

**Ohio Water Resources Center  
Annual Technical Report  
FY 2016**

# Introduction

Pursuant to the Water Resources Research Act of 1964, the Ohio Water Resources Center (WRC) is the federally-authorized and state-designated Water Resources Research Institute for the State of Ohio. The Ohio WRC was originally established at The Ohio State University in 1959, as part of the College of Engineering's Experiment Station. The Ohio WRC continues to be administered through the College of Engineering, in the Department of Civil, Environmental, and Geodetic Engineering.

The Ohio Water Resources Center promotes innovative, water-related research through research grant competitions, coordination of interdisciplinary research proposals, and educational outreach activities. In order to solve current and upcoming water issues, we are focusing on educating new water professionals and directing their efforts to local, state and regional water issues. The Ohio WRC is in ideal position to enable integration of ideas from different stakeholders and facilitate connection among diverse water stakeholders. Additionally, we strive to introduce innovation in water treatment technologies via fundamental research and improve communication of research results to broad audience.

Ohio WRC sponsored researchers enable ecologically and socially sound water management by investigating the sources of nutrients and algal blooms in our environment, developing novel methods and technologies to reduce nutrients and other pollutants in water, and characterizing and monitoring the effects of energy development on water resources. By funding researchers early in their careers and developing powerful alliances with partner institutions, Ohio WRC seeds innovative approaches that foster impactful outcomes.

Ohio WRC reaches out to water professionals, educators, and citizens to ensure current and future citizens are water smart. Ohio WRC leaders are active in local and national water research, education and policy organizations such as the Ohio Water Resources Council, Water Management Association of Ohio, National Institutes of Water Resources and University Council on Water Resources.

## Research Program Introduction

The Ohio Water Resources Center consistently invests in water related research in the State, growing the number of principal investigators involved in Ohio's water issues, and educating the next generation of water professionals by funding student work on water research projects. Over this past year's reporting period, we sponsored seven new projects and administered two ongoing research projects conducted at four different Ohio universities that totaled \$407,476 in research funding (direct and cost share). The PI's for these projects are three Assistant Professors, two Research Scientists, two Associate Professors and one Professor. In total, this research helped support directly and indirectly eleven students majoring in environmental engineering, biological sciences, environmental studies, natural resources and other water related fields.

The new funded research projects entail studies of important Ohio water resources problems. For example, Dr. Chaffin from the Ohio State University is investigating effectiveness of data buoys as early warning systems for harmful cyanobacterial blooms in Lake Erie and Dr. David Costello from Kent State University is looking at storage of nutrients by headwater streams and how that relates to trace metal concentrations and biofilm growth. Of the funded research projects, three projects were finalized during this fiscal year, six projects will be continued into next year. These include Dr. Cheng's and dr. Dwyers's project on developing nutrient interceptors to treat non-point sources, Dr. Buchberger's project improving estimates of peak water demands in buildings and Dr. Bohrer's project on methane emissions from lakes.

In summary, Ohio WRC administered nine research projects this reporting period, four of which were funded or co-funded by USGS 104(b) base grants. This resulted in the training of eleven students, 2 published manuscripts in peer-review journals and twenty one presentations or posters at local, national or international conferences. In this reporting period our PI's have been able to secure an additional \$381,556 in research awards using data generated with Ohio WRC funding.

# SEPARATION OF PHOSPHORUS- AND NITROGEN-NUTRIENTS FROM AGRICULTURAL DEGRADED WATERS USING PERVIOUS FILTER MATERIAL DEVELOPED FROM INDUSTRIAL BY-PRODUCTS

## Basic Information

<b>Title:</b>	SEPARATION OF PHOSPHORUS- AND NITROGEN-NUTRIENTS FROM AGRICULTURAL DEGRADED WATERS USING PERVIOUS FILTER MATERIAL DEVELOPED FROM INDUSTRIAL BY-PRODUCTS
<b>Project Number:</b>	2013OH4360
<b>Start Date:</b>	9/1/2016
<b>End Date:</b>	2/28/2018
<b>Funding Source:</b>	Other
<b>Congressional District:</b>	OH-12
<b>Research Category:</b>	Engineering
<b>Focus Category:</b>	Treatment, Agriculture, Water Quality
<b>Descriptors:</b>	Industrial by-rproducts, filter material, nutrients
<b>Principal Investigators:</b>	Linda Kay Weavers, ChinMin Cheng

## Publications

There are no publications.

SEPARATION OF PHOSPHORUS- AND NITROGEN-NUTRIENTS FROM AGRICULTURALLY DEGRADED  
WATERS USING PERVIOUS FILTER MATERIAL DEVELOPED FROM INDUSTRIAL BY-PRODUCTS

Progress Report

*Submitted to:*

Ohio Water Resources Center

*Submitted by:*

Principal Investigator:

Linda Weavers, Ph.D., P.E., BCEE.

