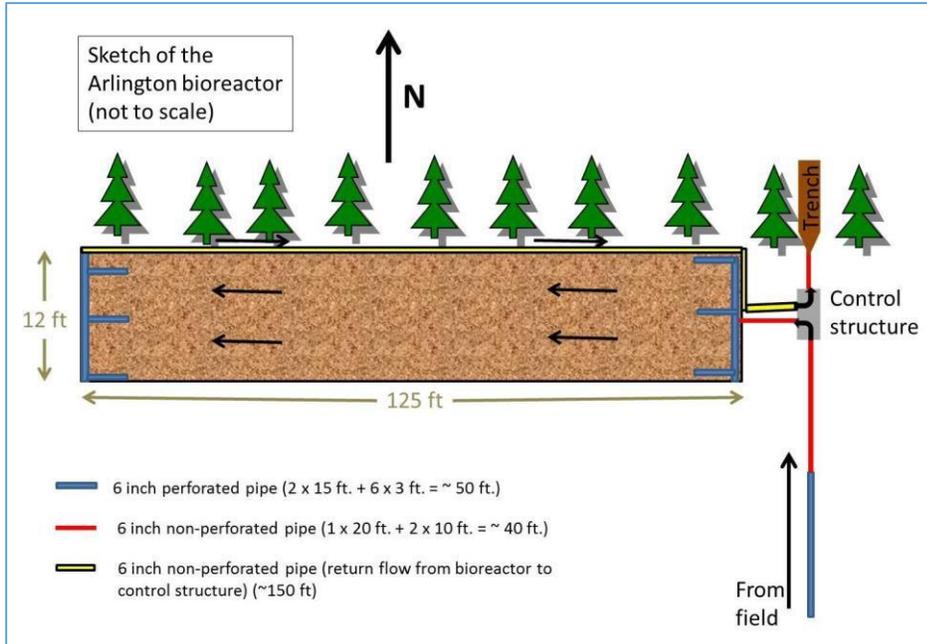


Figure 9. Diagram of Arlington bioreactor.

At the Arlington site, 4 observation wells/piezometers were fitted along the length of the bioreactor at the time of bioreactor installation in 2013 (Figure 10). The piezometers were constructed using 2 inch PVC pipe with well screen on the bottom 2 feet. When by-pass conditions occurred, water samples taken from observation well #4 (the furthest from the inlet) were used as the downstream outlet sample. In 2015, these occurred on 8 of the 12 sampling dates.



Figure 10. Photo of Arlington piezometers/observation wells.

Table 2 shows minimum, maximum, mean, and median nitrate-nitrogen concentrations (mg/L) from water samples taken in 2015 for each of the 4 bioreactor sites. Concentrations are not flow-weighted. Percent reductions for each site is based on mean concentrations.

Table 2. Upstream and downstream nitrate-nitrogen concentrations for water samples taken in 2015.

Bioreactor Site	Upstream NO <sub>3</sub> -N Concentrations (mg/L)				Downstream NO <sub>3</sub> -N Concentrations (mg/L)				Percent Reduction
	Min	Mean	Median	Max	Min	Mean	Median	Max	
Baltic	7.77	38.42	39.08	60.95	0.00	14.76	17.50	40.20	61.6%
Montrose	6.89	12.27	12.5	20.40	0.00	1.87	0.85	5.24	84.8%
Hartford	6.06	11.49	12.10	15.70	0.25	2.66	1.55	7.86	76.8%
Arlington	0.79	11.95	13.15	20.70	0.01	1.45	0.47	5.13	87.9%

Table 3 shows the flow-weighted nitrate-nitrogen loads (kg/day) for 3 of the 4 bioreactor sites in 2015. During 2015, the Arlington bioreactor site had a faulty pressure transducer used to measure stage height in the downstream control structure and was not replaced until July 9<sup>th</sup>. Because downstream flow rates are used to calculate nitrate-nitrogen loads (liters/day x mg/L), we were unable to determine daily loads for a majority of the samples taken at the Arlington site in 2015. Percent reductions for each site is based on the mean load.

Table 3. Upstream and downstream nitrate-nitrogen loads for water samples taken in 2015.

Bioreactor Site	Upstream NO <sub>3</sub> -N Load (kg/day)				Downstream NO <sub>3</sub> -N Load (kg/day)				Percent Reduction
	Min	Mean	Median	Max	Min	Mean	Median	Max	
Baltic	0.30	1.49	1.52	2.37	0.00	0.57	0.68	1.56	61.7%
Montrose	0.27	0.64	0.55	1.97	0.00	0.15	0.03	0.96	76.6%
Hartford	0.24	0.48	0.48	0.61	0.01	0.11	0.07	0.31	77.2%

A true downstream load calculation contains both the treated volume of drainage water that passes through the bioreactor plus any untreated water that passes over the upstream control structure by-pass. By-pass loads were not calculated for this progress report but will be for the final report due in 2016.

### Outreach Activities

- 10-11 Mar 2015. Extension Subsurface Drainage Design and Water Management Workshop, Grand Forks, ND. Coordinated with Tom Scherer and Hans Kandel (NDSU). 64 attendees consisting primarily of producers and contractors. Nine industry partners provided financial support.
- 13 Aug 2015. Kiwanis Club meeting. Presentation entitled *Ag Drainage: A Change in the SD Landscape*. ~ 15 attendees.
- 17 Nov 2015. ASA/SSA/CSSA Annual Meeting, Minneapolis, MN. Poster presentation entitled *Combine Treatment of Nitrogen & Phosphorus from Subsurface Drainage using Low-cost Industrial Byproducts and Woodchips Bioreactor*. ~ 25 attendees.
- 10 Dec 2015. AgOutlook Annual Meeting, Sioux Falls, SD. Poster presentation entitled *Combine Treatment of Nitrogen & Phosphorus from Subsurface Drainage using Low-cost Industrial Byproducts and Woodchips Bioreactor*. ~ 15 attendees.

# Nutrient Removal from Agricultural Subsurface Drainage Using Denitrification Bioreactors and Phosphate Adsorbents

## Basic Information

<b>Title:</b>	Nutrient Removal from Agricultural Subsurface Drainage Using Denitrification Bioreactors and Phosphate Adsorbents
<b>Project Number:</b>	2014SD235B
<b>Start Date:</b>	3/1/2014
<b>End Date:</b>	2/29/2016
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	South Dakota 1st
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Agriculture, Nutrients
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Guanghui Hua, Christopher Hay, Jeppe H Kjaersgaard, Christopher G Schmit

## Publications

1. Salo, Morgan, Weiss, Kody, Hua, Guanghui, Schmit, Christopher, Hay, Christopher, 2014, Nutrient removal from agricultural subsurface drainage using denitrification bioreactors and phosphate adsorbents. Eastern South Dakota Water Conference, Brookings, SD, October 29. (Poster Presentation)
2. Salo, Morgan, Weiss, Kody, Hua, Guanghui, Schmit, Christopher, Hay, Christopher, 2014, Nutrient removal from agricultural subsurface drainage using denitrification bioreactors and phosphate adsorbents. Eastern South Dakota Water Conference, Brookings, SD, October 29. (Poster Presentation)

# Nutrient Removal from Agricultural Subsurface Drainage Using Denitrification Bioreactors and Phosphate Adsorbents

Progress Report: March 1, 2015 to February 28, 2016

Report Submitted to the South Dakota Water Resources Institute under the USGS 104b program

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## Introduction

Agricultural subsurface drainage is a widely adopted water management practice to increase crop production in the Midwestern United States and many other areas (Fausey et al., 1995). Subsurface drainage removes excess water from the soil profile through a network of underground perforated pipes or surface ditches, which allows cultivation of agricultural fields with poor natural drainage. However, subsurface drainage systems also provide direct conduits that can transport nutrients from agricultural fields to surrounding natural water bodies (Sims et al., 1998; Jaynes et al., 2001). Elevated nutrient levels in surface waters can lead to a number of negative water quality impacts including harmful algal blooms, hypoxic zones in the ocean, and contamination of drinking water supplies (Sharpley et al., 1987; Anderson et al., 2002; Rabalais et al., 2002; Schilling, 2005).

Nitrate has been a major water quality concern for many subsurface drainage systems due to its high solubility and mobility in soils. Nitrate-nitrogen concentrations in subsurface drainage water often exceed the United States Environmental Protection Agency (USEPA) drinking water standard of 10 mg/L. Increased nitrate loading into the Mississippi River Basin from agricultural drainage in the Midwest has been identified as a major contributor to growing hypoxia in the Gulf of Mexico (Rabalais et al., 2002). Many nutrient management practices have been implemented in fields to reduce nitrate loads from subsurface drainage systems, including improved fertilizer application, controlled drainage, and denitrification bioreactors (Gilliam and Skaggs, 1986; Delgado et al., 2005; Schipper et al., 2010).

Phosphorus transport from agricultural fields to surface waters occurs through two primary pathways: surface runoff and subsurface drainage. Early work on agricultural phosphorus transport focused on soil erosion and surface pathways, and many studies have demonstrated that phosphorus loss occurs predominantly in surface runoff (Sharpley et al., 1993; Heathwaite and Dils, 2000). Recent studies suggest that subsurface drainage is also an important phosphorus transport pathway, and the leaching of phosphorus to subsurface drainage can be enhanced by low soil phosphorus adsorption capacity and development of preferential flows (Sims et al., 1998; Gentry et al., 2007; Kleinman et al., 2015). Smith et al. (2015) showed that 49% of soluble phosphorus and 48% of total phosphorus losses occurred through subsurface drainage in the St. Joseph River Watershed in northeastern Indiana. King et al. (2015) demonstrated that more than

90% of all measured phosphorus concentrations in subsurface drainage of a watershed in central Ohio exceeded recommended levels (0.03 mg/L) for minimizing harmful algal blooms. It is necessary to develop practices that can control the concentrations of both nitrogen and phosphorus in subsurface drainage to protect aquatic ecosystems and public health.

Denitrification bioreactors have emerged as an important edge-of-field treatment technology to reduce nitrate loads from subsurface drainage (Blowes et al., 1994; Greenan et al., 2006; van Driel et al., 2006; Schipper et al., 2010; Christianson et al., 2013). These bioreactors typically utilize an organic carbon medium to support the growth of denitrifying bacteria which use organic electron donors to reduce nitrate to nonreactive nitrogen gas. Woodchips are by far the most widely used materials in field-scale denitrification bioreactors and have shown the ability to deliver long-term (> 10 years) nitrate removal while requiring minimum maintenance (Blowes et al., 1994; Robertson, 2010; Christianson et al., 2011; Cooke and Bell, 2014). Under field operating conditions, woodchip bioreactors have demonstrated nitrate removal efficiencies ranging from 33 to 100%, and removal rates of 2 to 22 g N/m<sup>3</sup>/d (Schipper et al., 2010). Little information is available regarding the fate of phosphate in denitrification bioreactors and several studies suggest that wood-based bioreactors do not have the capability to substantially remove phosphate (Jaynes et al., 2008). Phosphate sorption materials such as drinking water treatment residuals and biochar have been used to amend laboratory-scale bioreactors to enhance phosphate removal (Zoski et al., 2013; Bock et al., 2015).

Emerging phosphate removal technologies are being developed to reduce phosphorus pollution using low-cost adsorption materials, such as natural minerals, synthetic filtration products, and industrial byproducts (steel slag, steel wool and turnings, fly ash, drinking water treatment residuals and others) (Penn et al., 2007; McDowell et al., 2008; Chardon et al., 2012; Erickson et al., 2012). The phosphorus adsorbents typically provide metal cations (iron, aluminum, or calcium) to bind with dissolved phosphorus to form insoluble compounds (Weng et al., 2012; Lyngsie et al., 2014). Steel chips, wools and turnings are common byproducts produced during metal processing, and they are typically recycled for steel production. These readily available steel byproducts are expected to possess high phosphate adsorption capacity due to their high iron content (Erickson et al., 2012; Weng et al., 2012). Therefore, recycled steel byproducts can be potentially used as cost-effective filtration materials to remove phosphate from subsurface drainage. Hence, we propose a two-stage treatment system using woodchip bioreactors followed by recycled steel byproduct filters to simultaneously remove nitrate and phosphate in subsurface drainage.

The objectives of this study were to determine the nitrate and phosphate removal efficiency of a woodchip bioreactor followed by a steel byproduct filter in the laboratory. In this study, batch adsorption experiments were conducted to determine the phosphate adsorption capacity of selected steel chips and turnings. Column experiments were performed to evaluate the nitrate and phosphate removal by woodchips and selected steel byproducts under continuous flow conditions. The impacts of influent nutrient concentrations and hydraulic retention times on the performance of the bioreactor and the steel filter were investigated. The results of this study may lead to the development of new edge-of-field treatment systems that combine woodchip denitrification and steel byproduct filtration for nitrate and phosphate removal in subsurface drainage.

## Materials and Methods

### *Woodchips and Steel byproducts*

Table 1 summarizes the characteristics of the steel byproducts and woodchips used for this study. Four different steel byproducts were collected from a metal machining factory located in Sioux Falls, SD. Small chips (0.1-2 mm), medium chips (1-10 mm), medium turnings (2.5-4.5 cm) and large turnings (3-5 cm) were produced by processing carbon steel using different machines. After collection, steel byproducts were washed using non-phosphate soap and air dried before use. Woodchips made from cottonwood trees were obtained from a supplier in Sioux Falls, SD. These woodchips (0.1-6 cm) were washed with distilled water to remove dirt and floating fine particles, and air dried before use.

Table 1 Characteristics of steel byproducts and woodchips

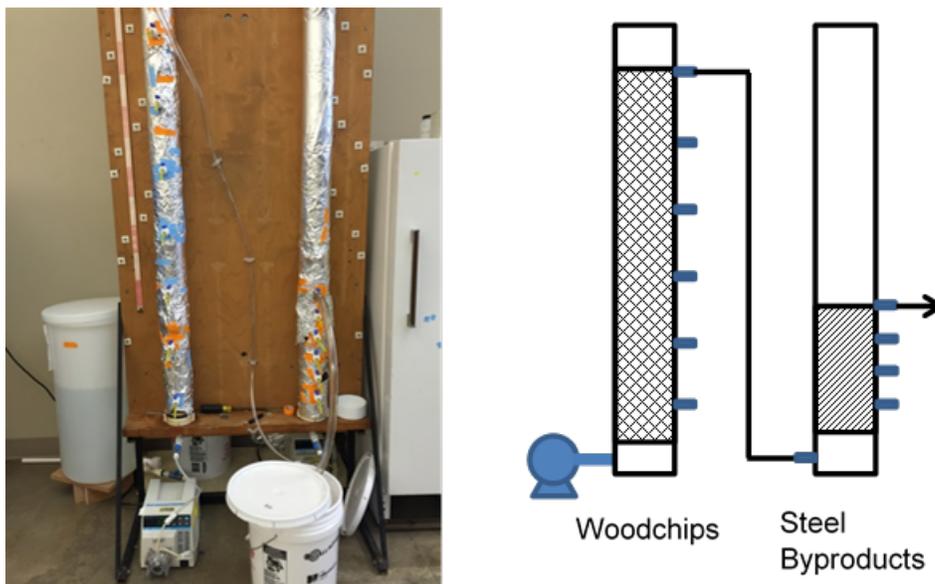
<b>Material</b>	<b>Name</b>	<b>Type</b>	<b>Size</b>
Steel Byproducts	Small Chips	Carbon Steel	0.1 – 2 mm
	Medium Chips	Carbon Steel	1 – 10 mm
	Medium Turnings	Carbon Steel	2.5-4.5 cm long, 2 mm thick
	Large Turnings	Carbon Steel	3-5 cm long, 5 mm thick
Woodchips	Woodchips	Cottonwood	36% large: 3-6 cm long, 0.5-2 cm wide 52% medium: 1-3 cm long, 0.5-1.5 cm wide 12% small: 0.1-1 cm long, 0.1-1 cm wide

### *Batch Phosphate Adsorption Experiments*

Batch adsorption experiments were conducted to determine the phosphate adsorption isotherm and kinetics of the steel byproducts. A temperature controlled orbital shaker (Model MaxQ 4000, Thermo Scientific, Waltham, MA) was used for the adsorption experiments. For the isotherm test, each steel byproduct (0.5 to 1 g) was placed in a 100 mL phosphate solution that had varying concentrations (10-40 mg P/L). The phosphate solution was prepared by dissolving  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in water and the pH was adjusted to 7 using 1.0 M NaOH solution. After 24 h of adsorption at 20 °C and 100 rpm shaking, the phosphate concentration of each sample was measured. The adsorption kinetics test was also conducted at a temperature of 20 °C and 100 rpm shaking. Each steel byproduct (0.5 to 1 g) was placed in a 100 mL phosphate solution with an initial concentration of 30 mg P/L and a pH of 7. Samples were collected at different time intervals (0.5, 1, 2, 3, 6, and 24 h) for phosphate measurement.

### *Column Reactor Experiments*

Figure 1 shows the schematic of the two-stage upflow column reactors with the woodchips and steel byproducts. Both reactors had an inside diameter of 8.7 cm. The woodchip reactor had 1.2 m of woodchips and 6 sampling ports. Medium steel chips were selected for the column experiments based on the batch adsorption experiments. The steel byproduct reactor contained 0.3 m of steel chips and 4 sampling ports. Sampling ports were evenly distributed along the height of each reactor. Drainable porosity was determined by draining each reactor for 1 h, and the resulting porosities were 50% and 80% for the woodchips and steel byproducts, respectively.



**Figure 1** The schematic and a picture of the column reactors

The woodchip bioreactor was inoculated by a soil sample collected from an agricultural field near Brookings, SD. The soil sample (50 g) was mixed with nanopure water (4 L) and the supernatant was pumped through the woodchips at a rate of 2.5 mL/min for 5 d before the column experiments. Simulated subsurface drainage was used for the column reactor experiments, and the drainage contained typical subsurface drainage ionic constituents including  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  at concentrations of 5, 2.5, 2.5, 1, 15.5, and 16.7 mg/L, respectively.

The long-term nutrient removal experiments were divided into two phases. In Phase 1, the influent nitrate and phosphate concentrations were kept at 20 mg N/L and 1 mg P/L, respectively. The influent concentrations were increased to 50 mg N/L and 10 mg P/L in Phase II as challenging conditions for the reactors. The reactors were operated continuously for 100 and 130 days under Phases I and II conditions, respectively. For both phases, the hydraulic retention time (HRT) was maintained at 24 and 9.5 h for the woodchips and steel byproducts, respectively, based on the flow rate and porosity of each material. Short-term nutrient removal experiments were also performed under Phase I nutrient concentrations to evaluate the impact of different HRTs and wet and dry cycles on the removal efficiency. During the HRT variation experiment, the HRT of the woodchips was decreased to 12 and 6 h, respectively, and the column reactors were operated for 10 days at each HRT. During the wet and dry cycle experiment, the two reactors were completely drained for 3 days, and the influent flow was restored for another 10 days (woodchip HRT=24 h). This cycle was repeated twice. During the column experiments, samples were collected from different sampling ports at different time intervals for the analysis of nitrate, nitrite, phosphate, and sulfate.

After the completion of the short and long-term column experiments, a phosphate breakthrough experiment was performed on the steel byproduct reactor to determine the total phosphate removal capacity. An influent concentration of 100 mg P/L and three HRTs (1.2 h, 0.5 h, and 0.17 h) were used during the phosphate breakthrough experiment. The reactor was operated for 36 h at each HRT.

### *Analytical Methods*

All solutions used in this study were prepared with ultrapure water (18 M $\Omega$ -cm) produced by a Barnstead NANOpure system. All solutions were adjusted to pH 7 using sodium hydroxide or sulfuric acid solutions. The chemicals used in this study were of American Chemical Society reagent grade and were purchased from Sigma Aldrich (St Luis, MO). Nitrate, nitrite, phosphate and sulfate were determined using a DX-500 ion chromatography system (Dionex, Sunnyvale, CA) equipped with a conductivity detector (CD-20, Dionex). Each sample was filtered through a 0.45  $\mu\text{m}$  filter before analysis. The pH of each solution was measured with an Orion 290A+ advanced ISE/pH/mV/OPR meter (Thermo Electron, Waltham, MA).

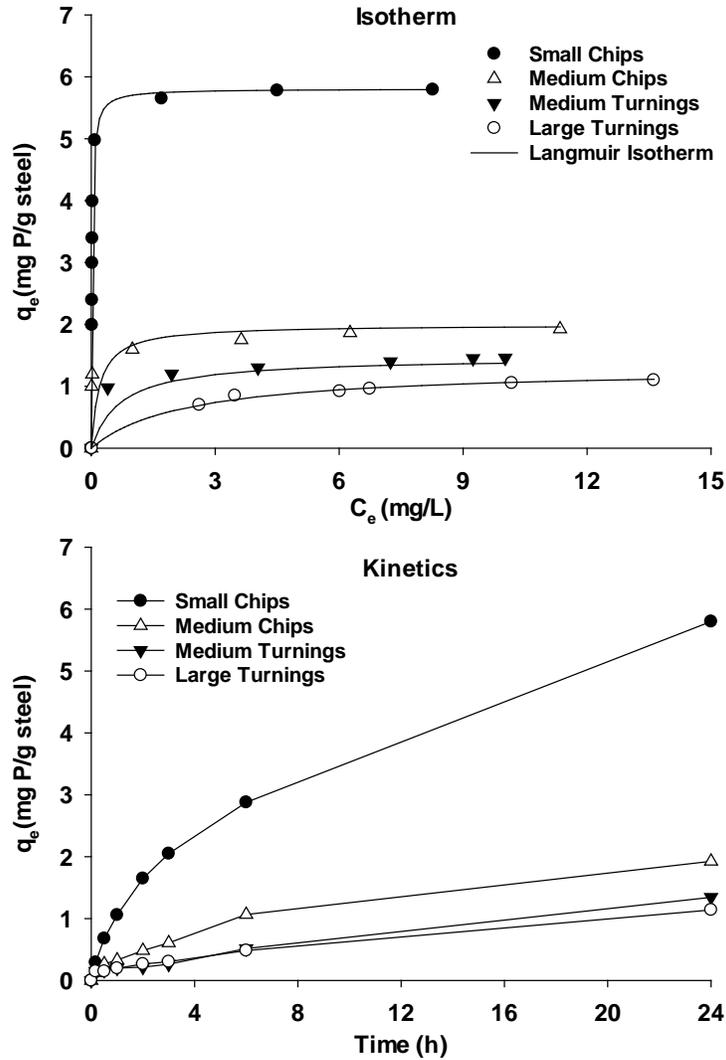
## Results and Discussion

### *Phosphate Adsorption Isotherm and Kinetics of Steel Byproducts*

Figure 2 shows the phosphate adsorption isotherm and kinetics of different steel byproducts. A Langmuir isotherm was used to model the phosphate adsorption capacity at different equilibrium concentrations. The phosphate adsorption rates were modeled using first-order reaction kinetics. Table 2 summarizes the model parameters of the Langmuir isotherm and first-order kinetics for each material. The phosphate adsorption by steel byproducts could be described by the two models as evidenced by the high linear regression coefficients ( $R^2 > 0.98$ ). The sizes of the steel byproducts exhibited large impacts on the phosphate adsorption capacities and rates. As shown in Figure 2, the adsorbed phosphate per unit mass ( $q_e$ ) of small and medium chips showed a sharp increase with increasing equilibrium concentrations ( $C_e$ ) and reached a constant value when the  $C_e$  was higher than 1 mg P/L. When medium and large turnings were used, the  $q_e$  showed a more gradual increase with increasing  $C_e$ , and reached a constant value when the  $C_e$  was higher than 3 mg P/L. The maximum  $q_e$  values determined from the Langmuir isotherm (Table 2) were 5.81, 2.00, 1.47, and 1.30 mg P/g for small chips, medium chips, medium turnings, and large turnings, respectively. This result suggests that smaller steel materials with larger surface areas have higher phosphate adsorption potential than larger steel materials. The phosphate adsorption capacities of these recycled steel byproducts were similar to several other industrial byproducts that showed good phosphate removal potential, such as drinking water treatment sludge (0.89-0.95 mg P/g, Leader et al., 2008), and various steel slags (1.35-6.56 mg P/g, Drizo et al., 2002; McDowell et al., 2008).

Kinetic analysis of the phosphate adsorption (Table 2) showed that the rate constant ( $k$ ) decreased with increasing steel particle sizes. In general, all selected steel byproducts exhibited fast phosphate removal rates. The phosphate removed within 6 hours amounted to 50, 55, 38, and 42% of the 24 h adsorption capacities, for small chips, medium chips, medium turnings, and large turnings, respectively (Figure 2). Leader et al. (2008) observed that iron-based drinking water residuals (0-2 mm) were able to adsorb phosphate to low levels within 4 h. Zeng et al. (2004) observed even faster phosphate adsorption kinetics using iron oxide tailing materials with an average size of 69  $\mu\text{m}$ , where 64-74% of the 24 h adsorption capacity occurred within the first 0.5 h. These results suggest that iron based industrial byproducts could quickly remove phosphate from water, and that the adsorption rate increases with decreasing particle sizes.

The results of the batch adsorption experiments indicate that the recycled steel byproducts exhibit relatively high phosphate adsorption capacity. Although small steel chips showed the highest phosphate removal potential, these materials may be prone to clogging during field applications due to their small size. Moreover, we observed that these small chips tended to solidify to form a single mass during the experiments. Therefore, medium chips were selected for the column experiments.



**Figure 2** Phosphate adsorption isotherm and kinetics of steel byproducts. (Experimental conditions: mass of materials=0.5-1 g; isotherm test initial P=10-40 mg/L; kinetics test initial P=30 mg/L; temperature=20 °C.)

**Table 2** Phosphate adsorption isotherm and kinetics of steel byproducts

Carbon Steel	Langmuir Isotherm			First Order Kinetics	
	$q_{max}$ (mg P/g)	$k$ (L/mg)	$R^2$	$k$ ( $min^{-1}$ )	$R^2$
Small Chips	5.81	46.5	0.999	0.276	0.978
Medium Chips	2.00	5.05	0.998	0.139	0.998
Medium Turnings	1.47	3.58	0.998	0.100	0.988
Large Turnings	1.30	0.44	0.999	0.084	0.995

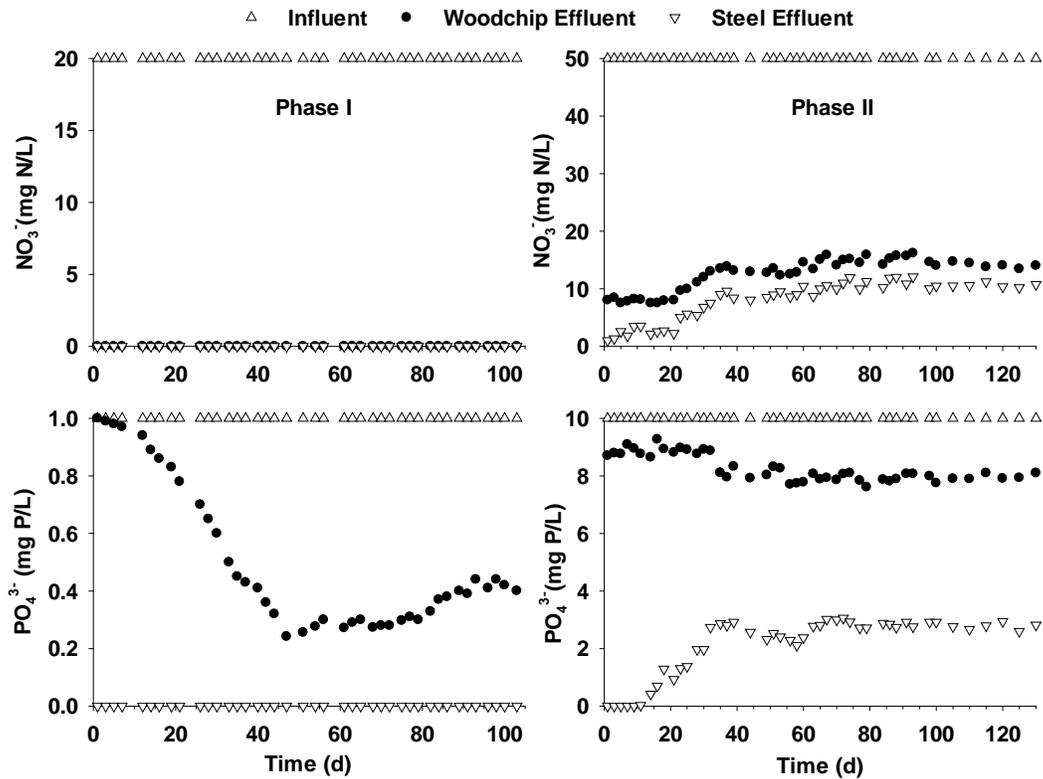
\*Experimental conditions: temperature=20 °C; adsorption time=24 h; shaking=100 rpm.

### *Long-term Nutrient Removal by Woodchip and Steel Byproduct Reactors*

Figure 3 presents the long-term performance of the woodchip bioreactor and steel byproduct filter under various influent concentrations. During the 100 days of the Phase I experiments (nitrate: 20 mg N/L, phosphate: 1 mg P/L), the woodchip bioreactor consistently achieved 100% removal of nitrate, with a removal rate of 10.1 g N/m<sup>3</sup>/d based on the reactor volume. The woodchip bioreactor did not exhibit apparent phosphate removal (< 3%) during the first 7 days. The bioreactor gradually developed the capability of phosphate removal and showed steady increases in the removal with increasing operation time after 7 days. The phosphate removal efficiency increased to a maximum of 75% on the 50th day. After that, the removal efficiency moderately decreased and reached an average of 60% during the last 20 days. This result suggests that woodchips may require relatively long operating times (e.g. > 50 days) to fully develop the capability to remove phosphate. The phosphate removal by the woodchip bioreactor may be explained by several mechanisms. First, the microbial growth within the bioreactor will consume certain amounts of phosphate. Second, the extracellular polymeric substances (EPS) produced by the biofilm on the woodchips may adsorb phosphate. Studies have shown that the EPS of activated sludge can accumulate considerable amounts of phosphate during wastewater treatment (Li et al, 2015). Third, woodchips may also have the ability to adsorb phosphate from the solution. It is possible that biofilm penetration and microbial degradation of woodchips (Cameron and Schipper, 2010) may be important in developing phosphate removal capability as evidenced by the increased phosphate removal with increasing operating time. Despite the variations of phosphate in the woodchip bioreactor effluent, the steel byproduct filter completely removed the remaining phosphate during the 100 days of operation. The removed phosphate by the steel chips varied from 0.25 to 1 mg P/L.

High nutrient concentrations (50 mg N/L and 10 mg P/L) were used during the 130 days of Phase II operation. The woodchip bioreactor achieved an average nitrate removal efficiency of 75% during the course of the experiments and the nitrate removal rate was 18.9 g N/m<sup>3</sup>/d, representing an 87% increase compared to Phase I conditions when influent nitrate was limiting. Both nitrate removal rates are well within the range observed in several other laboratory and field investigations (Robertson, 2010; Schipper et al., 2010; Woli et al., 2010). Steel chips showed the ability to further reduce the nitrate concentration and the removal extents varied from 2.59 to 7.10 mg N/L. The nitrate removal by steel filters may be attributed to the physical and chemical adsorption and/or denitrification by the biofilm in the steel media. Similar to the Phase I operation, the phosphate removal by woodchips also increased with increasing operating time and then stabilized. The phosphate removed by the woodchips averaged 1.13 mg P/L during the first 20 days and then gradually increased to 2.01 mg P/L during the last 20 days. These values are much higher than the Phase I experiments, suggesting that higher influent concentrations increased the phosphate removal potential of the woodchips. The steel byproduct reactor completely removed the phosphate during the initial 10 days and phosphate breakthrough occurred after that. The phosphate in the steel reactor effluent increased quickly from 10 to 30

days and then reached stable concentrations. An average of 5.23 mg P/L was removed by the steel chips during the last 20 days. The results in Figure 3 suggest that the two-stage treatment system using woodchips followed by steel byproducts is an effective approach to reduce nitrate and phosphate concentrations.



**Figure 3** Nitrate and phosphate removal by woodchip and steel byproduct reactors. (Phase I conditions: influent  $\text{NO}_3^- \text{-N} = 20 \text{ mg/L}$ ; influent  $\text{PO}_4^{3-} \text{-P} = 1 \text{ mg/L}$ ; woodchip HRT=24 h; steel byproduct HRT=9.5 h. Phase II conditions: influent  $\text{NO}_3^- \text{-N} = 50 \text{ mg/L}$ ; influent  $\text{PO}_4^{3-} \text{-P} = 10 \text{ mg/L}$ ; woodchip HRT= 24 h; steel byproduct HRT= 9.5 h.)

### *Effect of HRTs on Nutrient Removal*

Figure 4 presents the variations of nitrate, nitrite, phosphate and sulfate at different reactor locations during the long-term performance experiments and short-term HRT variation experiments. Figure 4a shows the average concentration profiles of the last 20 day operation under Phase I conditions. The nitrate decreased almost linearly from an initial 20 mg N/L to 3.3 mg N/L at 12 h in the woodchip bioreactor. However, it took another 12 h to completely remove nitrate. It appears that the nitrate removal kinetics by woodchips transitioned to the nitrate limiting conditions after 12 h, which necessitated long reaction times to reduce the nitrate to low levels. Christianson et al. (2011) also reported that 30-70% of nitrate was removed within 4-8 h

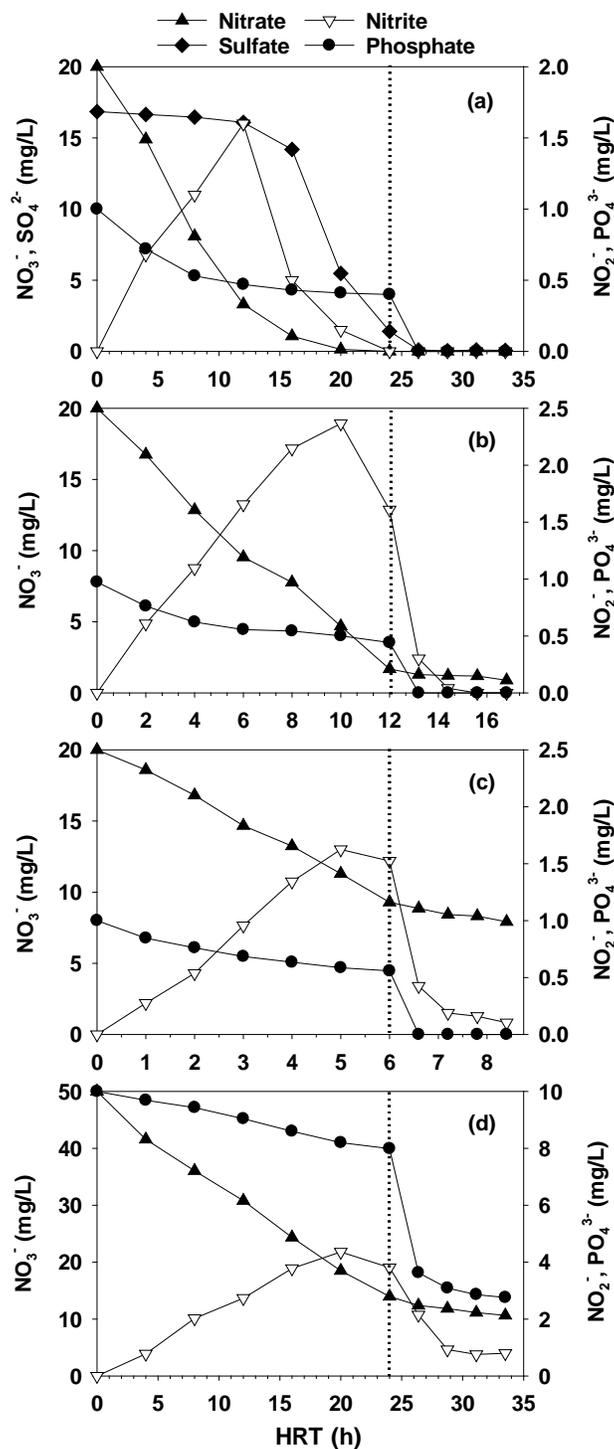
by pilot-scale drainage bioreactors and an HRT of 10 h was necessary for 90% removal for an initial concentration of 10.1 mg N/L. Biological denitrification can be described by the Michaelis–Menten kinetics which has been used to model nitrate removal by woodchips (Ghane et al., 2015). According to this model, nitrate removal follows zero-order kinetics when the concentration is higher than the half-saturation constant ( $K_m$ ) and first-order kinetics when the nitrate is lower than  $K_m$ . Based on the observation of nitrate variations in Figure 4a, zero-order and first-order kinetics were used to model the first and second 12 h nitrate reductions separately. The kinetic analysis showed that nitrate removal during the first 12 h followed zero-order with a rate constant of 1.42 mg N/L/h and a  $R^2$  value of 0.996. When the nitrate became limiting ( $< 3.3$  mg N/L) after 12 h, the nitrate removal changed to first-order kinetics with a rate constant of  $0.49 \text{ h}^{-1}$  and a  $R^2$  value of 0.971.

Biological denitrification is a sequential reaction involving reduction of nitrate to nitrite and eventually to nitrogen gas by the enzymes nitrate reductase, nitrite reductase, and others. Nitrite is an intermediate product during denitrification. Nitrite accumulation in the woodchip bioreactor was observed during this study. Figure 4a shows that nitrite increased near linearly from 0 to 1.60 mg N/L when increasing HRT from 0 to 12 h, which coincided with the zero-order reduction of nitrate. The accumulated nitrite accounted for 9.6% of the reduced nitrate. Nitrite quickly decreased after 12 h when nitrate became limiting and complete removal of nitrite was achieved by the woodchips at 24 h. This indicates that a 24 h HRT was necessary for the woodchips to completely remove nitrate and nitrite for an initial nitrate concentration of 20 mg N/L. Phosphate removal by woodchips primarily occurred within the first 8 h (1.00 to 0.50 mg P/L). Moderate reduction (0.50 to 0.40 mg P/L) was observed from 8 to 24 h. The phosphate in the woodchip effluent was quickly removed by the first 25% of the steel filter. Sulfate also declined within the woodchip reactor, but only after nitrate was depleted to less than 3.3 mg N/L. Accelerated sulfate reduction occurred when the nitrate decreased to less than 1.0 mg N/L. This indicates that nitrate at concentrations above 1 mg N/L inhibited the biological sulfate reduction. The sulfate (1.4 mg/L) in the woodchip bioreactor effluent was quickly removed by the steel filter through adsorption and/or biological sulfate reduction.

Figures 4b and 4c present the 10 day average profiles of nitrate, nitrite and phosphate at reduced HRTs. When the woodchip bioreactor HRT was reduced to 12 and 6 h, the nitrate removal efficiency decreased to 91.5% and 53.5%, respectively. The steel byproduct filter was able to further reduce the nitrate concentrations from 1.69 and 9.29 mg N/L to 0.90 and 7.92 mg N/L, respectively. Kinetic analysis suggests that nitrate removal by the woodchips followed zero-order ( $R^2=0.993-0.998$ ), and the rate constants were 1.50 and 1.80 mg N/L/h, respectively, for 12 and 6 h HRTs. Nitrite peaked at 2.37 mg N/L (10 h) and 1.62 mg N/L (5 h), respectively, for the two HRTs tested. The accumulated nitrite accounted for 15.5% and 18.7% of the reduce nitrate. Nitrite showed minor to moderate reductions at the end of the woodchip bioreactor and the effluent had nitrite concentrations of 1.62 and 1.52 mg N/L for the two HRTs tested, which exceeded the USEPA drinking water standard of 1 mg N/L. The nitrite decreased quickly in the

steel filter and reached the final concentrations of 0 and 0.10 mg N/L, respectively. When the HRT decreased to 12 h, phosphate removal by woodchips primarily occurred within the first 6 h (1 to 0.56 mg P/L) and reached 0.44 mg P/L in the effluent. The phosphate removal (1 to 0.55 mg P/L) was more evenly distributed along the woodchip reactor when the HRT was further reduced to 6 h. Therefore, the HRT had limited impact on the phosphate removal percentages by woodchips. It appears that the partition of phosphate from the solution to the woodchips became limited when the concentration was below 0.5 mg P/L. Despite the decrease of the retention time, the first 25% of steel filter depleted the remaining phosphate in the woodchip effluent for the two flow conditions.

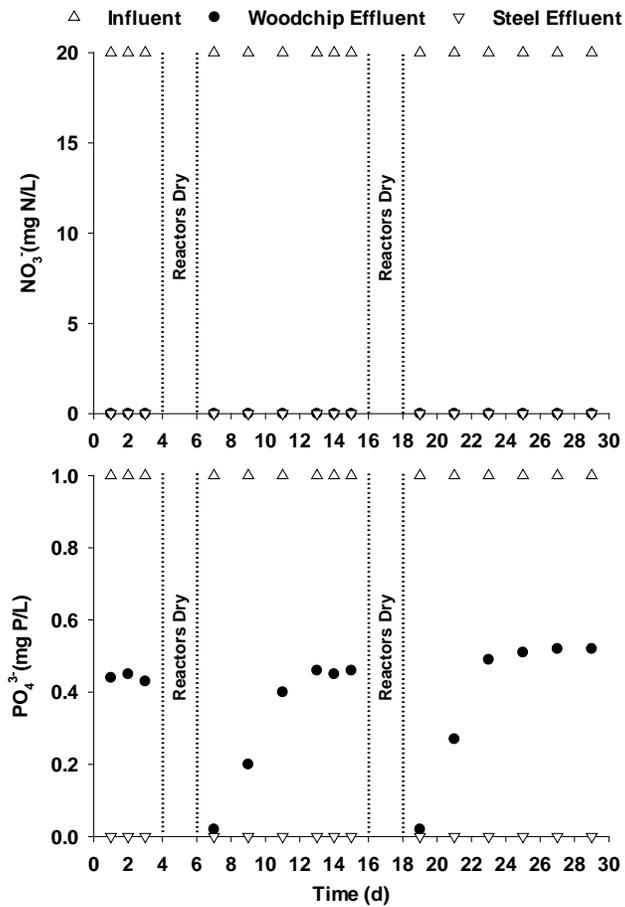
Figure 4d shows the average concentration profiles of the last 20 days of operation with high influent nutrient concentrations. Nitrate exhibited a zero-order reduction ( $R^2=0.995$ ) through woodchips with a rate constant of 1.48 mg N/L/h. Relatively high nitrite accumulation also occurred in the bioreactor which peaked at 4.36 mg N/L (13.8% of reduced nitrate) and led to an effluent concentration of 3.81 mg N/L. The phosphate decreased near linearly from 10 to 7.99 mg P/L within 24 h in the woodchip bioreactor. It is clear that high influent phosphate concentration substantially promoted more phosphate removal by the woodchips. The steel byproduct reactor moderately removed nitrate from 13.96 to 10.63 mg N/L, but substantially decreased nitrite to 0.80 mg N/L (79% removal), which was below the EPA drinking water standard. Phosphate breakthrough of the entire steel byproduct reactor occurred and 65% of the woodchip effluent phosphate was removed by the steel chips.



**Figure 4** Nitrate, nitrite, sulfate and phosphate profiles of woodchip and steel byproduct reactors. (Dash lines separate woodchips and steel byproducts. (a)  $\text{NO}_3^-$ -N=20 mg/L;  $\text{PO}_4^{3-}$ -P=1 mg/L; woodchip HRT=24 h. (b)  $\text{NO}_3^-$ -N=20 mg/L;  $\text{PO}_4^{3-}$ -P=1 mg/L; woodchip HRT=12 h. (c)  $\text{NO}_3^-$ -N=20 mg/L;  $\text{PO}_4^{3-}$ -P=1 mg/L; woodchip HRT=6 h. (d)  $\text{NO}_3^-$ -N=50 mg/L;  $\text{PO}_4^{3-}$ -P=10 mg/L; woodchip HRT=24 h.)

### Effect of Wet and Dry Cycles on Nutrient Removal

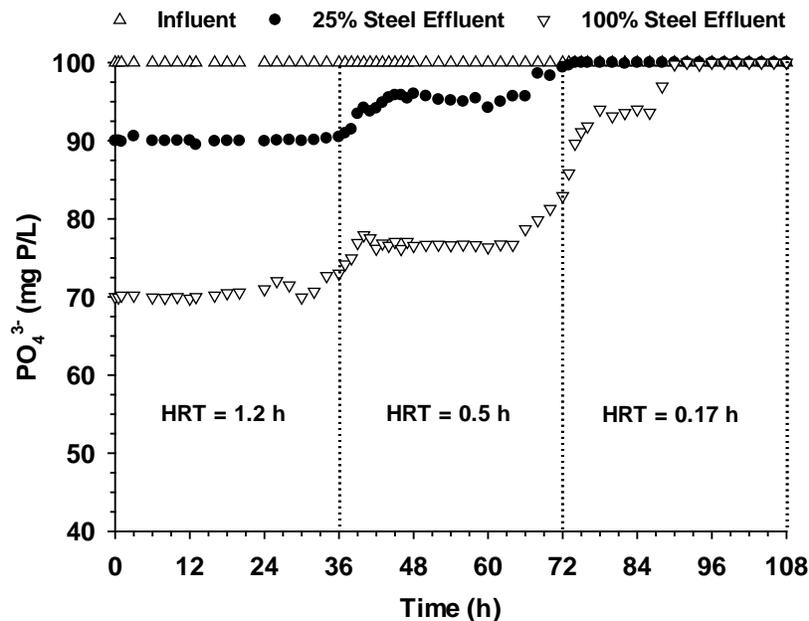
Figure 5 presents the impact of wet and dry cycles on the nutrient removal by the two reactors. After each 3-day dry period, the woodchip bioreactor consistently exhibited 100% removal of nitrate, suggesting that the denitrifying bacteria in the bioreactor can be reactivated quickly and no adaption time is required for the bioreactor. Other studies reported that the denitrification performance of woodchip bioreactors was even enhanced after drying periods presumably due to the high organic carbon content in the initial flush (Woli et al., 2010). The woodchip bioreactor showed a high phosphate removal capacity during the startup of the reactor. The phosphate was almost completely removed by woodchips during the first day operation. The removal efficiency gradually declined and reached stable conditions after seven days of operation (45-55% removal) during the two cycles. These results suggest that the preceding dry periods enhanced the phosphate removal capacity of the woodchips. However, this effect diminished quickly under continuous flow conditions. The steel byproduct reactor was not affected by the wet and dry cycles and completely removed the remaining phosphate in the woodchip bioreactor effluent.



**Figure 5** Nitrate and phosphate removal by woodchip and steel byproduct reactors during wet and dry cycle experiments

### Steel Byproduct Phosphate Breakthrough Experiment

A phosphate breakthrough test was performed on the steel byproduct reactor after the completion of nutrient removal experiments. The results are presented in Figure 6. During the first 36 h operation (HRT=1.2 h), the first 25% of steel filter removed approximately 10 mg P/L, and the rest removed an additional 20 mg P/L. When the HRT was decreased to 0.5 h, the phosphate removed by the first 25% of steel filter decreased to 5 mg P/L, and an additional 18 mg P/L was removed by the rest. Complete breakthrough of the 25% of the steel was observed at the end of 72 h. The entire steel filter showed complete breakthrough when the HRT was decreased to 0.17 h. The cumulative phosphate removal through the short and long-term experiments and the breakthrough test was calculated to determine the phosphate removal capacity of the steel chips. The total mass of the phosphate removed by the medium steel chips was 2071 mg as P. The calculated phosphate adsorption capacity of this steel byproduct was 3.70 mg P/g under continuous flow conditions. This value was much higher than the capacity (2.00 mg P/g) obtained through the batch adsorption experiments. It is possible that continued rusting or corrosion of the steel chips occurred during the column experiments, which created additional sites for phosphate adsorption. The high influent concentration (100 mg P/L) used during the breakthrough test may have also contributed to the high phosphate removal capacity. Drizo et al. (2002) reported that the maximum phosphate adsorption capacity of a steel slag increased 13 times when increasing the initial phosphate concentration from 20 to 320 mg P/L. Nonetheless, both batch and column experiments suggest that recycled steel byproducts can be used as effective adsorption materials for phosphate removal in subsurface drainage.



**Figure 6** Phosphate breakthrough curves of the steel byproduct reactor

## Conclusions

Nutrient loss from agricultural soils through subsurface drainage contributes to the deterioration of surface water quality. This study was conducted to investigate nitrate and phosphate removal in subsurface drainage using woodchip bioreactors and steel byproduct filters. The results of the batch adsorption experiments showed that phosphate adsorption capacity and kinetics of selected steel byproducts increased with decreasing particle sizes. The maximum phosphate adsorption capacity of the steel byproducts ranged from 1.30 to 5.81 mg P/g. The phosphate removed within 6 h amounted to 38 to 55% of the 24 h adsorption capacities for different steel byproducts.

The woodchip bioreactor demonstrated nitrate removal efficiencies of 75-100% and removal rates of 10.1 to 18.9 g N/m<sup>3</sup>/d for influent concentrations of 20 to 50 mg N/L. Woodchips fully developed their phosphate removal capacity after 50 d of operation and achieved average removal efficiencies of 60 and 20% for influent concentrations of 1 and 10 mg P/L, respectively. The phosphate removed by the steel byproduct filter varied from 0.25 to 8.9 mg P/L depending on the concentration in the woodchip bioreactor effluent. The total phosphate adsorption capacity of the medium steel chips was 3.70 mg P/g under continuous flow conditions. Nitrate removal by woodchips followed zero-order kinetics with rate constants of 1.42 to 1.80 mg N/L/h when nitrate was non-limiting. Nitrite accumulation was observed in the woodchip bioreactor, and the accumulated nitrite amounted to 9.6 to 18.7% of the reduced nitrate. Nitrite accumulation increased with decreasing HRTs and increasing nitrate concentrations. Substantial nitrite reduction occurred only after nitrate became limiting.

In addition to phosphate adsorption, the steel byproduct filter was also effective at removing nitrite in the woodchip bioreactor effluent. Wet and dry cycles did not affect the performance of the steel byproduct filter. Overall, the results of this study suggest that recycled steel byproducts can be used as effective adsorption materials for phosphate removal in subsurface drainage. The proposed two-stage treatment system using woodchip denitrification followed by steel byproduct filtration is a highly promising technology for field installations to remove nitrate and phosphate in subsurface drainage.

## Acknowledgments

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# Evaluating Nutrient Best Management Practices to Conserve Water Quality

## Basic Information

<b>Title:</b>	Evaluating Nutrient Best Management Practices to Conserve Water Quality
<b>Project Number:</b>	2014SD236B
<b>Start Date:</b>	3/1/2014
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<b>Research Category:</b>	Water Quality
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<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Laurent M. Ahiablame, Laurent M. Ahiablame, Sandeep Kumar

## Publications

There are no publications.

## **ANNUAL REPORT**

Reporting period: March 1, 2015 to February 28, 2016

Report submitted to the South Dakota Water Resources Institute under the USGS 104b Program.

### **Evaluating Nutrient Best Management Practices to Conserve Water Quality**

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## **INTRODUCTION**

Manure is an organic substance which is obtained from animal waste. Manure is rich source of nutrients that contributes to the soil fertility and are used in improving agricultural yields. It is shown that organic matter content is important for any soil, manure helps to increase the soil organic matter content, which in turn helps increase plant nutrient availability, promotes plant growth and facilitates nutrient cycling (Abawi and Widmer, 2000). South Dakota has extreme winter conditions during which the ground is mostly covered with snow and remains frozen for a longer period of time. The state leading in beef cattle, hogs, lambs, sheep and wool production, with substantial animal farms where a lot of agricultural wastes are generated. Therefore, managing agricultural wastes during winter months may be challenging.

Spreading manure on frozen soils has advantages and disadvantages. The advantages being that less of soil compaction occurs while driving heavy machinery, less storage space is required and reduced risk of concentrated spills into the streams occurs. The disadvantages of spreading manure on frozen soils include less manure wash off during snowmelt events. Manure application on frozen soils would lead to ammonia volatilization from the manure as frozen soils do not foster infiltration; thereby, reducing nutrient content in the soil profile.

Agriculture has shown to be a major contributor of nonpoint source pollution to streams and rivers in North America (USEPA, 1996; Kellogg *et al.*, 1994) (Berka *et al.*, 2001). While the USDA-NRCS (2012) reported that solid manure can be applied to frozen soils only if the slope is less than 4% and a setback distance of 91 meters for surface water or water conveyance systems

and 305 meters for lakes, rivers and perennial streams is observed, the South Dakota Department of Environment and Natural Resources does not recommended manure spreading on the frozen soils. (USDA-NRCS, 2012; SDDENR, 2012).

Pollution from agriculture activities has increased mainly as a result of intensification of food production (Hooda et al., 2000). Previous studies suggested that long-term experiments under field conditions are required to determine the impacts of manure application on surface runoff (Gilley and Risse, 2000). Runoff samples collected from natural precipitation events from field plots are appropriate for identifying the effects of manure on water quality (Gilley and Risse, 2000). According to studies conducted by Long et al. (1975), Wood et al. (1999) and Vories et al. (1999), runoff loss was significantly less from the fields treated with manure as compared to the fields without manure treatment (Gilley and Risse, 2000). Understanding the relationships between runoff water quantity and quality, and the type, timing, rates, and methods of manure applications will help develop improved manure management practices for water quality protection (Klinberg, 2008). The hypothesis for this study was that manure spread on high terrain results in less environmental risk than manure spread on lower terrain. Conducting research on this topic will provide science-based information on the environmental risk of spreading manure on frozen soils to help develop best management practices for agricultural waste management during winter months. The objectives of this study were to demonstrate and evaluate best management practices that minimize water quality impacts of winter manure spreading by reducing the nitrogen, phosphorus, and sediment exports due to surface runoff, and disseminate the results to producers and other stakeholders.

## **MATERIALS AND METHODS**

### **Study watershed**

The experiment was conducted at a field-scale in Egan Township, Moody County, South Dakota. Three different watersheds named North Watershed (NW), South Watershed (SW) and East Watershed (EW) were taken under study (Fig.1). The soil type of the watersheds is Egan-Ethan Complex (Fine - silty, mixed, superactive, mesic Udic Haplustolls). The area of the North Watershed is 2.71 hectares with an average slope of 13%. Similarly, the area of the South Watershed is 4.13 hectares with an average slope of 8%. The control watershed (East Watershed) has an area of 2.75 hectares with an average slope of 16%. The three watersheds are located in

the same field under the same field management and crop production (corn-soybean, two-year rotation). The North and South watersheds were treated with manure as follows: manure was spread on one-half of the North Watershed located lowest in the terrain, while on the South Watershed, manure was spread on one-half of the watershed located highest in the terrain. The East Watershed was the control and was left without any manure treatment. This treatment was used to test the hypothesis that the distance between the manure treatment location and runoff sampling point (i.e. the outlet of the watershed) will affect nutrient and sediment loss. Therefore, the South Watershed should have less nutrient and sediment loss compared to the North Watershed as the distance between the manure treatment and runoff sampling point in the South Watershed is longer than that of North Watershed, allowing more time for the water to infiltrate and thereby, reducing nutrient and sediment loss. A pull type spreader was used for spreading the manure. It should be noted that the manure was sufficient to meet Nitrogen demands in the field and nitrogen fertilizer was not as necessary.

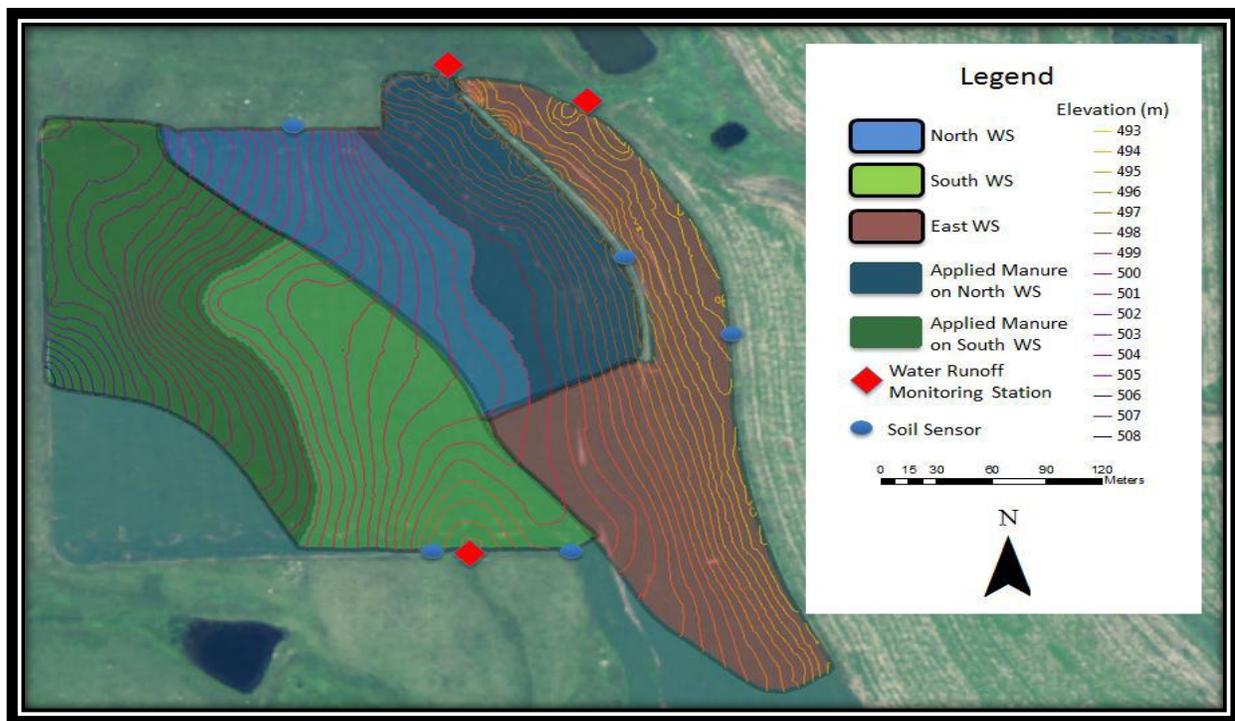


Fig. 1. Map showing the study watersheds

### Runoff Quantity

To monitor the runoff quantity, H flumes were installed at the outlet of each watershed. Peak flowS were recorded with the help of the H flumes and depth of the water flowing through the flumes was recorded by ultrasonic depth sensors (SR50A). Due to extreme weather

conditions in the state of South Dakota, runoff monitoring was difficult because the water gets frozen and could not flow through, leading to erroneous readings of runoff discharge. To avoid this problem, a Moultrie M80 GameSpy Digital Camera was installed near each flume location at the watersheds' outlet. This camera takes pictures every five minutes during the day and when it senses motion during night time. This addition helped to determine if runoff occurs and if the water freezes within the flume. Runoff depth in the H flume was measured by a bubbler system within the sampler powered by a 12 V battery, which is charged with the help of a 10-W solar panel.

### **Water Quality**

Water samples were collected by using Campbell Scientific automatic samplers during 2015; samples were collected during each runoff event and placed in a cooler and transported to the South Dakota Agricultural Laboratories in Brookings, South Dakota for further processing. The samples were analyzed for Total Kjeldahl nitrogen, nitrate-nitrogen, ammonia-nitrogen, total dissolved phosphorous, total phosphorus and total suspended solids using the following standard methods: EPA 351.3 (Colorimetric, Titrimetric, Potentiometric method) for Total Kjeldahl nitrogen, EPA 350.2 (Colorimetric, Titrimetric, Potentiometric Distillation Procedure) for ammonia; SM 4110B (Ion chromatography with chemical suppression of eluent conductivity) for nitrate, SM 4500PE (Ascorbic Acid method) for total phosphorous, SM 4500B&E (Sample digestion and Ascorbic acid method) for total dissolved phosphorous, and by SM 2540D (Total solids dried at 103-105<sup>0</sup>C) (Standard Methods for the Examination of Water and Wastewater , 21<sup>st</sup> Edition, 2005) for total suspended solids.

### **Climate**

Several instruments were used to measure climatic data at the study area. Rainfall was recorded by two standard CoCORaHS manual rain gauges and automated data logging tipping bucket rain gauge. A manual rain gauge was installed near the flume in the South Watershed and the other manual rain gauge along with a tipping bucket rain gauge was placed near the flume in the East Watershed. Air temperature was also recorded with sensors at the tipping bucket rain gauge and digital cameras.

## Soil

Soil data was collected for temperature and moisture with Decagon sensors, which were installed at five locations in the research site (two in the North Watershed, two in the South watershed, and one in the East Watershed).

## RESULTS AND DISCUSSIONS

Runoff events are depicted in Figure 2. The year 2015 had several runoff events that support the analysis on runoff as well as on water quality. There were many high intensity rainfalls during the summer from June to September. However, there was no snowmelt due to limited snowfall events in 2014. Around 10 runoff events were recorded in 2015 during summer months, starting from May to early August. There was a large runoff event on June 6 through 7, 2015, in which the total precipitation was approximately 7.5 inches which led to a lot of surface runoff.

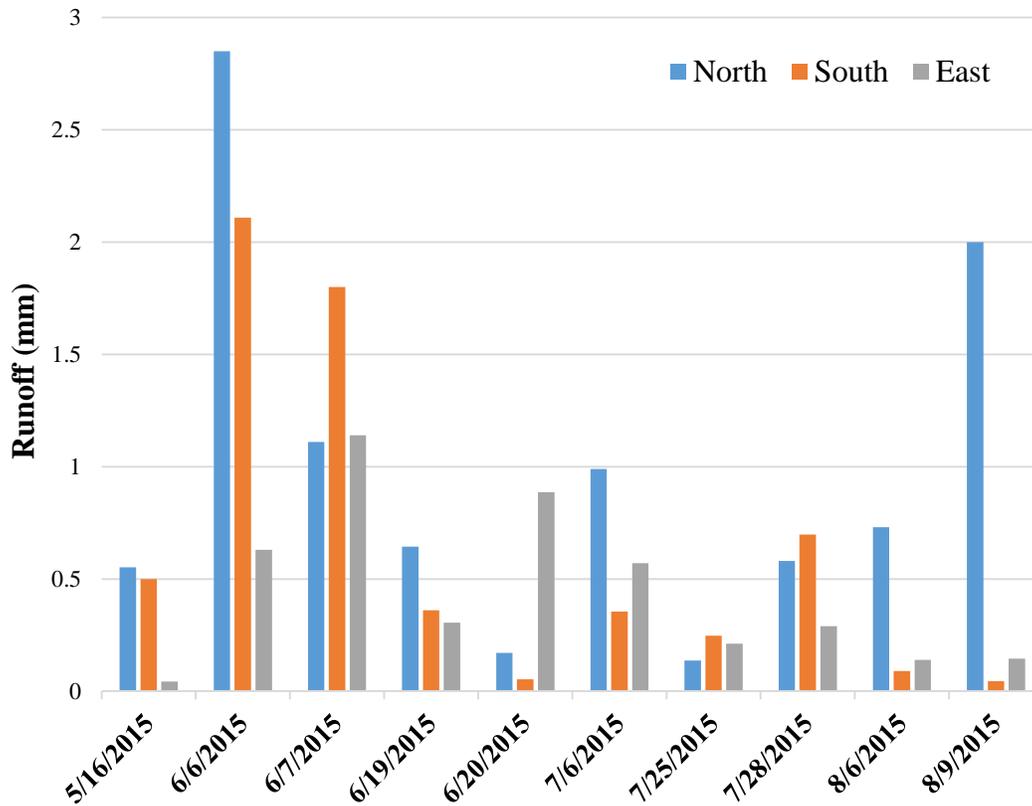


Fig. 2. Runoff events during the year 2015

The North and the East Watersheds were expected to have the highest nutrient losses among the three watersheds.

In 2015, there were five storm events on June 6, 7, 19 and 20, 2015 and July 6, 2015, during which water samples were collected. There were samples collected on the dates mentioned above for the North and South watershed while there were no samples for the East watershed on June 19 and 20, 2015.

Based on the results, it appears that nitrate-nitrogen in the South watershed had less concentration than the North and East Watersheds. The nitrate concentration ranges from 0.025 ppm in the South Watershed to 19 ppm in the North Watershed (Fig. 3). The highest nitrate-N concentration was recorded from the North Watershed while the least was recorded for the South Watershed (Fig. 3).

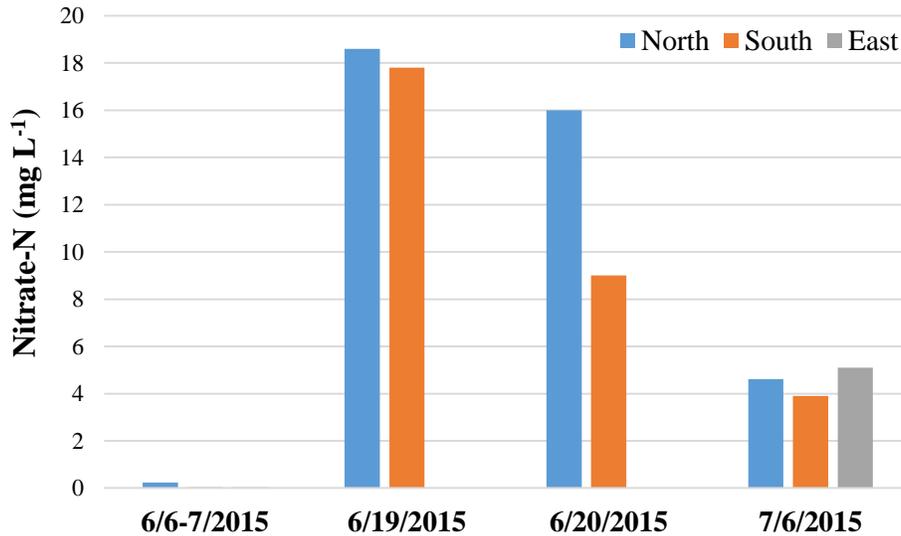


Fig. 3. Nitrate-N concentration in runoff from the three watersheds during 2015

Ammonia-nitrogen also has a similar trend as the nitrate-nitrogen concentration. However, the concentration was ranges from 0.03 ppm for South Watershed to 0.06 ppm for the North Watershed (Fig. 4). The ammonia – N loss was similar for the three watersheds within sampling events.

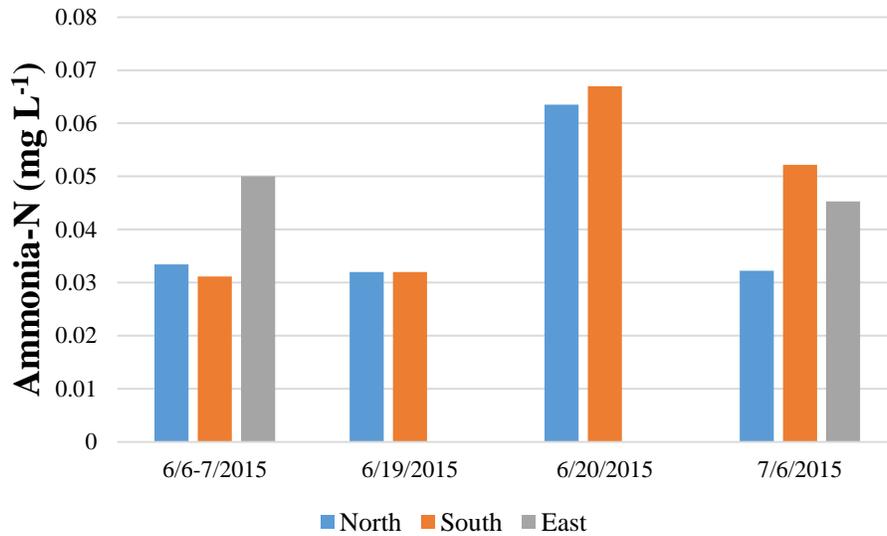


Fig. 4. Ammonia-N concentration in runoff from the three watersheds in 2015.

Total Kjeldahl nitrogen ranges from 1.06 ppm in the South Watershed to 10.5 ppm in the North Watershed for all the three watersheds (Fig. 5). This trend could be explained by the fact that manure placement was near the outlet in the North Watershed, leading to elevated levels of nutrient losses from this watershed (Fig. 5).

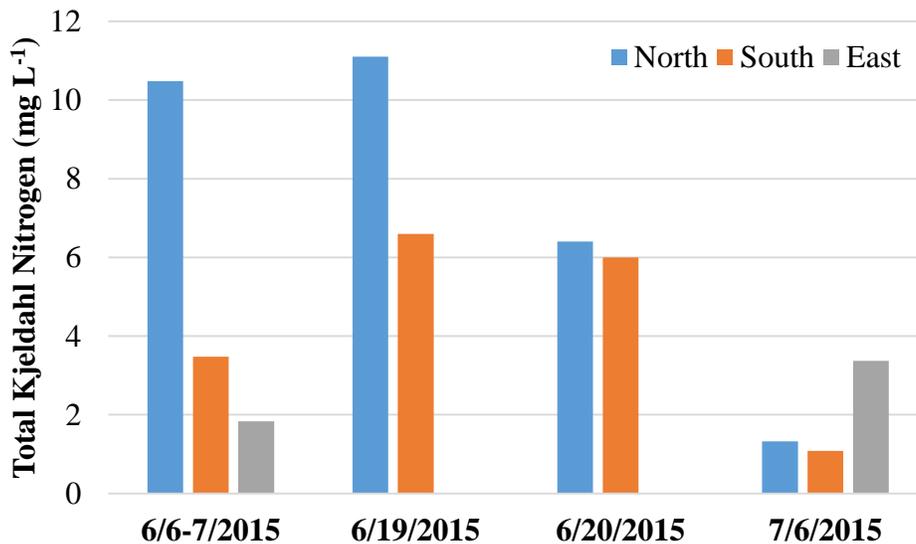


Fig. 5. Total Kjeldahl Nitrogen concentration in runoff from the three watersheds in 2015.

For total dissolved and total phosphorus, the North Watershed had the highest concentration while the East and South Watersheds had much less phosphorus (Figs. 6 and 7).

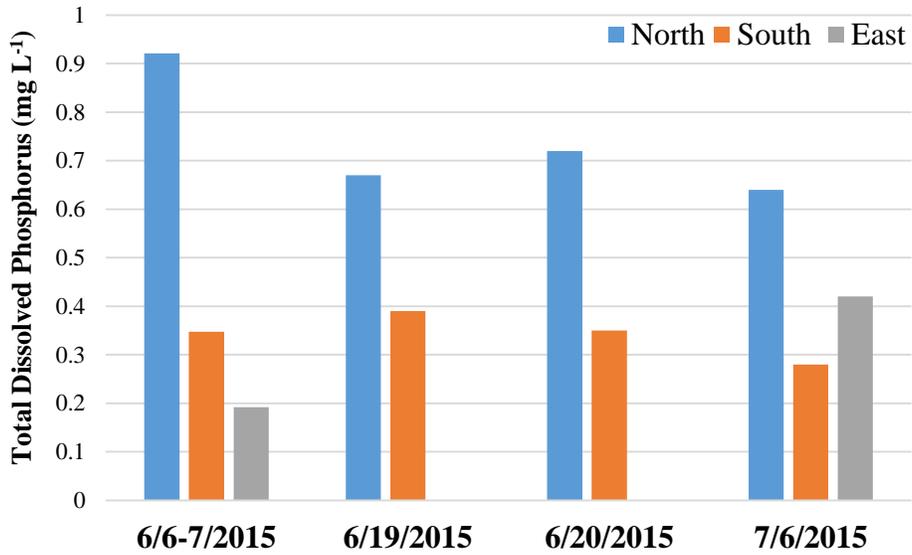


Fig. 6. Total Dissolved Phosphorus concentration in runoff from the three watersheds in 2015

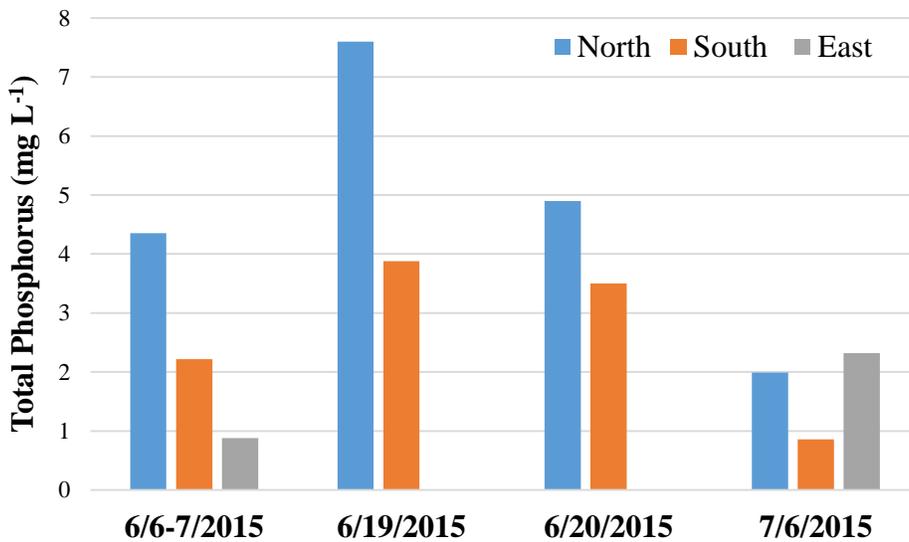


Fig. 7. Total Phosphorus concentration in runoff from the three watersheds in 2015

The total suspended solids also followed the same trend as total dissolved and total phosphorus. However, sediment loss was very high during all the sampling events. This may be due to the high intensity rainfalls that occurred during this year. The soils are fine silty clay loam with less infiltration capacity and could be susceptible to detachment depending on the intensity of rainfalls.

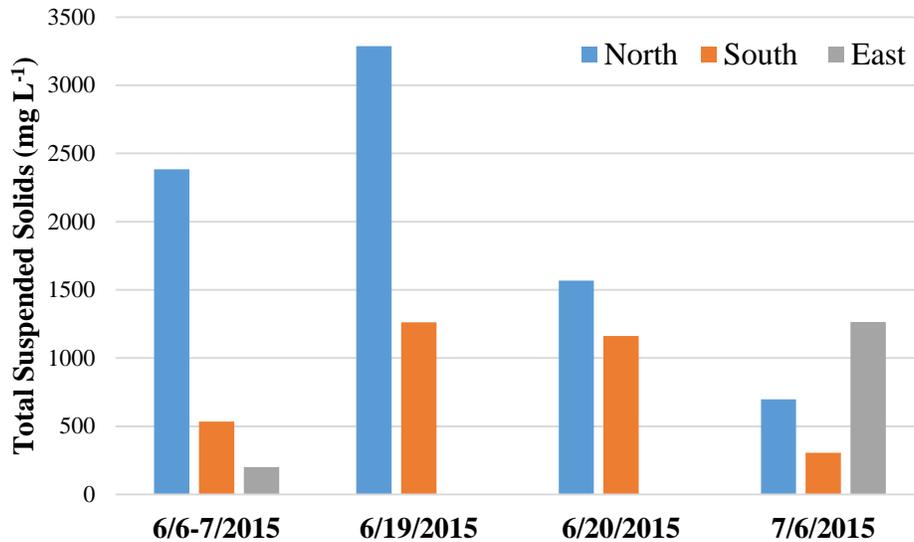


Fig. 8. Total Suspended Solids concentration in runoff from the three watersheds in 2015

Considering all the water quality parameters measured, the South Watershed had the least nutrient loss compared to the North and East Watersheds. This might be due to the fact that the manure was applied on the 50% terrain away from the outlet (upslope area) in South Watershed. In other words, there is a greater setback distance between the manured area and outlet of the watershed, leading to reduced nutrient loss. In the North Watershed, manure application was on the lower 50% of the watershed, near the outlet. The reduced distance between the application point and the outlet may result in more nutrient loss from this watershed. For the East Watershed, nutrient loss was also high compared to South Watershed. Overall, it appears that the North and East Watersheds had higher nutrient loss. However, there was not much difference between nutrient losses for the East and the North Watersheds. Based on the comparison of nutrient loss from the three watersheds, it appears that the point and rate of application of manure would play an important role in determining nutrient losses to downstream watershed. According to Chinkuyu et al. (2002), nitrate-nitrogen was greater in high application manured soils than low application manured soils and soils receiving other types of fertilizer. Similarly, the study reported that phosphorus content was high in soils that received manure applied at high rate compared to soils with low application manure. Evanylo et al. (2008) studied poultry litter, compost and poultry litter with yard waste application on Fauquier silty clay loam (Ultic Hapludalfs) at Virginia Tech's Northern Piedmont

agricultural research and education center in Orange, Virginia. They concluded that the time required for runoff to begin litter fields with compost and poultry was eight times less than the time required for the control fields. . The compost treatment allowed more water to infiltrate into the soils and remain in the soils before runoff began in the treatment site compared to the control site, possibly due to an increase in soil porosity and a decrease in bulk density resulted from increase in soil organic carbon in the compost treated soil.

## **CONCLUSIONS**

This study assessed the impacts of winter manure application on different landscape positions under a paired watershed design. Results showed that applying manure on part of the watershed would lead to less runoff and more infiltration. Water quality improved in the South Watershed where manure treatment was away from the outlet compared to the North Watershed, where manure treatment was near the outlet. Applying manure with a setback distance in the field may lead to reduced nutrient loss into nearby streams, conserving water quality.

## **ACKNOWLEDGEMENTS**

This study is supported by the South Dakota Water Research Institute (SDWRI) United States Geological Survey (USGS) 104b program, USEPA Section 319 via South Dakota Department of Environmental and Natural Resources, South Dakota Cattlemen's Association, South Dakota Farm Bureau, and East Dakota Water Development District.

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## Source water implications associated with the current Black Hills mountain pine-beetle infestation

### Basic Information

<b>Title:</b>	Source water implications associated with the current Black Hills mountain pine-beetle infestation
<b>Project Number:</b>	2014SD237B
<b>Start Date:</b>	3/1/2014
<b>End Date:</b>	9/21/2015
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	South Dakota 1st
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Surface Water, Water Supply, Management and Planning
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	James Stone, John Stamm

### Publications

1. Vik, E., Stone, J.J., 2015. Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak. Presented at the South Dakota School of Mines Research Symposium Poster Presentation, Rapid City, SD April 2015
2. Vik, E., Stone, J.J., Kenner, S., Sieverding, H., Kunza, L., Stamm, J. 2015. Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak. Presented at the 2015 Western South Dakota Hydrology Conference, Rapid City, SD, April 2015
3. Stone, J., 2016 Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak - targeting Journal of Environmental Quality.
4. Vik, E., Stone, J.J., 2015. Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak. Presented at the South Dakota School of Mines Research Symposium Poster Presentation, Rapid City, SD April 2015
5. Vik, E., Stone, J.J., Kenner, S., Sieverding, H., Kunza, L., Stamm, J. 2015. Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak. Presented at the 2015 Western South Dakota Hydrology Conference, Rapid City, SD, April 2015
6. Stone, J., 2016 Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak - targeting Journal of Environmental Quality.

## South Dakota USGS 104B 2015 Annual Report

**Project Title:** Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak

**Investigators:** Dr. James Stone, South Dakota School of Mines and Technology  
Erik Vik, South Dakota School of Mines and Technology  
Dr. Scott Kenner, South Dakota School of Mines and Technology  
Dr. Lisa Kunza, South Dakota School of Mines and Technology  
Heidi Sieverding, South Dakota School of Mines and Technology  
Dr. John Stamm, USGS, South Dakota Water Science Center

### Introduction:

The following report addresses the progress to date and findings of significance related to the project titled “Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak” during the funding period of May 2015 to February 2016. Funding for this project has supported research efforts examining natural organic matter (NOM) increases and surface water quality changes taking place in the upper reaches of the Rapid Creek watershed.

### Summary:

Since 1996, Mountain pine beetle (MPB) (*Dendroctonus ponderosae*) infestation has impacted 174,000 hectares of forest within the Black Hills of South Dakota. The goal of this research was to investigate the water quality implications of MPB infestation, and to create a foundation by which additional Black Hills MPB studies can be built. Sampling was conducted from Rapid Creek, Castle Creek, Rhoades Fork Spring, and small tributaries contributing to these streams throughout times of different precipitation and stream flow. Total organic carbon (TOC) and dissolved organic carbon (DOC) testing was completed using a Shimadzu® TOC-L CSN TOC analyzer for all collected samples. Generally, an increase in stream flow rate resulted in an increase in TOC and DOC concentration. A more general water chemistry analysis was also carried out using field probes (ExStik® II EC 500, Oakton® ORP testr, and Orbeco® TB 200) and laboratory Hach® reagent methods. Hardness parameters were highest for groundwater influenced sites, and experienced a dilution during high precipitation times. Certain sites with heavy acid mine and bog iron influence showed great variability with general water chemistry. Pearson product-moment correlations showed that organic carbon concentration correlated highly with stream flow rate, however correlated rather weakly with MPB impacted area. In some instances, organic carbon did correlate with MPB impacted area from the year 2012. This could indicate that 3 years of decomposition (2012 to 2015), is optimal for organic carbon leaching. Aside from organic carbon, water chemistry appeared to be unrelated to MPB impact. Additionally, disinfection by-product (DBP) formation potential, resulting from chlorine

disinfection, was evaluated using empirical predictor models produced by Rathbun (1996b), Rodriguez et al. (2000), Ates et al. (2007), and Semerjian et al. 2008, for collected samples. DBP concentrations varied widely, however nearly all DBP results fell under EPA regulatory limits of 80 µg/L and 60 µg/L, respectively, indicating that organic carbon in this study area was not particularly prone to forming DBPs upon chlorination.

**Deliverables:**

The project provided partial support for 2 MS CEE students (Vik and Freed) at SD Mines, and resulted in two MS theses (attached as Appendices) and one peer review publication that currently in draft form and will be submitted during 2016.

**Presentations:**

Vik, E., Stone, J.J., Kenner, S., Sieverding, H., Kunza, L., Stamm, J. Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak. Presented at the 2015 Western South Dakota Hydrology Conference, Rapid City, SD, April 2015

Vik, E., Stone, J.J. Potential organic carbon exports within the upper Rapid Creek watershed due to the current mountain pine beetle outbreak. Presented at the 2015 South Dakota Water and Wastewater Association Annual Meeting, Spearfish, SD, September 2015.

# Nutrient Removal from Agricultural Subsurface Drainage Using Denitrification Bioreactors and Phosphate Adsorbents (Year 2)

## Basic Information

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<b>Principal Investigators:</b>	Guanghai Hua, Christopher Hay

## Publications

There are no publications.

# Nutrient Removal from Agricultural Subsurface Drainage Using Denitrification Bioreactors and Phosphate Adsorbents

Progress Report: March 1, 2015 to February 28, 2016

Report Submitted to the South Dakota Water Resources Institute under the USGS 104b program

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## Introduction

Agricultural subsurface drainage is a widely adopted water management practice to increase crop production in the Midwestern United States and many other areas (Fausey et al., 1995). Subsurface drainage removes excess water from the soil profile through a network of underground perforated pipes or surface ditches, which allows cultivation of agricultural fields with poor natural drainage. However, subsurface drainage systems also provide direct conduits that can transport nutrients from agricultural fields to surrounding natural water bodies (Sims et al., 1998; Jaynes et al., 2001). Elevated nutrient levels in surface waters can lead to a number of negative water quality impacts including harmful algal blooms, hypoxic zones in the ocean, and contamination of drinking water supplies (Sharpley et al., 1987; Anderson et al., 2002; Rabalais et al., 2002; Schilling, 2005).

Nitrate has been a major water quality concern for many subsurface drainage systems due to its high solubility and mobility in soils. Nitrate-nitrogen concentrations in subsurface drainage water often exceed the United States Environmental Protection Agency (USEPA) drinking water standard of 10 mg/L. Increased nitrate loading into the Mississippi River Basin from agricultural drainage in the Midwest has been identified as a major contributor to growing hypoxia in the Gulf of Mexico (Rabalais et al., 2002). Many nutrient management practices have been implemented in fields to reduce nitrate loads from subsurface drainage systems, including improved fertilizer application, controlled drainage, and denitrification bioreactors (Gilliam and Skaggs, 1986; Delgado et al., 2005; Schipper et al., 2010).

Phosphorus transport from agricultural fields to surface waters occurs through two primary pathways: surface runoff and subsurface drainage. Early work on agricultural phosphorus transport focused on soil erosion and surface pathways, and many studies have demonstrated that phosphorus loss occurs predominantly in surface runoff (Sharpley et al., 1993; Heathwaite and Dils, 2000). Recent studies suggest that subsurface drainage is also an important phosphorus transport pathway, and the leaching of phosphorus to subsurface drainage can be enhanced by low soil phosphorus adsorption capacity and development of preferential flows (Sims et al., 1998; Gentry et al., 2007; Kleinman et al., 2015). Smith et al. (2015) showed that 49% of soluble phosphorus and 48% of total phosphorus losses occurred through subsurface drainage in the St. Joseph River Watershed in northeastern Indiana. King et al. (2015) demonstrated that more than

90% of all measured phosphorus concentrations in subsurface drainage of a watershed in central Ohio exceeded recommended levels (0.03 mg/L) for minimizing harmful algal blooms. It is necessary to develop practices that can control the concentrations of both nitrogen and phosphorus in subsurface drainage to protect aquatic ecosystems and public health.

Denitrification bioreactors have emerged as an important edge-of-field treatment technology to reduce nitrate loads from subsurface drainage (Blowes et al., 1994; Greenan et al., 2006; van Driel et al., 2006; Schipper et al., 2010; Christianson et al., 2013). These bioreactors typically utilize an organic carbon medium to support the growth of denitrifying bacteria which use organic electron donors to reduce nitrate to nonreactive nitrogen gas. Woodchips are by far the most widely used materials in field-scale denitrification bioreactors and have shown the ability to deliver long-term (> 10 years) nitrate removal while requiring minimum maintenance (Blowes et al., 1994; Robertson, 2010; Christianson et al., 2011; Cooke and Bell, 2014). Under field operating conditions, woodchip bioreactors have demonstrated nitrate removal efficiencies ranging from 33 to 100%, and removal rates of 2 to 22 g N/m<sup>3</sup>/d (Schipper et al., 2010). Little information is available regarding the fate of phosphate in denitrification bioreactors and several studies suggest that wood-based bioreactors do not have the capability to substantially remove phosphate (Jaynes et al., 2008). Phosphate sorption materials such as drinking water treatment residuals and biochar have been used to amend laboratory-scale bioreactors to enhance phosphate removal (Zoski et al., 2013; Bock et al., 2015).

Emerging phosphate removal technologies are being developed to reduce phosphorus pollution using low-cost adsorption materials, such as natural minerals, synthetic filtration products, and industrial byproducts (steel slag, steel wool and turnings, fly ash, drinking water treatment residuals and others) (Penn et al., 2007; McDowell et al., 2008; Chardon et al., 2012; Erickson et al., 2012). The phosphorus adsorbents typically provide metal cations (iron, aluminum, or calcium) to bind with dissolved phosphorus to form insoluble compounds (Weng et al., 2012; Lyngsie et al., 2014). Steel chips, wools and turnings are common byproducts produced during metal processing, and they are typically recycled for steel production. These readily available steel byproducts are expected to possess high phosphate adsorption capacity due to their high iron content (Erickson et al., 2012; Weng et al., 2012). Therefore, recycled steel byproducts can be potentially used as cost-effective filtration materials to remove phosphate from subsurface drainage. Hence, we propose a two-stage treatment system using woodchip bioreactors followed by recycled steel byproduct filters to simultaneously remove nitrate and phosphate in subsurface drainage.

The objectives of this study were to determine the nitrate and phosphate removal efficiency of a woodchip bioreactor followed by a steel byproduct filter in the laboratory. In this study, batch adsorption experiments were conducted to determine the phosphate adsorption capacity of selected steel chips and turnings. Column experiments were performed to evaluate the nitrate and phosphate removal by woodchips and selected steel byproducts under continuous flow conditions. The impacts of influent nutrient concentrations and hydraulic retention times on the performance of the bioreactor and the steel filter were investigated. The results of this study may lead to the development of new edge-of-field treatment systems that combine woodchip denitrification and steel byproduct filtration for nitrate and phosphate removal in subsurface drainage.

## Materials and Methods

### *Woodchips and Steel byproducts*

Table 1 summarizes the characteristics of the steel byproducts and woodchips used for this study. Four different steel byproducts were collected from a metal machining factory located in Sioux Falls, SD. Small chips (0.1-2 mm), medium chips (1-10 mm), medium turnings (2.5-4.5 cm) and large turnings (3-5 cm) were produced by processing carbon steel using different machines. After collection, steel byproducts were washed using non-phosphate soap and air dried before use. Woodchips made from cottonwood trees were obtained from a supplier in Sioux Falls, SD. These woodchips (0.1-6 cm) were washed with distilled water to remove dirt and floating fine particles, and air dried before use.

Table 1 Characteristics of steel byproducts and woodchips

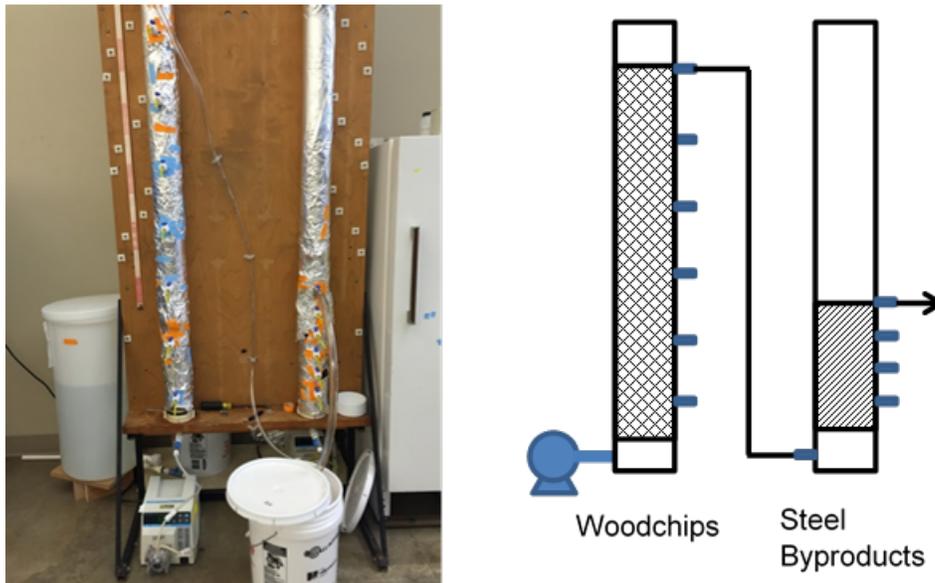
<b>Material</b>	<b>Name</b>	<b>Type</b>	<b>Size</b>
Steel Byproducts	Small Chips	Carbon Steel	0.1 – 2 mm
	Medium Chips	Carbon Steel	1 – 10 mm
	Medium Turnings	Carbon Steel	2.5-4.5 cm long, 2 mm thick
	Large Turnings	Carbon Steel	3-5 cm long, 5 mm thick
Woodchips	Woodchips	Cottonwood	36% large: 3-6 cm long, 0.5-2 cm wide 52% medium: 1-3 cm long, 0.5-1.5 cm wide 12% small: 0.1-1 cm long, 0.1-1 cm wide

### *Batch Phosphate Adsorption Experiments*

Batch adsorption experiments were conducted to determine the phosphate adsorption isotherm and kinetics of the steel byproducts. A temperature controlled orbital shaker (Model MaxQ 4000, Thermo Scientific, Waltham, MA) was used for the adsorption experiments. For the isotherm test, each steel byproduct (0.5 to 1 g) was placed in a 100 mL phosphate solution that had varying concentrations (10-40 mg P/L). The phosphate solution was prepared by dissolving  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in water and the pH was adjusted to 7 using 1.0 M NaOH solution. After 24 h of adsorption at 20 °C and 100 rpm shaking, the phosphate concentration of each sample was measured. The adsorption kinetics test was also conducted at a temperature of 20 °C and 100 rpm shaking. Each steel byproduct (0.5 to 1 g) was placed in a 100 mL phosphate solution with an initial concentration of 30 mg P/L and a pH of 7. Samples were collected at different time intervals (0.5, 1, 2, 3, 6, and 24 h) for phosphate measurement.

### *Column Reactor Experiments*

Figure 1 shows the schematic of the two-stage upflow column reactors with the woodchips and steel byproducts. Both reactors had an inside diameter of 8.7 cm. The woodchip reactor had 1.2 m of woodchips and 6 sampling ports. Medium steel chips were selected for the column experiments based on the batch adsorption experiments. The steel byproduct reactor contained 0.3 m of steel chips and 4 sampling ports. Sampling ports were evenly distributed along the height of each reactor. Drainable porosity was determined by draining each reactor for 1 h, and the resulting porosities were 50% and 80% for the woodchips and steel byproducts, respectively.



**Figure 1** The schematic and a picture of the column reactors

The woodchip bioreactor was inoculated by a soil sample collected from an agricultural field near Brookings, SD. The soil sample (50 g) was mixed with nanopure water (4 L) and the supernatant was pumped through the woodchips at a rate of 2.5 mL/min for 5 d before the column experiments. Simulated subsurface drainage was used for the column reactor experiments, and the drainage contained typical subsurface drainage ionic constituents including  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  at concentrations of 5, 2.5, 2.5, 1, 15.5, and 16.7 mg/L, respectively.

The long-term nutrient removal experiments were divided into two phases. In Phase 1, the influent nitrate and phosphate concentrations were kept at 20 mg N/L and 1 mg P/L, respectively. The influent concentrations were increased to 50 mg N/L and 10 mg P/L in Phase II as challenging conditions for the reactors. The reactors were operated continuously for 100 and 130 days under Phases I and II conditions, respectively. For both phases, the hydraulic retention time (HRT) was maintained at 24 and 9.5 h for the woodchips and steel byproducts, respectively, based on the flow rate and porosity of each material. Short-term nutrient removal experiments were also performed under Phase I nutrient concentrations to evaluate the impact of different HRTs and wet and dry cycles on the removal efficiency. During the HRT variation experiment, the HRT of the woodchips was decreased to 12 and 6 h, respectively, and the column reactors were operated for 10 days at each HRT. During the wet and dry cycle experiment, the two reactors were completely drained for 3 days, and the influent flow was restored for another 10 days (woodchip HRT=24 h). This cycle was repeated twice. During the column experiments, samples were collected from different sampling ports at different time intervals for the analysis of nitrate, nitrite, phosphate, and sulfate.

After the completion of the short and long-term column experiments, a phosphate breakthrough experiment was performed on the steel byproduct reactor to determine the total phosphate removal capacity. An influent concentration of 100 mg P/L and three HRTs (1.2 h, 0.5 h, and 0.17 h) were used during the phosphate breakthrough experiment. The reactor was operated for 36 h at each HRT.

### *Analytical Methods*

All solutions used in this study were prepared with ultrapure water (18 M $\Omega$ -cm) produced by a Barnstead NANOpure system. All solutions were adjusted to pH 7 using sodium hydroxide or sulfuric acid solutions. The chemicals used in this study were of American Chemical Society reagent grade and were purchased from Sigma Aldrich (St Luis, MO). Nitrate, nitrite, phosphate and sulfate were determined using a DX-500 ion chromatography system (Dionex, Sunnyvale, CA) equipped with a conductivity detector (CD-20, Dionex). Each sample was filtered through a 0.45  $\mu\text{m}$  filter before analysis. The pH of each solution was measured with an Orion 290A+ advanced ISE/pH/mV/OPR meter (Thermo Electron, Waltham, MA).

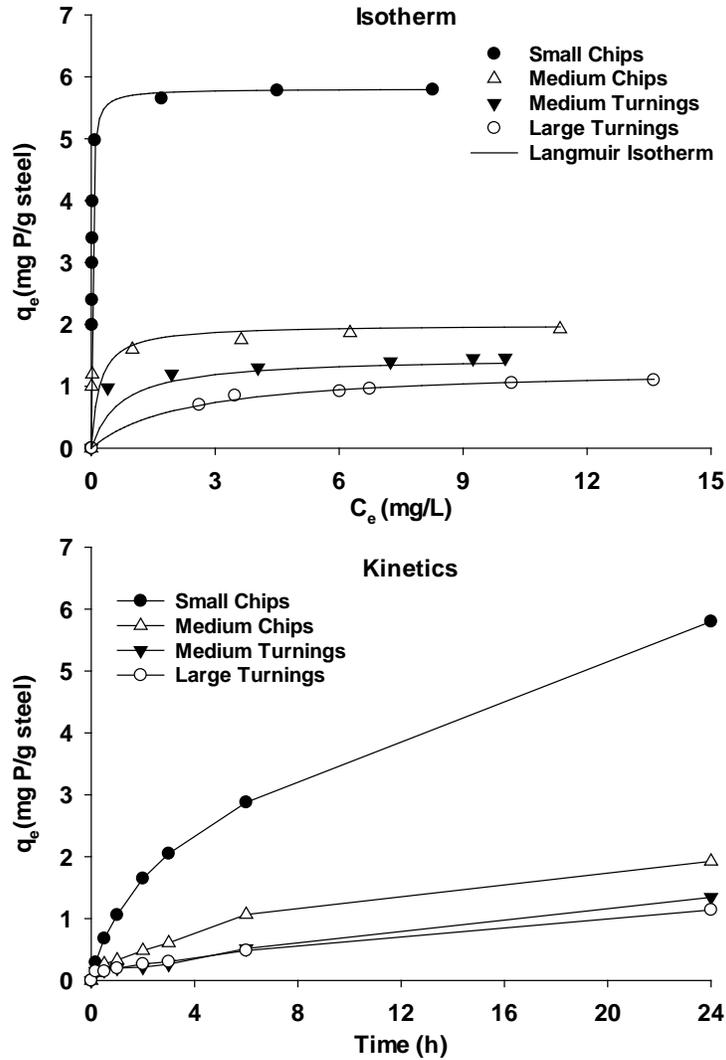
## Results and Discussion

### *Phosphate Adsorption Isotherm and Kinetics of Steel Byproducts*

Figure 2 shows the phosphate adsorption isotherm and kinetics of different steel byproducts. A Langmuir isotherm was used to model the phosphate adsorption capacity at different equilibrium concentrations. The phosphate adsorption rates were modeled using first-order reaction kinetics. Table 2 summarizes the model parameters of the Langmuir isotherm and first-order kinetics for each material. The phosphate adsorption by steel byproducts could be described by the two models as evidenced by the high linear regression coefficients ( $R^2 > 0.98$ ). The sizes of the steel byproducts exhibited large impacts on the phosphate adsorption capacities and rates. As shown in Figure 2, the adsorbed phosphate per unit mass ( $q_e$ ) of small and medium chips showed a sharp increase with increasing equilibrium concentrations ( $C_e$ ) and reached a constant value when the  $C_e$  was higher than 1 mg P/L. When medium and large turnings were used, the  $q_e$  showed a more gradual increase with increasing  $C_e$ , and reached a constant value when the  $C_e$  was higher than 3 mg P/L. The maximum  $q_e$  values determined from the Langmuir isotherm (Table 2) were 5.81, 2.00, 1.47, and 1.30 mg P/g for small chips, medium chips, medium turnings, and large turnings, respectively. This result suggests that smaller steel materials with larger surface areas have higher phosphate adsorption potential than larger steel materials. The phosphate adsorption capacities of these recycled steel byproducts were similar to several other industrial byproducts that showed good phosphate removal potential, such as drinking water treatment sludge (0.89-0.95 mg P/g, Leader et al., 2008), and various steel slags (1.35-6.56 mg P/g, Drizo et al., 2002; McDowell et al., 2008).

Kinetic analysis of the phosphate adsorption (Table 2) showed that the rate constant ( $k$ ) decreased with increasing steel particle sizes. In general, all selected steel byproducts exhibited fast phosphate removal rates. The phosphate removed within 6 hours amounted to 50, 55, 38, and 42% of the 24 h adsorption capacities, for small chips, medium chips, medium turnings, and large turnings, respectively (Figure 2). Leader et al. (2008) observed that iron-based drinking water residuals (0-2 mm) were able to adsorb phosphate to low levels within 4 h. Zeng et al. (2004) observed even faster phosphate adsorption kinetics using iron oxide tailing materials with an average size of 69  $\mu\text{m}$ , where 64-74% of the 24 h adsorption capacity occurred within the first 0.5 h. These results suggest that iron based industrial byproducts could quickly remove phosphate from water, and that the adsorption rate increases with decreasing particle sizes.

The results of the batch adsorption experiments indicate that the recycled steel byproducts exhibit relatively high phosphate adsorption capacity. Although small steel chips showed the highest phosphate removal potential, these materials may be prone to clogging during field applications due to their small size. Moreover, we observed that these small chips tended to solidify to form a single mass during the experiments. Therefore, medium chips were selected for the column experiments.



**Figure 2** Phosphate adsorption isotherm and kinetics of steel byproducts. (Experimental conditions: mass of materials=0.5-1 g; isotherm test initial P=10-40 mg/L; kinetics test initial P=30 mg/L; temperature=20 °C.)

**Table 2** Phosphate adsorption isotherm and kinetics of steel byproducts

Carbon Steel	Langmuir Isotherm			First Order Kinetics	
	$q_{max}$ (mg P/g)	$k$ (L/mg)	$R^2$	$k$ ( $min^{-1}$ )	$R^2$
Small Chips	5.81	46.5	0.999	0.276	0.978
Medium Chips	2.00	5.05	0.998	0.139	0.998
Medium Turnings	1.47	3.58	0.998	0.100	0.988
Large Turnings	1.30	0.44	0.999	0.084	0.995

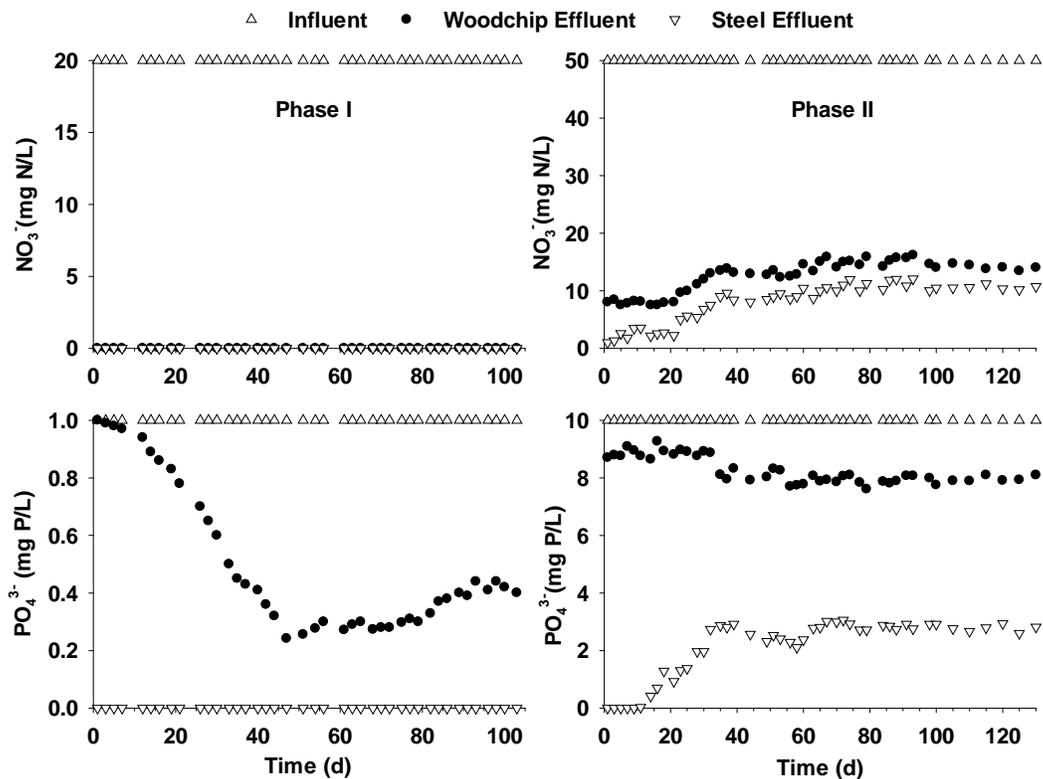
\*Experimental conditions: temperature=20 °C; adsorption time=24 h; shaking=100 rpm.

### *Long-term Nutrient Removal by Woodchip and Steel Byproduct Reactors*

Figure 3 presents the long-term performance of the woodchip bioreactor and steel byproduct filter under various influent concentrations. During the 100 days of the Phase I experiments (nitrate: 20 mg N/L, phosphate: 1 mg P/L), the woodchip bioreactor consistently achieved 100% removal of nitrate, with a removal rate of 10.1 g N/m<sup>3</sup>/d based on the reactor volume. The woodchip bioreactor did not exhibit apparent phosphate removal (< 3%) during the first 7 days. The bioreactor gradually developed the capability of phosphate removal and showed steady increases in the removal with increasing operation time after 7 days. The phosphate removal efficiency increased to a maximum of 75% on the 50th day. After that, the removal efficiency moderately decreased and reached an average of 60% during the last 20 days. This result suggests that woodchips may require relatively long operating times (e.g. > 50 days) to fully develop the capability to remove phosphate. The phosphate removal by the woodchip bioreactor may be explained by several mechanisms. First, the microbial growth within the bioreactor will consume certain amounts of phosphate. Second, the extracellular polymeric substances (EPS) produced by the biofilm on the woodchips may adsorb phosphate. Studies have shown that the EPS of activated sludge can accumulate considerable amounts of phosphate during wastewater treatment (Li et al, 2015). Third, woodchips may also have the ability to adsorb phosphate from the solution. It is possible that biofilm penetration and microbial degradation of woodchips (Cameron and Schipper, 2010) may be important in developing phosphate removal capability as evidenced by the increased phosphate removal with increasing operating time. Despite the variations of phosphate in the woodchip bioreactor effluent, the steel byproduct filter completely removed the remaining phosphate during the 100 days of operation. The removed phosphate by the steel chips varied from 0.25 to 1 mg P/L.

High nutrient concentrations (50 mg N/L and 10 mg P/L) were used during the 130 days of Phase II operation. The woodchip bioreactor achieved an average nitrate removal efficiency of 75% during the course of the experiments and the nitrate removal rate was 18.9 g N/m<sup>3</sup>/d, representing an 87% increase compared to Phase I conditions when influent nitrate was limiting. Both nitrate removal rates are well within the range observed in several other laboratory and field investigations (Robertson, 2010; Schipper et al., 2010; Woli et al., 2010). Steel chips showed the ability to further reduce the nitrate concentration and the removal extents varied from 2.59 to 7.10 mg N/L. The nitrate removal by steel filters may be attributed to the physical and chemical adsorption and/or denitrification by the biofilm in the steel media. Similar to the Phase I operation, the phosphate removal by woodchips also increased with increasing operating time and then stabilized. The phosphate removed by the woodchips averaged 1.13 mg P/L during the first 20 days and then gradually increased to 2.01 mg P/L during the last 20 days. These values are much higher than the Phase I experiments, suggesting that higher influent concentrations increased the phosphate removal potential of the woodchips. The steel byproduct reactor completely removed the phosphate during the initial 10 days and phosphate breakthrough occurred after that. The phosphate in the steel reactor effluent increased quickly from 10 to 30

days and then reached stable concentrations. An average of 5.23 mg P/L was removed by the steel chips during the last 20 days. The results in Figure 3 suggest that the two-stage treatment system using woodchips followed by steel byproducts is an effective approach to reduce nitrate and phosphate concentrations.



**Figure 3** Nitrate and phosphate removal by woodchip and steel byproduct reactors. (Phase I conditions: influent  $\text{NO}_3^-$ -N=20 mg/L; influent  $\text{PO}_4^{3-}$ -P = 1 mg/L; woodchip HRT=24 h; steel byproduct HRT=9.5 h. Phase II conditions: influent  $\text{NO}_3^-$ -N=50 mg/L; influent  $\text{PO}_4^{3-}$ -P=10 mg/L; woodchip HRT= 24 h; steel byproduct HRT= 9.5 h.)

### *Effect of HRTs on Nutrient Removal*

Figure 4 presents the variations of nitrate, nitrite, phosphate and sulfate at different reactor locations during the long-term performance experiments and short-term HRT variation experiments. Figure 4a shows the average concentration profiles of the last 20 day operation under Phase I conditions. The nitrate decreased almost linearly from an initial 20 mg N/L to 3.3 mg N/L at 12 h in the woodchip bioreactor. However, it took another 12 h to completely remove nitrate. It appears that the nitrate removal kinetics by woodchips transitioned to the nitrate limiting conditions after 12 h, which necessitated long reaction times to reduce the nitrate to low levels. Christianson et al. (2011) also reported that 30-70% of nitrate was removed within 4-8 h

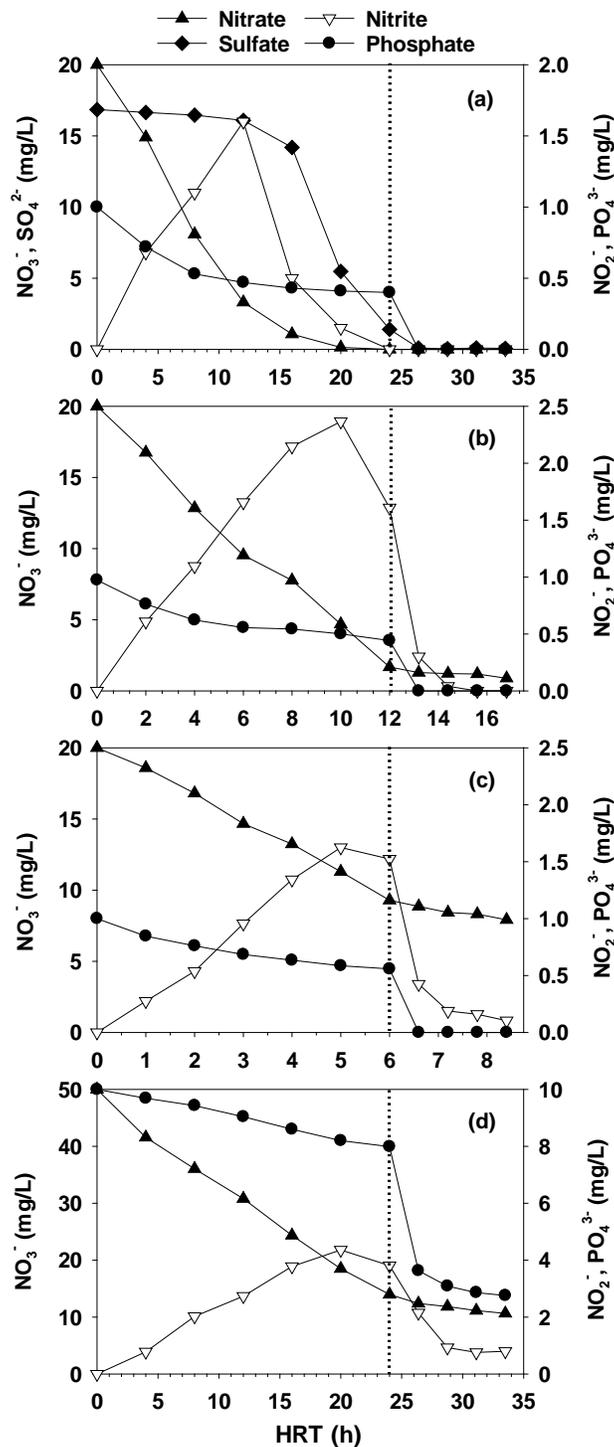
by pilot-scale drainage bioreactors and an HRT of 10 h was necessary for 90% removal for an initial concentration of 10.1 mg N/L. Biological denitrification can be described by the Michaelis–Menten kinetics which has been used to model nitrate removal by woodchips (Ghane et al., 2015). According to this model, nitrate removal follows zero-order kinetics when the concentration is higher than the half-saturation constant ( $K_m$ ) and first-order kinetics when the nitrate is lower than  $K_m$ . Based on the observation of nitrate variations in Figure 4a, zero-order and first-order kinetics were used to model the first and second 12 h nitrate reductions separately. The kinetic analysis showed that nitrate removal during the first 12 h followed zero-order with a rate constant of 1.42 mg N/L/h and a  $R^2$  value of 0.996. When the nitrate became limiting ( $< 3.3$  mg N/L) after 12 h, the nitrate removal changed to first-order kinetics with a rate constant of  $0.49 \text{ h}^{-1}$  and a  $R^2$  value of 0.971.

Biological denitrification is a sequential reaction involving reduction of nitrate to nitrite and eventually to nitrogen gas by the enzymes nitrate reductase, nitrite reductase, and others. Nitrite is an intermediate product during denitrification. Nitrite accumulation in the woodchip bioreactor was observed during this study. Figure 4a shows that nitrite increased near linearly from 0 to 1.60 mg N/L when increasing HRT from 0 to 12 h, which coincided with the zero-order reduction of nitrate. The accumulated nitrite accounted for 9.6% of the reduced nitrate. Nitrite quickly decreased after 12 h when nitrate became limiting and complete removal of nitrite was achieved by the woodchips at 24 h. This indicates that a 24 h HRT was necessary for the woodchips to completely remove nitrate and nitrite for an initial nitrate concentration of 20 mg N/L. Phosphate removal by woodchips primarily occurred within the first 8 h (1.00 to 0.50 mg P/L). Moderate reduction (0.50 to 0.40 mg P/L) was observed from 8 to 24 h. The phosphate in the woodchip effluent was quickly removed by the first 25% of the steel filter. Sulfate also declined within the woodchip reactor, but only after nitrate was depleted to less than 3.3 mg N/L. Accelerated sulfate reduction occurred when the nitrate decreased to less than 1.0 mg N/L. This indicates that nitrate at concentrations above 1 mg N/L inhibited the biological sulfate reduction. The sulfate (1.4 mg/L) in the woodchip bioreactor effluent was quickly removed by the steel filter through adsorption and/or biological sulfate reduction.

Figures 4b and 4c present the 10 day average profiles of nitrate, nitrite and phosphate at reduced HRTs. When the woodchip bioreactor HRT was reduced to 12 and 6 h, the nitrate removal efficiency decreased to 91.5% and 53.5%, respectively. The steel byproduct filter was able to further reduce the nitrate concentrations from 1.69 and 9.29 mg N/L to 0.90 and 7.92 mg N/L, respectively. Kinetic analysis suggests that nitrate removal by the woodchips followed zero-order ( $R^2=0.993-0.998$ ), and the rate constants were 1.50 and 1.80 mg N/L/h, respectively, for 12 and 6 h HRTs. Nitrite peaked at 2.37 mg N/L (10 h) and 1.62 mg N/L (5 h), respectively, for the two HRTs tested. The accumulated nitrite accounted for 15.5% and 18.7% of the reduce nitrate. Nitrite showed minor to moderate reductions at the end of the woodchip bioreactor and the effluent had nitrite concentrations of 1.62 and 1.52 mg N/L for the two HRTs tested, which exceeded the USEPA drinking water standard of 1 mg N/L. The nitrite decreased quickly in the

steel filter and reached the final concentrations of 0 and 0.10 mg N/L, respectively. When the HRT decreased to 12 h, phosphate removal by woodchips primarily occurred within the first 6 h (1 to 0.56 mg P/L) and reached 0.44 mg P/L in the effluent. The phosphate removal (1 to 0.55 mg P/L) was more evenly distributed along the woodchip reactor when the HRT was further reduced to 6 h. Therefore, the HRT had limited impact on the phosphate removal percentages by woodchips. It appears that the partition of phosphate from the solution to the woodchips became limited when the concentration was below 0.5 mg P/L. Despite the decrease of the retention time, the first 25% of steel filter depleted the remaining phosphate in the woodchip effluent for the two flow conditions.

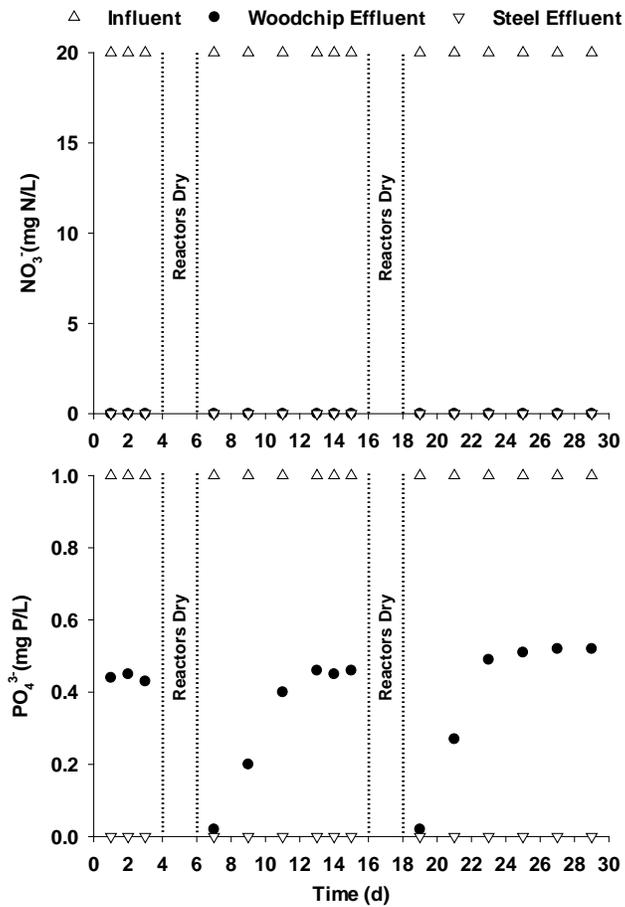
Figure 4d shows the average concentration profiles of the last 20 days of operation with high influent nutrient concentrations. Nitrate exhibited a zero-order reduction ( $R^2=0.995$ ) through woodchips with a rate constant of 1.48 mg N/L/h. Relatively high nitrite accumulation also occurred in the bioreactor which peaked at 4.36 mg N/L (13.8% of reduced nitrate) and led to an effluent concentration of 3.81 mg N/L. The phosphate decreased near linearly from 10 to 7.99 mg P/L within 24 h in the woodchip bioreactor. It is clear that high influent phosphate concentration substantially promoted more phosphate removal by the woodchips. The steel byproduct reactor moderately removed nitrate from 13.96 to 10.63 mg N/L, but substantially decreased nitrite to 0.80 mg N/L (79% removal), which was below the EPA drinking water standard. Phosphate breakthrough of the entire steel byproduct reactor occurred and 65% of the woodchip effluent phosphate was removed by the steel chips.



**Figure 4** Nitrate, nitrite, sulfate and phosphate profiles of woodchip and steel byproduct reactors. (Dash lines separate woodchips and steel byproducts. (a)  $\text{NO}_3^-$ -N=20 mg/L;  $\text{PO}_4^{3-}$ -P=1 mg/L; woodchip HRT=24 h. (b)  $\text{NO}_3^-$ -N=20 mg/L;  $\text{PO}_4^{3-}$ -P=1 mg/L; woodchip HRT=12 h. (c)  $\text{NO}_3^-$ -N=20 mg/L;  $\text{PO}_4^{3-}$ -P=1 mg/L; woodchip HRT=6 h. (d)  $\text{NO}_3^-$ -N=50 mg/L;  $\text{PO}_4^{3-}$ -P=10 mg/L; woodchip HRT=24 h.)

### Effect of Wet and Dry Cycles on Nutrient Removal

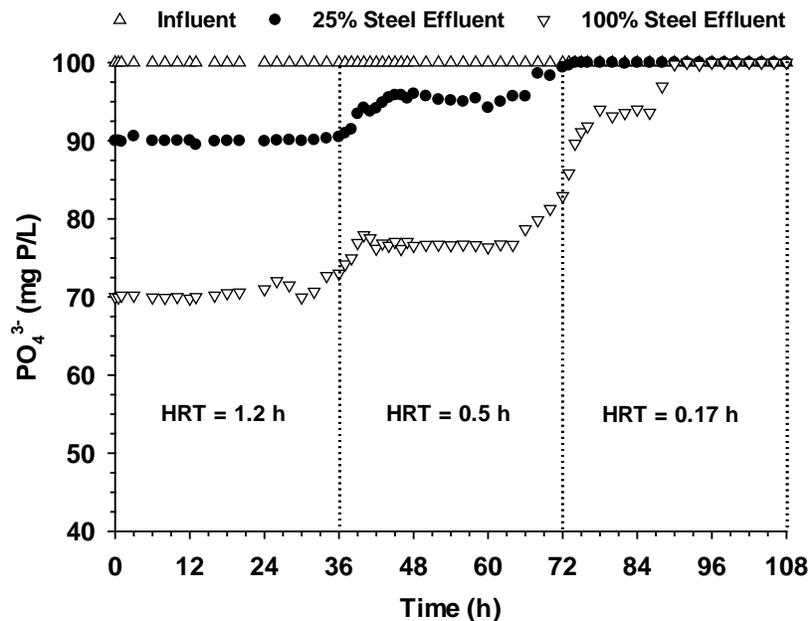
Figure 5 presents the impact of wet and dry cycles on the nutrient removal by the two reactors. After each 3-day dry period, the woodchip bioreactor consistently exhibited 100% removal of nitrate, suggesting that the denitrifying bacteria in the bioreactor can be reactivated quickly and no adaption time is required for the bioreactor. Other studies reported that the denitrification performance of woodchip bioreactors was even enhanced after drying periods presumably due to the high organic carbon content in the initial flush (Woli et al., 2010). The woodchip bioreactor showed a high phosphate removal capacity during the startup of the reactor. The phosphate was almost completely removed by woodchips during the first day operation. The removal efficiency gradually declined and reached stable conditions after seven days of operation (45-55% removal) during the two cycles. These results suggest that the preceding dry periods enhanced the phosphate removal capacity of the woodchips. However, this effect diminished quickly under continuous flow conditions. The steel byproduct reactor was not affected by the wet and dry cycles and completely removed the remaining phosphate in the woodchip bioreactor effluent.



**Figure 5** Nitrate and phosphate removal by woodchip and steel byproduct reactors during wet and dry cycle experiments

### Steel Byproduct Phosphate Breakthrough Experiment

A phosphate breakthrough test was performed on the steel byproduct reactor after the completion of nutrient removal experiments. The results are presented in Figure 6. During the first 36 h operation (HRT=1.2 h), the first 25% of steel filter removed approximately 10 mg P/L, and the rest removed an additional 20 mg P/L. When the HRT was decreased to 0.5 h, the phosphate removed by the first 25% of steel filter decreased to 5 mg P/L, and an additional 18 mg P/L was removed by the rest. Complete breakthrough of the 25% of the steel was observed at the end of 72 h. The entire steel filter showed complete breakthrough when the HRT was decreased to 0.17 h. The cumulative phosphate removal through the short and long-term experiments and the breakthrough test was calculated to determine the phosphate removal capacity of the steel chips. The total mass of the phosphate removed by the medium steel chips was 2071 mg as P. The calculated phosphate adsorption capacity of this steel byproduct was 3.70 mg P/g under continuous flow conditions. This value was much higher than the capacity (2.00 mg P/g) obtained through the batch adsorption experiments. It is possible that continued rusting or corrosion of the steel chips occurred during the column experiments, which created additional sites for phosphate adsorption. The high influent concentration (100 mg P/L) used during the breakthrough test may have also contributed to the high phosphate removal capacity. Drizo et al. (2002) reported that the maximum phosphate adsorption capacity of a steel slag increased 13 times when increasing the initial phosphate concentration from 20 to 320 mg P/L. Nonetheless, both batch and column experiments suggest that recycled steel byproducts can be used as effective adsorption materials for phosphate removal in subsurface drainage.



**Figure 6** Phosphate breakthrough curves of the steel byproduct reactor

## Conclusions

Nutrient loss from agricultural soils through subsurface drainage contributes to the deterioration of surface water quality. This study was conducted to investigate nitrate and phosphate removal in subsurface drainage using woodchip bioreactors and steel byproduct filters. The results of the batch adsorption experiments showed that phosphate adsorption capacity and kinetics of selected steel byproducts increased with decreasing particle sizes. The maximum phosphate adsorption capacity of the steel byproducts ranged from 1.30 to 5.81 mg P/g. The phosphate removed within 6 h amounted to 38 to 55% of the 24 h adsorption capacities for different steel byproducts.

The woodchip bioreactor demonstrated nitrate removal efficiencies of 75-100% and removal rates of 10.1 to 18.9 g N/m<sup>3</sup>/d for influent concentrations of 20 to 50 mg N/L. Woodchips fully developed their phosphate removal capacity after 50 d of operation and achieved average removal efficiencies of 60 and 20% for influent concentrations of 1 and 10 mg P/L, respectively. The phosphate removed by the steel byproduct filter varied from 0.25 to 8.9 mg P/L depending on the concentration in the woodchip bioreactor effluent. The total phosphate adsorption capacity of the medium steel chips was 3.70 mg P/g under continuous flow conditions. Nitrate removal by woodchips followed zero-order kinetics with rate constants of 1.42 to 1.80 mg N/L/h when nitrate was non-limiting. Nitrite accumulation was observed in the woodchip bioreactor, and the accumulated nitrite amounted to 9.6 to 18.7% of the reduced nitrate. Nitrite accumulation increased with decreasing HRTs and increasing nitrate concentrations. Substantial nitrite reduction occurred only after nitrate became limiting.

In addition to phosphate adsorption, the steel byproduct filter was also effective at removing nitrite in the woodchip bioreactor effluent. Wet and dry cycles did not affect the performance of the steel byproduct filter. Overall, the results of this study suggest that recycled steel byproducts can be used as effective adsorption materials for phosphate removal in subsurface drainage. The proposed two-stage treatment system using woodchip denitrification followed by steel byproduct filtration is a highly promising technology for field installations to remove nitrate and phosphate in subsurface drainage.

## Acknowledgments

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# Controlling Harmful Algal Blooms in Eutrophic Lakes by Combined Phosphorus Precipitation and Sediment Capping

## Basic Information

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<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Kyungnan Min, Guanghui Hua

## Publications

There are no publications.

# **Controlling Harmful Algal Blooms in Eutrophic Lakes by Combined Phosphorus Precipitation and Sediment Capping**

Progress Report: March 1, 2015 to February 28, 2016

Investigators: Kyungnan Min and Guanghui Hua, South Dakota State University

Report Submitted to the South Dakota Water Resources Institute under the USGS 104b program

Written by: Kyungnan Min, Sepideh Sadeghi, Guanghui Hua

## **INTRODUCTION**

South Dakota Department of Environment and Natural Resources (DENR) assessed 143 lakes in South Dakota based on numeric water quality standards and nutrient-related narrative standards (SD DENR, 2014). Approximately 60% of the assessed lakes do not support one or more assigned beneficial uses. Lakes in South Dakota are impaired by excessive nutrients and siltation generated from non-point source pollution. The trophic status indicates that 118 out of 143 lakes are characterized as eutrophic to hypereutrophic condition. Eutrophication can lead to the development of harmful algal blooms of cyanobacteria (blue-green algae), which will result in detrimental effects on lake water quality including increased turbidity, dissolved oxygen depletion, and scum layers formation (Smith et al., 1999). Moreover, cyanobacteria can release potent toxins that pose significant threats to ecosystem and public health.

Phosphorus (P) loading reduction is critical to eutrophication control because phosphorus frequently limits the primary production in lakes. It is generally accepted that the first step to control harmful algal blooms in eutrophic lakes is to reduce the external nutrient loading from point and non-points sources. However, many studies have shown that the lake recovery is a slow process even when the external P loading has substantially reduced. The internal P loading from P-rich sediment is one major factor that is responsible for enhanced eutrophication process (Gulati and Van Donk, 2002; Berg et al., 2004; Cooke et al., 2005). The phosphorus released from the sediment can delay the lake recovery for years to decades (Sondergaard et al., 2001; Cooke et al., 2005). Therefore, effective internal P loading control strategies are necessary to accelerate lake recovery and achieve long-term lake eutrophication mitigation.

Sediment dredging is one of the in-lake restoration methods that can be used to reduce the internal P loading from the sediment (Peterson, 1982). However, sediment removal is relatively expensive and often cannot provide a permanent solution (Welch and Cooke, 2005). The in-situ sediment capping technology has been developed to control the P cycling from the sediment. This technology involves placement of a layer of particulate materials at the sediment-water interface to create a barrier between the sediment and overlaying water. The in-situ sediment capping is a promising technology that can stabilize sediment, minimize re-suspension, and reduce nutrient release from the sediment (Simpson et al., 2002; Kim et al., 2007; Lin et al., 2011). Clean sand has traditionally been used for in situ capping of sediment for eutrophication

control. Recently, active barrier system has been developed to improve the effectiveness of sediment capping. In this system, reactive materials are used to bind contaminants in the sediments by adsorption or precipitation, thereby improving the capping efficiency. These reactive materials include activated carbon, gypsum, modified sand, natural and modified zeolite, calcite and others (Berg et al., 2004; Jacobs and Waite, 2004; Park et al., 2007; Viana et al., 2008; Pan et al., 2012). Several studies have shown that calcite is effective in preventing phosphorus release from sediment under anaerobic conditions (Hart et al., 2003; Berg et al., 2004). Lin et al. (2011) used a mixed calcite and zeolite medium for sediment capping in a laboratory study. The results showed that the mixture was able to simultaneously control phosphorus and ammonium release from the sediment. A lanthanum-enriched bentonite clay (Phoslock®) has been proven to be a strong P binding material in several laboratory and field experiments (Lurling and Van Oosterhout 2013). These P binding materials can be used as active barrier systems for sediment capping in eutrophic lakes to provide long-term inhibition of P recycling from the sediments.

Direct precipitation of P and algae cells is an effective remedial method that can quickly reduce the lake water P content and mitigate lake algal blooms. Aluminium-, calcium-, and iron salts are the common chemical coagulants that have been applied for algal bloom control and P reduction in lakes (Cooke et al., 2005). Phytoplankton can be precipitated more effectively when these coagulants are used together with clay particles as ballast (Wang et al., 2012). Although chemical and physical precipitation can remove the total P from the water column, it does not provide a long-term prevention of P release from the sediment due to the re-suspension of the precipitated flocs. The combined phosphorus precipitation and sediment capping technology is a promising method to control harmful algal blooms in eutrophic lakes. The treatment involves precipitation of dissolved and particulate P from water column and subsequent immobilization of any P released from the sediment using reactive materials (Pan et al., 2012; Lurling and Van Oosterhout, 2013). The precipitation-capping technology could also promote the development of sandy sediment and facilitate a sustainable improvement of sediment-water environment.

The objective of this study is to develop an effective technology using precipitation and sediment capping to control harmful algal blooms and P levels in eutrophic lakes. Laboratory coagulation experiments were performed to evaluate factors affecting the dissolved P and algal cells precipitation using coagulants and reactive P binding particles to precipitate dissolved P and algal cells. The long-term sediment incubation experiments will be conducted in the second year to measure P flux from the sediment-water interfaces after capping with reactive P-binding particles. The results of this project will provide critical information on the application of the P precipitation and sediment capping technology for in lake restoration in South Dakota. This may eventually lead to the development of an effective lake management tool that can be used as a sustainable eutrophication control strategy to accelerate the lake recovery in South Dakota and many other areas.

## MATERIALS AND METHODS

### Lake Water Samples and Natural Minerals

The lake water samples were collected from Lake Kampeska located in Watertown, South Dakota, and used as raw water for the coagulation experiments. The characteristics of the lake are shown in Table 1. Aluminum sulfate (98% purity, Fisher Scientific) was used as the coagulant for this study. Calcite (97.9% CaCO<sub>3</sub>), Zeolite, Silica Sand (99.7% SiO<sub>2</sub>) and limestone were obtained from Great Lakes Calcium Co., Bear River Zeolite Co., U.S Silica Company, and Martin Marietta Co., respectively. A six position jar tester (Phipps & Bird) was used for the coagulation experiments using 500 mL glass beakers.

Table 1. Lake Kampeska Water Characteristics

Parameters	Values
pH	8.5
Alkalinity	250 mg/L as CaCO <sub>3</sub>
Phosphate	0.65 mg P/L
Total Phosphate	2.7 mg P/L
Nitrate	0.2 mg N/L
Ammonia	0.5 mg N/L

### Cyanobacteria Strains, Maintenance, and Culture Conditions

*Anabaena sp.* PCC 7120 (here in referred to as *Anabaena sp.* 7120), a model species for filamentous cyanobacteria, was obtained from the Pasteur Culture Collection of Cyanobacteria (Paris, France). For long term storage, strains were frozen at -80°C in 5% v/v methanol. For short-term maintenance, the cyanobacteria were grown on BG11 agar (1.5% agar) (Allen and Stanier, 1968) at pH 7.1, incubated at room temperature of 20 to 22° C under constant illumination of 24 µmol/m<sup>2</sup>-s using fluorescent lights and then stored at room temperature. Light intensity was measured with a Heavy Duty Light Meter with PC Interface (Extech Instruments, Waltham MA, USA).

Cyanobacterial cultures were grown in 40 L fiberglass photobioreactors (Solar Components Corp., Manchester, NH, USA) that were sparged with a mixture of 95-5% air-CO<sub>2</sub> gas at a rate of 0.25 L/min. The culture medium consisted of 30 L BG11 and was inoculated with 1.5 L (5%) of an *Anabaena sp.* 7120 culture that had been grown to mid-log phase. The reactors were incubated for up to 2 days after stationary phase was reached at room temperature under constant illumination of approximately 40 µE/m<sup>2</sup>-s.

### Experimental Procedure

All particles were sieved with Sieves #100 (0.15 mm), #140 (0.106 mm), #200 (0.075 mm) and #325 (0.044 mm), and washed with deionized water to remove any fine particles and impurities. They were then dried before use. In Phase I, different amounts of cyanobacteria (*Anabaena sp.*

7120) were dosed into 500 mL lake water to provide an initial turbidity of 20 NTU or 50 NTU. Alum and particles were applied to the water sample at different dosage. The coagulation tests proceeded with rapid mixing at 250 rpm for 2 minutes followed by slow mixing at 30 rpm for 20 minutes. Sedimentation was allowed to occur for 24 hours. In Phase II, the settling kinetics were evaluated by taking supernatant of coagulated samples after 1, 2, 5, 10, 30, and 1440 minutes intervals. In Phase III, the resuspension of coagulated flocs were investigated at different velocity gradients of zero to 500/s for 5 minutes after 24-hour settlement. The stirrer was located at about 3 cm above the sediment layer. For all experiments, supernatant was taken from 1 cm below the top water surface to measure different water quality parameters.

### Analytical Methods

The analysis of ammonia, nitrate, and phosphate was carried out using UV-visible spectrophotometer (HACH, DR 4000, USA). *Chlorophyll a* was analyzed using UV-visible spectrophotometer (Shimadzu, UV-160/160A, Japan) based on the Standard Methods for Examination of Water and Wastewater (Clesceri et al, 1998). A turbidity meter (HACH, 2100P, USA) was used to measure turbidity.

## **RESULTS AND DISCUSSION**

### Impact of Alum and Particle Dosage on P and *Chlorophyll a* Removal

Figure 1 shows the impact of different alum dosages from zero to 8 mg Al/L on P and *chlorophyll a* removal. Alum coagulation effectively removed total P, orthophosphate and *chlorophyll a* especially when the dose was higher than 4 mg Al/L. At the alum dosage of 8 mg Al/L, more than 90% removal rates were observed for these parameters. However, alum coagulation did not affect the nitrate removal. The maximum removal efficiency of 60% was achieved for ammonium-N at the highest dose of 8 mg Al/L.

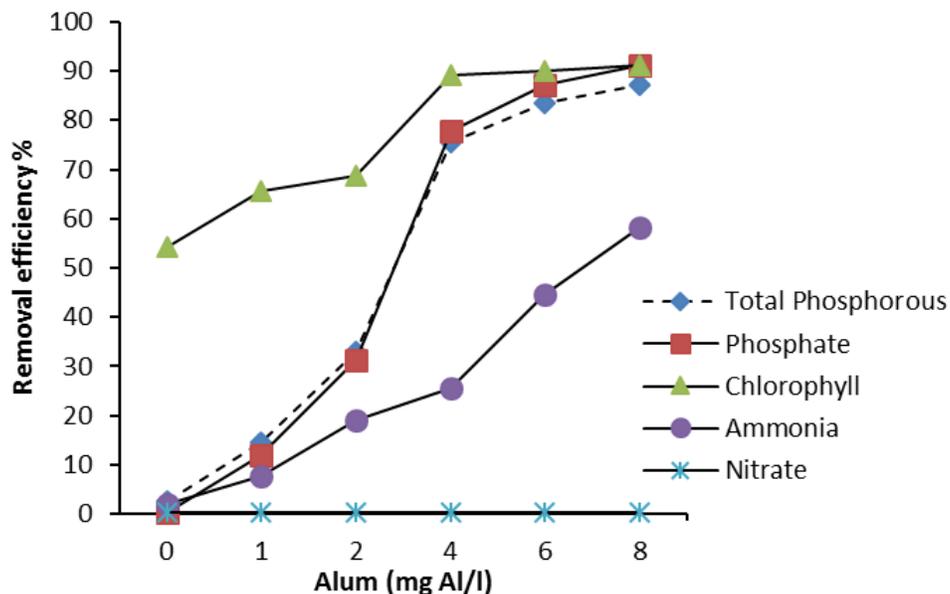


Figure 1 Effect of alum dosage on P, *Chlorophyll-a*, nitrogen removal efficiency

Table 2 shows the effect of different particles doses on the orthophosphate and *chlorophyll a* removal efficiency. In this test, alum dosage was fixed at 4 mg Al/L and dosages of sand, calcite, zeolite and limestone varied. Particle sizes were 45 to 75  $\mu\text{m}$  and supernatant was taken after 24-hour settling. The added particles has limited impact on the *chlorophyll a* removal efficiency. However, the P removal gradually decreased with increasing particle doses. This is likely caused by the competitive adsorption of alum by these particles. Zeolite showed the largest reduction in P removal whereas sand showed the least.

Table 2 Effect of Particle Dose on *Chlorophyll a* and Phosphate Removal

Coagulant + Particles (g/L)	<i>Chlorophyll- a</i> Removal Rate (%)	Phosphate Removal Rate (%)
Alum (4 mg Al/L)	89.5	78.2
Alum + 0.2 g/L Calcite	90.6	77.9
Alum + 0.4 g/L Calcite	90.0	77.5
Alum + 1 g/L Calcite	88.8	74.7
Alum + 2 g/L Calcite	88.1	76.0
Alum + 5 g/L Calcite	87.7	71.4
Alum + 0.2 g/L Zeolite	90.6	75.8
Alum + 0.4 g/L Zeolite	89.5	73.9
Alum + 1 g/L Zeolite	89.1	72.9
Alum + 2 g/L Zeolite	88.4	69.7
Alum + 5 g/L Zeolite	85.6	62.9
Alum + 0.2 g/L Lime stone	89.8	77.1
Alum + 0.4 g/L Lime stone	89.9	78.4
Alum + 1 g/L Lime stone	90.2	76.2
Alum + 2 g/L Lime stone	89.5	70.7
Alum + 5 g/L Lime stone	89.1	71.7
Alum + 0.2 g/L Sand	90.6	78.2
Alum + 0.4 g/L Sand	90.9	76.9
Alum + 1 g/L Sand	90.2	78.6
Alum + 2 g/L Sand	89.8	75.2
Alum + 5 g/L Sand	90.3	74.3

## Impact of Particle Addition on Settling Kinetics

Figure 2 shows the effect of particle sizes on the supernatant turbidity at different settling times. The particle sizes ranged from 0.044 to 0.075 mm did not affect the settling of the coagulated flocs. However, addition of particles enhanced floc settling when the particles size was higher than 0.0106 mm. The added particles in the size of 0.15 mm substantially improved the settling kinetics of the flocs, especially during the first 5 minutes. The effect of the enhanced settling by these particles diminished when the settling time was more than 30 minutes.

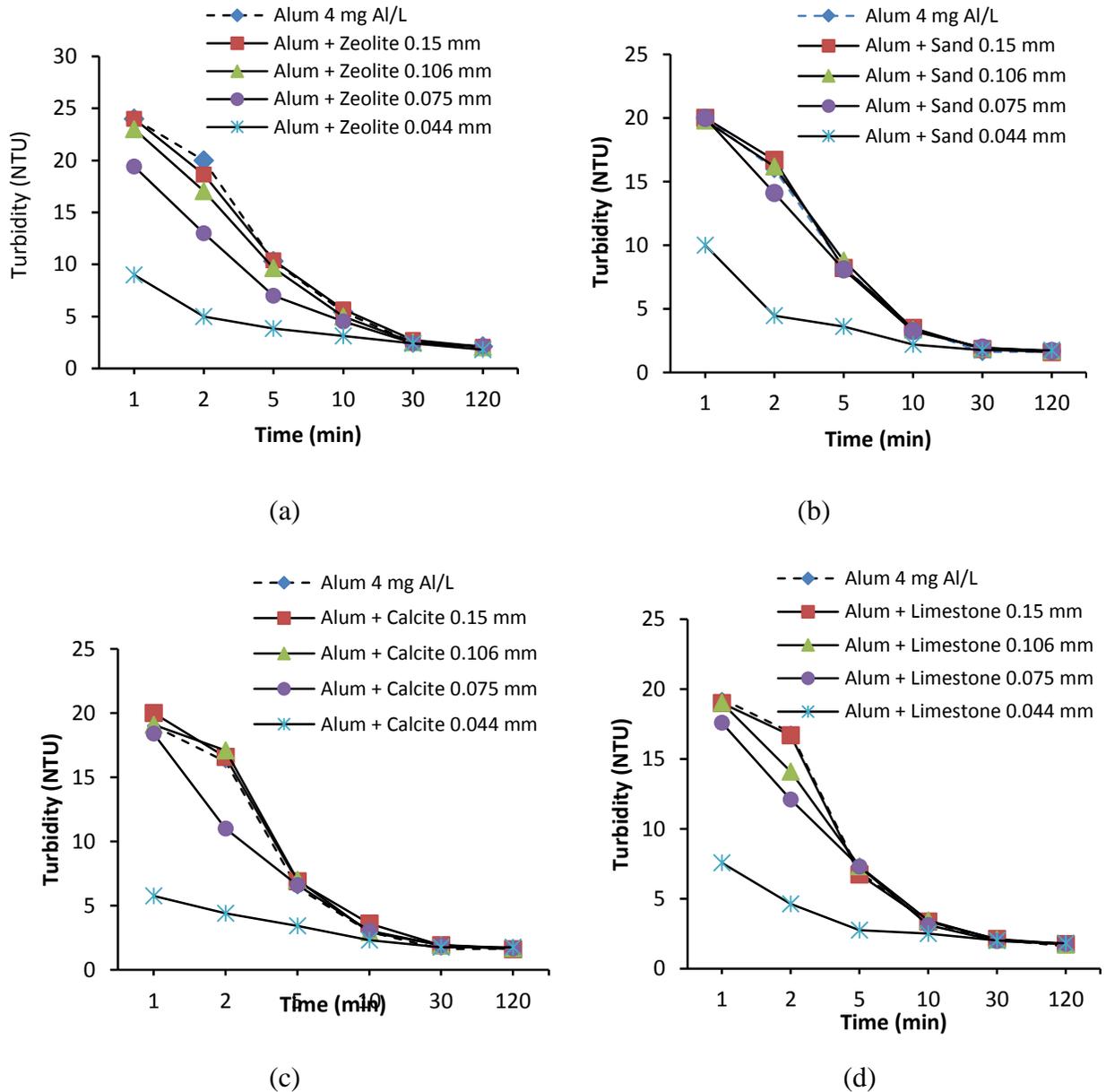


Figure 2 Effect of different particle sizes on settling kinetics; (a) zeolite, (b) sand, (c) calcite and (d) limestone

The influence of particle dosage of zeolite on settling kinetics is shown in Figure 3. Compared to alum alone, the zeolites addition improved the floc settling. The optimum zeolite dosage was determined to be 1 g/L. When further increasing zeolite dosage to 5 g/L, the performance of the floc settling reduced which could be attributed to the turbidity caused by zeolite itself at the higher dosage.

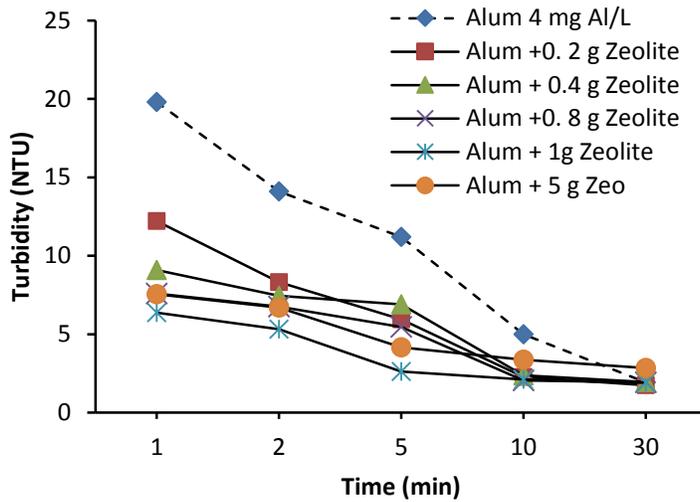


Figure 3 Effect of zeolite dosages on settling kinetics

When the Lake Kampeska water was spiked with higher concentration of *Anabaena* sp. to reach initial turbidity levels of 40 to 50 NTU, the alum coagulation with particles showed faster floc settling kinetics compared to alum only as shown in Figure 4. This indicate that particle-assisted coagulation can help the settling of the cyanobacteria and flocs for a wide range of initial cyanobacteria concentrations. Different particles and doses in the range of 1 to 5 g/L had similar impact on turbidity reduction.

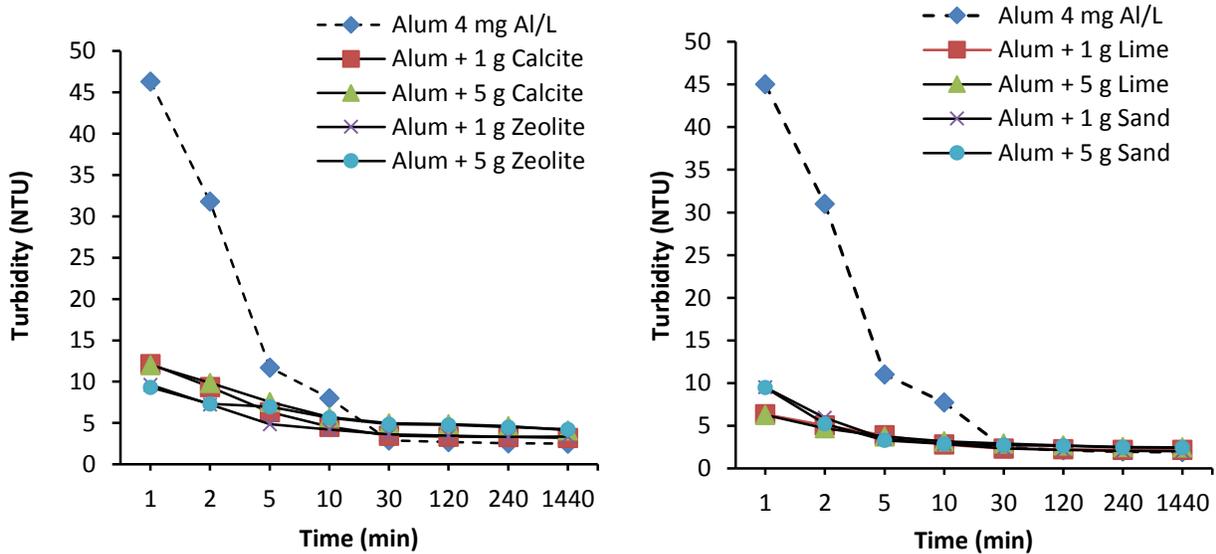


Figure 4 Effect of particle-assisted coagulation on settling kinetics at high turbidity of 50 NTU

## Impact of Particle-assisted Coagulation on Resuspension of Floccs

Figure 5 shows the *chlorophyll a* concentrations during the resuspension tests. Coagulated floccs by alum alone were easily disturbed by the stirring at 10 rpm and were fully mixed when the stirring increased to 30 rpm. However, the particle-assisted coagulation floccs were much more resistant to the disturbance by the mixing. The *chlorophyll a* concentrations started to increase at the mixing speed of 30 rpm and became completely mixed at 100 to 150 rpm.

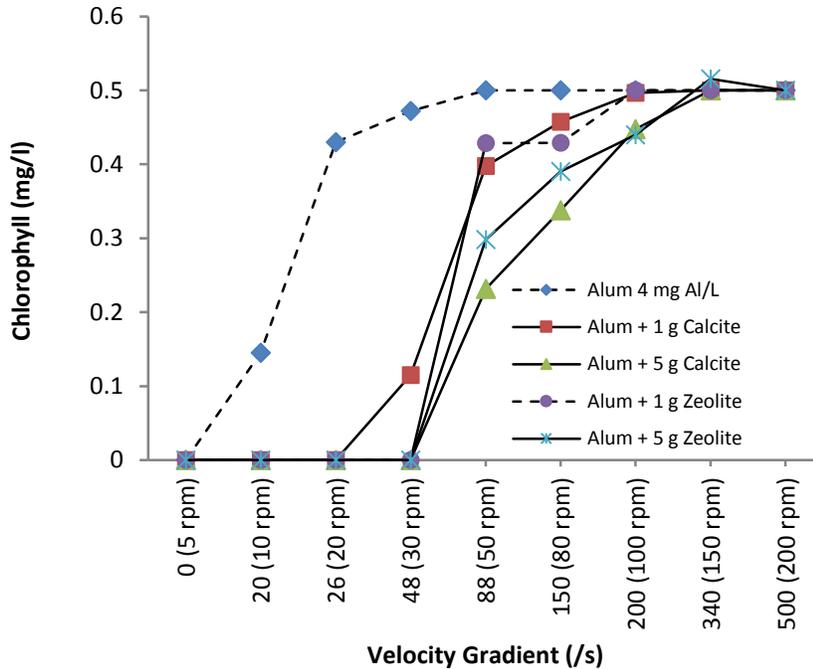


Figure 5 Effect of different velocity gradient on floc resuspension

## CONCLUSION

The effect of alum-alone coagulation and particle-assisted coagulation on *chlorophyll a*, P, and turbidity removal was investigated using laboratory coagulation experiments. The results showed that alum coagulation was able to remove 85 to 90% of P and *chlorophyll a* from *Anabaena sp.* enriched lake water. The added particles did not substantially affect the removal of P and *chlorophyll a* during combined alum and particle coagulation. However, the particles substantially improved the floc settling kinetics. The combined treatment with alum and particles also significantly enhanced the resistance of the settled floccs to disturbance by mixing. The results of this study showed that ballasted alum coagulation using natural minerals can increase the floc settling kinetics and prevent the resuspension of the settled floccs.

## **ACKNOWLEDGEMENTS**

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## **STUDENT INVOLVEMENT IN PROJECT**

A Ph.D. student, Sepideh Sadeghi has worked on this project and will develop a doctoral dissertation based on the results of this project. This project provided the opportunity for her to gain knowledge on eutrophication, algal blooms, water quality criteria, and physical/chemical processes as well as to develop an innovative engineered solution for algal bloom control. She is working on a manuscript for a peer-review journal based on results of coagulation and re-suspension experiments. Three undergraduate students, Cole Gebhart, Mitchell Shearer, and Tanner Odegaard also worked on this project. They helped Sepideh conduct lab experiments which will have long-term benefits on their career.

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## Establishing Gene Fingerprints of Pathogenic Bacteria Along Selected Reaches of Rapid Creek

### Basic Information

<b>Title:</b>	Establishing Gene Fingerprints of Pathogenic Bacteria Along Selected Reaches of Rapid Creek
<b>Project Number:</b>	2015SD245B
<b>Start Date:</b>	3/1/2015
<b>End Date:</b>	2/29/2016
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	First
<b>Research Category:</b>	Biological Sciences
<b>Focus Category:</b>	Water Quality, Wastewater, Water Use
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Linda DeVeaux, Lisa Kunza

### Publications

There are no publications.

# ***Establishing Gene Fingerprints of Pathogenic Bacteria along Selected Reaches of Rapid Creek***

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## **Introduction**

Bacterial levels, particularly fecal coliforms such as *Escherichia coli*, are standard water quality indicators of fecal contamination. The EPA estimates that 25% of national groundwater systems exceed the Total Coliform Rule, suggesting a widespread dissemination of enteric organisms into the environment [1]. South Dakota surface water is not immune to fecal contamination, and according to the 2014 South Dakota Integrated Report for Surface Water Quality Assessment, sections of Rapid Creek are affected by unacceptably high levels of indicator bacteria, particularly *E. coli* [2].

Certain *E. coli* strains are commensal organisms that are part of the normal microflora of the human intestinal tract, and when ingested do not have any adverse health effects. However, infection by pathogenic variants, particularly Shiga-toxicogenic *E. coli* serotype O157:H7, accounts for approximately 73,000 annual cases of reported illnesses in the U.S. alone [1]. Such strains are considered emerging zoonotic infectious agents, and have been linked to outbreaks of severe diarrhea and hemolytic uremic syndrome, an often lethal condition in small children.

Routine testing provides a snapshot of microbial abundance and content; however, such sampling does not take into account the pathogenic profile of the bacteria.

Though disease-causing in humans, many of the pathogenic *E. coli* strains are common inhabitants of the guts of both domestic and wild animals, particularly ruminants, where they appear to cause no symptoms. Cattle are the major reservoir of Shiga toxin-producing *E. coli* (STEC), and transmission to humans often occurs through fecally-contaminated water sources. The ability of *E. coli* to cause disease is directly related to its genetic make-up, and ‘horizontal gene transfer’ is a source of evolution that allows genes to be passed easily between even distantly related species of bacteria. Shiga-toxigenic *E. coli* possess a gene for Shiga toxin, a virulence factor that contributes to the disease-causing potential. The Shiga toxin gene originated in *Shigella dysenteriae*, and has been found in *Enterobacter*, *Citrobacter*, *Acineobacter*, *Campylobacter*, and *Hamitonella* bacterial species [3]. Since horizontal gene transfer has been observed where bacterial levels are high, it is expected that the number of copies of pathogenic genes will increase as they are shared between individuals. The more potentially harmful genes a bacterium acquires, the more likely it will be to cause disease. Worldwide, both municipal drinking water and water used recreationally are known to harbor Shiga toxin-producing organisms, and have been linked to a number of STEC outbreaks [4]. There are two antigenically distinct Shiga toxin variants: the highly conserved Stx1, and the more diverse Stx2, which has five subtypes (stx2, stx2c, stx2d, stx2e, and stx2g) and 11 variants. Other known virulence factors often carried in tandem with the Shiga toxins include heat-labile and heat-stable toxins, cytotoxic necrotizing factors, attaching and effacing mechanisms, enteroaggregative mechanisms and enteroinvasive mechanisms [5].

Parts of Rapid Creek have fecal coliform impairment presumably due to multiple influences including the sewage treatment plant, septic tanks, and cattle. In this study, we applied a novel water quality metric to create a genetic fingerprint of Shiga-toxin and related pathogenicity genes at 6 sites along Rapid Creek from above Canyon Lake to just above the confluence of the creek with the Cheyenne River. Additionally, we collected samples from potential contaminating sources, including livestock and wildlife feces. The goal of this project was to establish a pathogenicity profile for each sample that may be correlated with potential sources of contamination, and to determine if the contamination present in Rapid Creek presents a potential human health risk. The information generated by this project and future work could lead to guidance for implementation of new best management practices for these watersheds.

## **Objectives**

Total fecal coliforms, and more recently, *E. coli* alone, have been used as an indicator of fecal contamination of aquatic environments; however, such testing does not take the pathogenic

potential of the bacterial load into account. Rapid Creek is listed as impaired from Canyon Lake to the Cheyenne River. What is less clear are the sources of this contamination, as well as the potential for serious illness from contamination. In this project, we applied our novel pathogenicity metric, which consists of assays to determine the presence/absence as well as relative abundance of approximately 30 genes, to establish a molecular profile within microorganisms present at various locations along Rapid Creek at two time points. The profiles were then compared to profiles obtained from potential sources of contamination, including stool samples from wildlife, cattle, and other domestic animals. Comparison of samples from the same site collected at two different times allowed for the establishment of a temporal distribution of each gene, and provided an indication of the persistence of each pathogenic source. From the data, we determined the abundance, distribution, and persistence of pathogenic genes in Rapid Creek.

## Materials and Methods

### *Sampling Scheme*

The sampling analysis in this study mimicked those in place by state agencies for water quality assessment of total fecal coliforms/*E. coli*. In the first phase of this study, water samples were sterilely collected in triplicate from six sites along Rapid Creek: Braeburn Dog Park above Canyon Lake (DP), immediately below Canyon Lake, Memorial Park (MP), Anderson Road (AR), Radar Hill Road (RHR), and Farmingdale (FD) (Figure 1). We sampled Rapid Creek on July 20<sup>th</sup> and September 30<sup>th</sup>, 2015. Additionally, on September 30<sup>th</sup>, 10 fecal samples (3 birds, 1 horse, 2 cows, 2 dogs, and 2 deer) were collected from the sampling vicinities. All 46 samples were processed in the lab within three hours of collection.

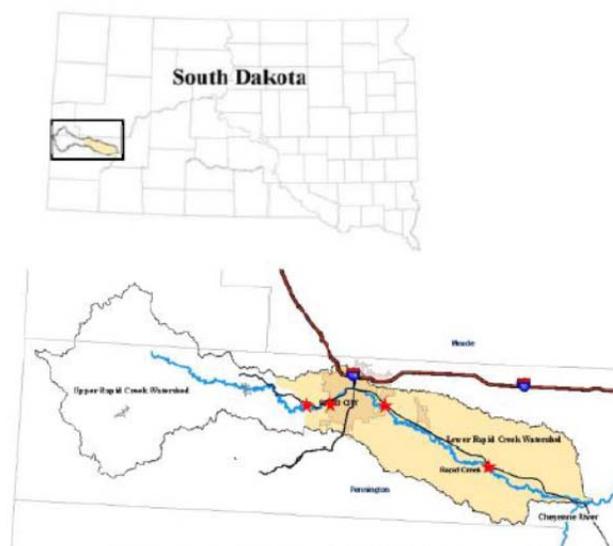


Figure 1: Rapid Creek Watershed. Sampling sites are denoted with a red star.

### *Sampling Processing and DNA Extraction*

Creek water samples were agitated prior to filtration to resuspend settled solids and homogenize the sample. A subsample of 100 mLs of each creek water sample was filtered through 0.45µm mixed cellulose ester membranes using a vacuum manifold (Figure 2). Total DNA was extracted from the filter paper using a PowerWater DNA Extraction Kit per the manufacturer protocol (MoBio). Total DNA was extracted from feces using a PowerFecal DNA Extraction kit per the manufacturer protocol (MoBio). DNA samples were stored at -20°C.

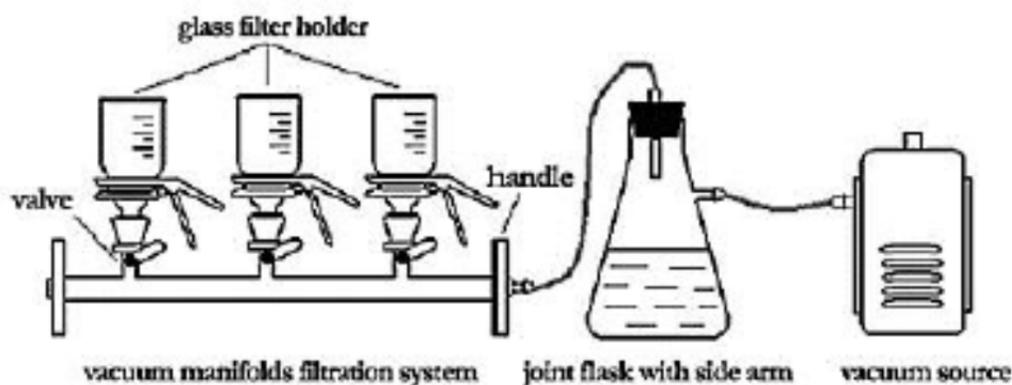


Figure 2: General set-up for vacuum filtration of creek samples.

### PCR and Gel Electrophoresis

Each DNA sample was used as the template in polymerase chain reactions (PCR) using oligonucleotide primer pairs (Fisher Scientific) specific for each of the 30 pathogenicity genes. Presence of a particular gene was then verified if the appropriately sized DNA fragment was visible when the amplified DNA samples were separated by gel electrophoresis. The relative abundance of each gene present in a particular sample was subsequently measured using quantitative PCR (qPCR) using the same unique oligonucleotide primers, on a PikoReal Real-Time PCR system.

## Results

### Presence of Pathogenicity Genes

Genes encoding Shiga toxins and analogous verotoxins (*stx1/VT1*, *stx2/VT2*), in addition to an intimin-encoding gene (*eaeA*), an enteroinvasin-encoding gene (*einV*), and a serine protease-encoding gene (*espP*) were detected in water samples during the course of this study (Figure 3). The *stx1/VT1* and *einV* genes were detected in 100% of water samples, the *stx2/VT2* genes was detected in 72% of samples, the *eaeA* gene was detected in 64% of samples, and the *espP* gene was detected in 53% of samples. In fecal samples, the *stx1*, *stx2*, *eaeA*, and *espP* genes were determined to be present in some of the samples, however the *einV* gene was absent from all feces tested in this experiment, thus the source of *einV* contamination into water samples is unknown at this time (Figure 4).

**stx2/VT2 gene**

Site	7/20/2015		9/30/2015	
	# Positive Samples	% Positive	# Positive Samples	% Positive
DP	(2/3)	66	(2/3)	66
CL	(2/3)	66	(3/3)	100
MP	(2/3)	66	(3/3)	100
AR	(3/3)	100	(1/3)	33
RHR	(2/3)	66	(1/3)	33
FD	(2/3)	66	(3/3)	100

**stx1/VT1 gene**

Site	7/20/2015		9/30/2015	
	# Positive Samples	% Positive	# Positive Samples	% Positive
DP	(3/3)	100	(3/3)	100
CL	(3/3)	100	(3/3)	100
MP	(3/3)	100	(3/3)	100
AR	(3/3)	100	(3/3)	100
RHR	(3/3)	100	(3/3)	100
FD	(3/3)	100	(3/3)	100

**eaеA gene**

Site	7/20/2015		9/30/2015	
	# Positive Samples	% Positive	# Positive Samples	% Positive
DP	(2/3)	66	(1/3)	33
CL	(2/3)	66	(3/3)	100
MP	(1/3)	33	(2/3)	66
AR	(2/3)	66	(2/3)	66
RHR	(2/3)	66	(2/3)	66
FD	(1/3)	33	(2/3)	66

**einV gene**

Site	7/20/2015		9/30/2015	
	# Positive Samples	% Positive	# Positive Samples	% Positive
DP	(3/3)	100	(3/3)	100
CL	(3/3)	100	(3/3)	100
MP	(3/3)	100	(3/3)	100
AR	(3/3)	100	(3/3)	100
RHR	(3/3)	100	(3/3)	100
FD	(3/3)	100	(3/3)	100

**espP gene**

Site	7/20/2015		9/30/2015	
	# Positive Samples	% Positive	# Positive Samples	% Positive
DP	(2/3)	66	(0/3)	100
CL	(2/3)	66	(1/3)	33
MP	(3/3)	100	(1/3)	33
AR	(3/3)	100	(1/3)	33
RHR	(3/3)	100	(0/3)	0
FD	(2/3)	66	(1/3)	33

Figure 3: Presence and temporal distribution of pathogenic genes *stx2/VT2*, *stx1/VT1*, *eaеA*, *einV*, and *espP*.

Fecal Source	<i>stx1</i>	<i>stx2</i>	<i>eaeA</i>	<i>espP</i>	<i>EinV</i>
Bird	✓	✓	✓		
Bird	✓		✓		
Bird		✓	✓	✓	
Horse			✓	✓	
Cow	✓	✓	✓	✓	
Cow					
Dog	✓	✓	✓	✓	
Dog	✓	✓		✓	
Deer					
Deer	✓	✓	✓	✓	

Figure 4: Pathogenicity genes detected in fecal samples collected on September 30, 2015.

#### Relative Abundance of Pathogenicity Genes

Quantitative PCR was used to determine the relative abundance of pathogenicity genes present in water samples. In qPCR, a cycle threshold (Ct) value is obtained that is inversely proportional to the amount of target DNA for the gene of interest in a sample. For purpose of this experiment, Ct values up to 29 indicated an abundance of target DNA, Ct values from 30 to 37 indicated a moderate amount of target DNA, and Ct values from 38 to 40 indicated a low amount of target DNA.

For the *stx1* gene, which was detected in all creek water samples by conventional PCR, qPCR Ct values ranged from 23.46 to 27.86, indicating an abundance of target DNA. For the *stx2* gene, which was detected in 72% of samples, Ct values ranged from 20.24 to 27.09, indicating an abundance of target DNA. For the *eaeA* gene, Ct values ranged from 24.77 to 27.38, indicating an abundance of target DNA. For the *einV* gene, Ct values ranged from 21.59 to 37.86. Four of the water samples indicated an abundance of target DNA, 31 samples indicated a moderate amount of target DNA, and 1 sample indicated a low amount of target DNA.

#### Discussion

*E. coli* is a diverse and abundant bacterium generally associated with the intestinal tract of warm-blooded mammals. Though *E. coli* generally act in a symbiotic manner with their host, some strains have acquired the ability to cause disease in humans, with an array of clinical symptoms ranging from mild diarrhea to severe bloody diarrhea, hemolytic uremic syndrome, and death. The pathogenic capacity of a bacterium such as *E. coli* is directly related to the acquisition and expression of various pathogenicity genes. Horizontal gene transfer is a source of bacterial

evolution that allows for pathogenic genes to be passed easily between bacteria, even among distantly related or unrelated species.

A wide and diverse array of microorganisms are capable of producing Shiga toxin (and analogous verotoxin), including Shiga-toxigenic *E. coli* (STEC), a human pathogen. Such bacteria possess at least one gene for Shiga toxin, a critical virulence factor that contributes to the disease-causing potential. The Shiga toxin genes (*stx*), which comprise two antigenically distinct variants (*stx1* and *stx2*), have not only been found in the coliform bacteria *E. coli*, *Enterobacter*, and *Citrobacter*, and the aquatic bacterium *Aeromonas*, but in the soil bacterium *Acinetobacter*, the food pathogens *Campylobacter* and *Shigella*, and even an insect endosymbiont, *Hamiltonella* [4,5]. Bacteria, particularly *E. coli*, are capable of encoding and expressing more than one Shiga toxin variant. For example, both *E. coli* O157:H7 and *E. coli* O91:H21 contain multiple copies of the *stx2* gene, and up to 30% of *stx* positive bacteria have been shown to express both *stx1* and *stx2* [6,7]. The infectious threshold of STEC is extremely low, where only 10-100 cells are required to cause disease [8].

In addition to Shiga toxin, other virulence factors including adhesins, toxins, invasins, cytotoxic necrotizing factors, protein secretion systems, and iron uptake systems may be shared between individuals in a given bacterial population [7]. These virulence factors in pathogenic bacteria originated from horizontal gene transfer events, and such gene sharing is observed in environments where bacterial levels are high [1].

In the current study, three such pathogenicity genes, in addition to the *stx* were detected: *eaeA*, *einV*, and *espP*.

- The virulence factor *eaeA* encodes a protein necessary for the attaching and effacing lesions in the gut mucosa, a hallmark of enteropathogenic *E. coli* (EPEC) and enterohemorrhagic *E. coli* (EHEC) infections. Approximately 45% of known STEC strains also harbor the *eaeA* gene [9].
- *einV* gene presence is indicative of enteroinvasive *E. coli* (EIEC), which can cause a Shigellosis-like disease with watery diarrhea and dysentery. EIEC's mechanism of pathogenesis involves epithelial invasion of the colon leading to inflammation and ulceration of the mucosal lining.
- The *espP* gene encodes a serine protease which has homologs in *Neisseria gonorrhoeae*, *Haemophilus influenzae*, and *E. coli* O157:H7. *espP* contributes to mucosal hemorrhage in hemorrhagic colitis and hemolytic uremic syndrome, and likely invokes an antibody response during EHEC infection [10].

Clearly, the presence of these genes within Rapid Creek indicates significant horizontal gene transfer among the resident bacteria, and their presence may indicate a potential risk to human health. While this study did not distinguish between one single bacterium carrying all the positive virulence gene versus each gene being carried by different organisms, the elevated levels of total *E. coli* in Rapid Creek indicates a significant potential to create new combinations of these genes through horizontal gene transfer, and thus, new human pathogens. Such evolution has been documented recently in Germany, where the acquisition of the *stx2* gene by an *E. coli* subtype containing the *eaeA* gene caused an outbreak in which more than 50 people died from ingestion of the pathogen [7]. In Rapid Creek, the *einV* gene presence alone may be indicative of mild to moderate health risk. The *stx1*, *stx2*, and *eaeA* genes occur concurrently in many strains of pathogenic *E. coli*, and are all found in *E. coli* O157:H7, and thus their presence in Rapid Creek indicates a significant potential risk to human health.

### **Relevant Presentations**

6<sup>th</sup> Annual SDSMT Research Symposium, March 31, 2015

Poster Presentation: Kelsey Murray, Lisa Kunza, Linda DeVeaux

Title: *Gene Fingerprinting: A Method to Assess the Pathogenicity Potential of Microbes and Source of Contamination in Selected Reaches of Rapid Creek*

2015 Western South Dakota Hydrology Conference, April 15, 2015

Poster Presentation: Kelsey Murray, Lisa Kunza, Linda DeVeaux, **First Place Student Presentation Award**

Title: *Establishing Gene Fingerprints of Pathogenic Bacterial along Selected Reaches of Rapid Creek*

### **Acknowledgements**

We are grateful for WRI for funding this project. This work was completed in part with support from South Dakota School of Mines and Technology. We would also like to extend a sincere thank you to Sydney Sayler for her work in collecting and analyzing samples for this study.

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# Hydrologic Life Cycle Impact of Mountain Pine Bark Beetle Infestations

## Basic Information

<b>Title:</b>	Hydrologic Life Cycle Impact of Mountain Pine Bark Beetle Infestations
<b>Project Number:</b>	2015SD248G
<b>USGS Grant Number:</b>	2015SD248G
<b>Start Date:</b>	9/1/2015
<b>End Date:</b>	8/30/2018
<b>Funding Source:</b>	104G
<b>Congressional District:</b>	1
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Water Use, Surface Water
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	James Stone, Scott J Kenner, Heidi Leah Sieverding

## Publications

There are no publications.

## **Introduction**

This project is assessing the dissolved organic carbon (DOC) runoff from mountain pine beetle (MPB) impacted catchments within the ponderosa pine forest of the Black Hills of South Dakota. This project primarily involves field work measuring runoff water quality and soil changes due to MPB as well as hydrologic modeling.

## **Research Program**

### *Problem*

Across the Western US, both large and small population centers are situated in the foothills and mountains at the heart of the MPB epidemic. These cities are also heavily dependent on storage of surface water for drinking water resources; smaller urban areas lack the leverage, capital and resources that larger municipalities have. DOC exports from MPB-impacted forest ecosystems contain precursor compounds that can react during drinking water purification (in treatment facilities) with disinfectants such as chlorine to form highly toxic and regulated disinfection by-products (DBPs).

### *Research Objectives*

The project objectives include the following:

- Better elucidate how and why the timing of organic matter and carbon loading occurs during various stages of MPB mortality stages in ponderosa pine forests;
- Determine whether the expected increase in watershed runoff efficiencies during MPB stages may result in increased metal, carbon, and nutrient loading may occur;
- Determine changes in the 'embodied energy' of drinking water supplies using life cycle assessment (LCA) modeling due to MPB water resources impairment; and
- Provide a watershed assessment that integrates changes in organic and carbon loading, drinking water environmental footprints (embodied energy), and ponderosa pine forestry MPB management options that addresses 'triple bottom line' alternatives for forestry managers and municipalities.

### *Methodology*

Five hydrologic sub-basins based on hydrologic unit code (HUC) cataloging unit level (12-digit) representing each of the four phases of MPB infestation (green, red, gray, toppled) with similar geology have been identified within the upper Rapid Creek watershed. Due to the pervasiveness of the infestation, it was not possible to identify un-impacted areas in the all of the general watershed zones outlined in the proposal. After assessing the sub-basins during sample site selection, it was also discovered that the sub-basins with significant active acid mine drainage (iron bogs) and karst impacts created unique, basin-level situations that could not be replicated in different zones or sub-basins and did not represent the entire watershed. So, in order to create a realistic representation of overall watershed interactions, these unique

areas were avoided for intensive sub-basin sampling and dynamics modeling. These unique areas were characterized by a water pH of 5 or lower and lack of or intermittent surface flow (sink areas). Watersheds with similar degrees of impact were selected through aerial photographic analysis, screening with USGS-EROS' new land cover mapping tool LCMMap, GIS analysis (soil, geology, tree stand density and age distribution, harvest and MPB infection history), and physical site visits. The sub-basins which meet these constraints generally do not have year-round access.

As part of the site selection process, LCMMap change detection was contrasted with USFS MPB infestation records. LCMMap analyzes the reflectance value of all images in the Landsat archive on a per pixel basis. This tool then detects the annual reflectance pattern for each of the bands and when there is a statistically significant change in the reflectance. Based on the comparison with USFS MPB annually mapped impact areas, this tool can effectively determine the month of red phase onset and subsequent forest response.

Baseflow water quality samples prior to annual high spring flow events have been collected and are being analyzed. These baseline samples were analyzed by USFS at the Rocky Mountain Research Station (Fort Collins CO) and analyzed at SDSM&T using total organic carbon (TOC) standard operating procedures (SOP) developed under the USGS 104B grant by recent MS graduate, Erik Vik.

A sampling protocol defining the number and volume of samples collected, analyses to be conducted on each volume and detailing labeling system, storage and disposal has been developed. New MS student funding on the project, Jesse Punsal, has been trained on SDSM&T's TOC analyzer. Jesse will be trained on SDSM&T's AquaLog to conduct organic carbon characterization analyses this summer. As part of his training, he will be developing a SOP for the instrument.

### *Significance*

Development of SOPs, sampling protocols, and the study site selection process has provided valuable learning experiences for students. Active participation of the students in this process ensures that sample collection will be properly collected and processed.

Data is currently being collected and being used to determine the timing of DOC loading due to MPB and associated runoff efficiencies. Once data is processed and incorporated into models, watershed assessments and impacts to water resources and associated LCA impact and energy consumption will be evaluated.

### *Principal Findings*

Preliminary assessments conducted through preceding USGS 104B grant detected a pattern of DOC release roughly coinciding with MPB stages. A statistically significant correlation between runoff and DOC migration for three and five to six years after the red phase, presumed to correlate with the decay of needles and wood respectively, has been made for most of the

upper Rapid Creek basin. A peer review manuscript has been written and submitted to peer-reviewed publication summarizing this finding (Timing of Organic Carbon Release from Mountain Pine Beetle Impacted Ponderosa Pine Forests: Erik S. Vik, Heidi L. Sieverding, Jesse J. Punsal, Scott J. Kenner, Lisa A. Kunza, and James J. Stone to *Water Environment Research*). Due to the discovery of this correlation and the current, widespread nature of the infection - sub-basin hydrologic monitoring plan has been slightly altered to further investigate if this correlation is present consistently in the watershed.

It has been determined that the new USGS-EROS LCmap tool can be used detect the current and historical (back to 1984) spatial and temporal spread of MPB mortality and document recovery.

## **Information Transfer Program**

The project is in its first year. As part of the information transfer to the public, four related presentations and a paper was submitted to peer-review (listed under prior projects) on preliminary results.

Students rehearsed their presentations at the SDSM&T Student Research Symposium (<http://www.sdsmt.edu/Research/Student-Research-Symposium/>) with a smaller audiences prior to the Hydrology Conference.

Western South Dakota Hydrology Conference (<http://sd.water.usgs.gov/WSDconf/>) had approximately 300 attendees from the region. Presentations included:

- Oral Presentation: Sensitivity of Black Hills Hydrology to Land-use Change Using WRF-Hydro. Lucas Barrett and William Capehart
- Oral Presentation: Simulation of the effects of deforestation on headwater streams in the Black Hills, western South Dakota. Brian Freed, Galen Hoogestraat, and Scott Kenner
- Oral Presentation: Geochemical impacts of mountain pine beetles on Rapid Creek, SD. Jesse Punsal, Erik Vik, Heidi Sieverding, Scott Kenner, Lisa Kunza, and James Stone
- Poster Presentation: Modeling the hydrological impact with land cover change over time. Patrick Shaw and Scott Kenner

## **Student Support**

Jesse Punsal and Patrick Shaw, M.S. graduate student in Civil Engineering started graduate research assistanceships on the project during January 2016. Patrick is also a volunteer at the USGS South Dakota Water Science Research Center. During the first six months they have been working on the project, they have made significant strides and have learned several new instruments and analysis tools. Jesse traveled to Fort Collins, CO and received instrument and sample collection training from Chuck Rhoades with the USFS in March 2016. In April 2016, Patrick Shaw and Heidi Sieverding traveled to Garretson, SD and received training on the new USGS-EROS' Landsat-based land cover change detection tool.

Preliminary work on the project was conducted with the support of USGS CESU-funded students, Brian Freed and Lucas Barrett as well as USGS 104B-funded student, Erik Vik. Their work is being continued and expanded by current students.

## **Notable Awards and Achievements**

N/A

## **Publications from Prior Projects**

Timing of Organic Carbon Release from Mountain Pine Beetle Impacted Ponderosa Pine Forests: Erik S. Vik, Heidi L. Sieverding, Jesse J. Punsal, Scott J. Kenner, Lisa A. Kunza, and James J. Stone submitted to *Water Environment Research*.

SDSMT M.S. Thesis: Erik Vik - Potential organic carbon exports within the upper Rapid Creek watershed due to mountain pine beetle infestation

SDSMT M.S. Thesis: Brian Freed - Hydrologic Impacts of the Mountain Pine Beetle in Headwater Streams in the Black Hills of Western South Dakota.

## **Information Transfer Program Introduction**

The SDWRI Information Transfer Program includes public outreach; steering committee representation and leading involvement in the Big Sioux Water Festival hosting about 1,100 fourth grade students; interactions with extension agents and local, state and federal agencies; participation and presentations at regional and national conferences; youth education, adult education and university student training and education. Publications, such as pamphlets, educational materials, reports and peer-reviewed journal entries are made available in paper format and electronically through the Institute's website and are designed to support the mission of the Institute.

# South Dakota Water Resources Institute FY2015 Information Transfer Program

## Basic Information

<b>Title:</b>	South Dakota Water Resources Institute FY2015 Information Transfer Program
<b>Project Number:</b>	2015SD246B
<b>Start Date:</b>	3/1/2015
<b>End Date:</b>	2/28/2016
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	SD-001
<b>Research Category:</b>	Biological Sciences
<b>Focus Category:</b>	Education, Management and Planning, Conservation
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Van Kelley, Rachel McDaniel, Scott Cortus

## Publications

There are no publications.

## **SDWRI FY2015 Information Transfer Program**

South Dakota Water Resources Institute

### **PUBLIC OUTREACH**

Public outreach and dissemination of research results are cornerstones of the South Dakota Water Resources Institute's (SDWRI) Information Transfer Program. The Institute distributes information through a variety of outlets, including interactive information via the Internet, pamphlets and reports, direct personal communication, hands-on demonstrations and through presentations and discussions at meetings, symposia, and conferences. These outlets are described below.

#### ***SDWRI Website***

The SDWRI website is accessible through <http://www.sdstate.edu/abe/wri/>. The website contains information relating to water resources, current and past research projects, reference materials, and extension publications. One feature of the SDWRI website is it allows users access to links which include publications and on-line tools to help diagnose and treat many water quality problems. The "Research Projects" section of the SDWRI website contains past and present research projects, highlighting the Institute's commitment to improving water quality.

#### ***Annual Mayors Big Sioux River Water Summit***

The SDWRI was a sponsor of the Third Annual Mayors Big Sioux River Water Summit. The event was held Sept. 10 at the Days Inn Hotel in Brookings. The event was open to the public, and included presentations on water quality; water resources and conservation; urban, rural, government, and nongovernment watershed partnerships; and storm water management. The keynote speaker was Barr Engineering's Fred Rozumalski, who discussed the benefits of low-impact development and green infrastructure design. In addition, Dr. Dennis Todey, associate professor at South Dakota State University and the SDSU Extension Climate Specialist, presented on "Climate, Precipitation, and Water Quality".

#### ***Conference Proceedings***

Cortus, E. and Embertson, N. 2015. The Pathways Project. Waste to Worth: Spreading Science and Solutions. Seattle, WA. March 31-April 3, 2015.  
<http://articles.extension.org/pages/73244/the-pathways-project>.

Reyes-Gonzalez, A, C. Hay, J. Kjaersgaard, and C. Neale. 2015. Use of remote sensing to generate crop coefficient and estimate actual crop evapotranspiration. ASABE Paper No. 152190105. St. Joseph, Mich.: ASABE.

Salo, M., G. Hua, C. Schmit, and C. Hay. 2015. Nutrient removal from agricultural subsurface drainage using denitrification bioreactors and phosphate adsorbents. ASABE Paper No. 152156408. St. Joseph, Mich.: ASABE.

Schmitz, H., D. Todey, and M. Widhalm, (2015). The Agronomic Content of U2U's Climate Responsive Decision Tools. American Society of Agronomy Annual Meeting, Minneapolis, MN. 15-18 November 2015.

Todey, D., J. Andresen, J. Angel, B. Gramig, P. Guinan, C. Hart, M. Widhalm, O. Kellner, L. Biehl and D. Niyogi, (2015). Climate Information for Agronomic Decision Tools. American Society of Agronomy Annual Meeting, Minneapolis, MN. 15-18 November 2015.

Troop, C., D. Todey, and W. Capehart (2015). Changes in Water Balance in the Corn Belt over the Past 30 Years. Climate and Corn CAP Next Generation of Scientists Poster Symposium. Washington, D.C. 15 October 2015.

### ***Conference Papers or Posters Presented, Invited Lectures***

Embertson, N., Jacquet, J., Heemstra, J. and Cortus, E. Pathways for Effective Information Transfer Between Manure Management Professionals. Livestock and Poultry Environmental Learning Center. 15 November 2015 [Webcast – Embertson, Jacquet and Heemstra]

Jacquet, J., Kasu, B., Cortus, E. and Embertson, N. The Pathways for Information Transfer Among Manure Nutrient Management Professionals. The Current Webinar Series, North Central Region Water Network. 17 February 2016. [Oral presentation – Jacquet]

Hay, Christopher. Oral presentation at the Extension Subsurface Drainage Design and Water Management Workshop on March 10-11, 2015 in Grand Forks, N. D.

Kringen, David. 2015. Demonstrating the Nitrate Removal Effectiveness of Bioreactors for Improved Drainage Water Management in Eastern South Dakota. Oral presentation at the SDSU Crop Production Clinic in Faulkton, SD

McDaniel, Rachel. 2015. Persistence of *E. coli* in stream sediments and the impact on water quality. Oral presentation at the December EDWDD Board of Directors Meeting in Brookings, SD.

O'Neill, M. 2015. South Dakota Lakes - A Look from Above. AmericaView Fall Technical Meeting, Sioux Falls, S.D. 22 October. [Poster presentation].

Singh, S., Brandenburg, N., Gonzalez A., Kjaersgaard, J., Trooien, T., Ahiablame, L. and Kumar, S. (2015). Response of Winter Manure Application to Surface Water Quantity and Quality from Small Watersheds. Oral Presentation at ASA/SSA/CSSA Annual meeting, November 15-18, Minneapolis, MN.

Singh, S., Brandenburg, N., Gonzalez A., Kjaersgaard, J., Trooien, T., Ahiablame, L., Kumar, S. (2015). Response of Winter Manure Application to Runoff Quantity and

Phosphate loss from field scale watersheds in South Dakota. Poster presented at Plant Science Research Day at South Dakota State University, December 9, 2015, Brookings, SD.

Strock, J. S., J. Magner, A. Gacia y Garcia, B. J. Dalzell, T. P. Trooien, C. Hay, and G. Sands. 2015. Hydrologic impacts of agricultural drainage in the Upper Midwest, USA. ASA, CSSA and SSSA International Annual Meetings, Minneapolis, Minn.

Thapa, U., Ahiablame, L., Trooien, T., Hay, C. Kjaersgaard, J., Hua, G. (2015). Combined Treatment of Nitrogen and Phosphorus from Subsurface Drainage Using Low-cost Industrial By-products and Woodchip Bioreactors. Poster presented at ASA/SSA/CSSA Annual meeting, November 15-18, Minneapolis, MN.

Thapa, U., Ahiablame, L., Trooien, T., Hay, C. Kjaersgaard, J., Hua, G. (2015). Combined Treatment of Nitrogen and Phosphorus from Subsurface Drainage Using Low-cost Industrial By-products and Woodchip Bioreactors. Poster presented at AgOutlook annual meeting, December 10, Sioux Fall, SD.

Trooien, TP and R Beck. 2015. Development of subsurface drip irrigation in South Dakota. Highly-Efficient water use in agriculture project (111 Plan) Workshop. "Irrigation in Action". Beijing, China. 11 October 2015. [Oral presentation- Trooien]

### ***Peer-Reviewed Publications Currently in the Review Process***

Carlton, J. S., Mase, A. S., Knutson, C. L., Lemos, M. C., Haigh, T., Todey, D. P., & Prokopy, L. S. (2015). The effects of extreme drought on climate change beliefs, risk perceptions, and adaptation attitudes. *Climatic Change*, 1-16.

McDaniel, Rachel, Clyde Munster, and Tom Cothren. (under review). Crop and Location Specific Agricultural Drought Quantification: Part I – Method Development. *Transactions of the ASABE*.

McDaniel, Rachel, Clyde Munster, and Tom Cothren. (under review). Crop and Location Specific Agricultural Drought Quantification: Part II – Case Study. *Transactions of the ASABE*.

McDaniel, Rachel, Clyde Munster, and John Nielsen-Gammon. (under review). Crop and Location Specific Agricultural Drought Quantification: Part III - Forecasting Water Stress and Yield Trends. *Transactions of the ASABE*.

Prokopy, L. S., Hart, C. E., Massey, R., Widhalm, M., Klink, J., Andresen, J., Angel, J., Blewet, T., Doerin, O.C., Elmore, R., Gramig, B. M. Guinan, P., Hall, B.L., Jain, A., Knutson, C.L., Lemos, C.L., Morton, L.W., Niyogi, D., Power, R., Shulski, M.D., Song, C.X., Takle, E.S., Todey, D. (2015). Using a team survey to improve team communication for enhanced delivery of agro-climate decision support tools. *Agricultural Systems*, 138, 31-37.

### ***Extension Articles***

Cortus, Erin. 2015. Runoff Management Considerations for Pastures and Lots. SDSU iGrow Article.

Kringen, David. 2016. Immobilizing Nitrogen through the Use of Cover Crops. SDSU iGrow Article.

Kringen, David. 2015. From the Top Down. SDSU iGrow Article.

Kringen, David. 2015. Taking Steps for Cleaner Water on SD Grazing Lands. SDSU iGrow Article.

### **AGENCY INTERACTIONS**

SDWRI staff and affiliates served on several technical committees and boards, including:

- Member of the AmericaView Board of Directors
- Steering Committee for the National eXtension Conference
- Steering Committee for the Big Sioux Water Festival

Several other local, state, and federal agencies conduct cooperative research with SDWRI or contribute funding for research. Feedback to these agencies is often given in the form of reports and presentations at state meetings, service through committees and local boards, and public informational meetings for non-point source and research projects.

### **YOUTH EDUCATION**

Non-point source pollution contributes to the loss of beneficial uses in many impaired water bodies in South Dakota. An important part of reducing non-point pollution is modifying the behavior of people living in watersheds through education. Programs designed to educate youth about how their activities affect water are important because attitudes regarding pollution and the human activities that cause it are formed early in life. For these reasons, Youth Education is an important component of SD WRI's Information Transfer Program.

#### ***Big Sioux Water Festival***

Water Festivals provide an opportunity for fourth grade students to learn about water. SDWRI personnel were part of the organizing committee for the 2015 Big Sioux Water Festival held on May 12, 2015 with about 1000 fourth grade students from eastern South Dakota participating. SDWRI was responsible for coordination of volunteers and helpers, and co-coordinating the exhibit hall.

## **ADULT EDUCATION**

As part of SDWRI's outreach to the agricultural community, WRI affiliates host a booth at DakotaFest, a three-day agricultural fair held in August each year near Mitchell, SD, which each draws approximately 30,000 people. Personnel field a variety of questions concerning water quality and current research for farm and ranch families.

SDWRI staff and affiliates additionally participated in and presented at several regional and national meetings and conferences, including:

<b>Conference Name</b>	<b>Organizing Organization</b>	<b>Location</b>	<b>Date</b>
Annual Mayors Big Sioux River Water Summit	City of Sioux Falls	Brookings, SD	9/10/2015
Western SD Hydrology Conference	USGS	Rapid City, SD	4/6/2015
Highly-Efficient Water Use in Agriculture Project (111 Plan) Workshop. "Irrigation in Action"	China Agricultural University, Center for Agricultural Water Research in China, and Kansas State University	Beijing, China	10/11/2015
Waste to Worth: Spreading Science and Solutions	Livestock and Poultry Environmental Learning Center	Seattle, WA	3/31/2015

# 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>	4	0	0	0	4
<b>Masters</b>	3	2	0	0	5
<b>Ph.D.</b>	0	0	0	0	0
<b>Post-Doc.</b>	0	0	0	0	0
<b>Total</b>	7	2	0	0	9

## **Notable Awards and Achievements**