Professor

Department of Civil, Environmental, and Geodetic Engineering

e-mail: [weavers.1@osu.edu](mailto:weavers.1@osu.edu); Telephone: 614-292-8263; Fax: 614-292-3780

Co-PI:

Chin-Min Cheng, Ph.D., P.E.

Research Associate II-Engineer

Department of Civil, Environmental, and Geodetic Engineering

ABSTRACT

End-of-tail filtration has been suggested as a more aggressive and effective approach to reduce losses of nutrients from crop lands compared to current best management practices (BMPs) focusing on source reduction and minimizing transportation. A number of industrial by-products, e.g., coal combustion by-products and bauxite leaching residual, have been proven chemically effective in trapping P- and/or N-nutrients, and therefore, are potential low-cost nutrient sorbents for the end-of-tail filtration approach. However, the application of these industrial by-products as the filtration media is limited due to unfavorable hydraulic properties, as well as unknown associated environmental impacts. In this proposed study, pervious filter materials owning both reactivity to nutrients and adequate hydraulic properties are developed using fly ash, stabilized FGD materials, and bauxite leaching residual as the feedstock. By modifying the composition of these industrial by-products, the pervious materials are expected to have selective nutrient-sequestering capabilities, which can be used to separate and recycle phosphorus- and nitrogen-nutrients from agricultural drainage waters (ADWs). This study is carried out in three tasks to (1) investigate the adsorption efficiency and service lifetime of selected pervious materials with synthetic ADW; (2) evaluate the physical and chemical integrity of the pervious materials before and after service; and (3) study the interactions between the prepared filter materials and emerging pollutants commonly found in ADW (e.g., estrone). The goal of this study is to demonstrate the feasibility of applying a low-cost and environmentally-sustainable approach to ADW handling and treatment. This alternative to current BMPs is able to convert agricultural and industrial wastes to value-added products containing concentrated and specific nutrients. Currently, the project is still on going. Results obtained from this study will be used to develop a competitive proposal for external funding.

## 1. Introduction

Eutrophication of water bodies, a result of release of excessive phosphorous (P) and nitrogen (N) from soil to drainages<sup>1</sup>, has been an increasing environmental issue in the US, especially in the Midwest, northeast, and Gulf coast area where the watersheds of major freshwater bodies involve rapid growth and intensification of crop and livestock farming<sup>2</sup>. Not only eutrophication posts unpleasant aesthetic characteristics to water bodies, accumulation of toxic, volatile chemicals produced by algae can cause neurological damage in people and animals being exposed to them. Consequently, eutrophication of water resources results in losses of biodiversity, as well as their amenities and services<sup>3</sup>. For example, the recent outbreaks of Cyanobacteria, or blue-green algae, in the Grand Lake at St. Mary's area in Ohio has led to state officials to issue water contact and fish consumption advisories.

The major cause of many eutrophication incidents can be directly correlated to fertilizer application<sup>4</sup>. To prevent accumulation of nutrients in surface waters, reduction of nutrients present in the agricultural degraded waters (ADW, i.e., livestock wastewater overflow, subsurface drainages, and surface runoffs from cropland) is perceived as necessary approach<sup>5</sup>. Although many best management practices (BMPs) focusing on source reduction and minimizing transportation have been implemented to reduce losses of nutrients from crop lands, these approaches have shown no control on dissolved phosphorus losses<sup>6,7</sup>, which is the most readily available form of phosphorus to aquatic organisms<sup>8</sup>. Instead, end-of-tail filtration has been suggested as a more aggressive and effective approach<sup>6</sup>. However, the application is limited. Ideal filter materials, i.e., material with both favorable nutrient-sequestering capability and hydraulic property, have yet been identified<sup>9</sup>.

In this study, low-cost pervious sorption materials prepared from a self-geopolymerization process using agricultural wastes and industrial by-products are tested for their potential as an alternative to current BMPs. The self-geopolymerization process enchains agricultural wastes with chemically-effective, nutrient-sorbing industrial by-products (e.g., coal ash, flue gas desulfurization materials, and bauxite residual) and forms pervious materials. By modifying the composition, the pervious materials are expected to have selective sorption capabilities to nitrogen (N-) and phosphorus (P-) nutrients with adjustable hydraulic properties, which can be used to separate and recycle nutrients from ADWs.

## 2. Objectives

In this study, a geopolymerization procedure is developed to convert coal combustion by-products (i.e., fly ash and flue gas desulfurization (FGD) material) and alkaline bauxite leaching

residual (bauxite red mud) to pervious filter materials. The materials are tested in a bench-scale setting for their effectiveness and capacity on removing nutrients from simulated agricultural drainage waters. The specific objectives of this proposed project are to:

- (1) Assess the performance of the industrial by-product-derived pervious filter materials with respect to their nutrient removal efficiencies, service lifetime, and hydraulic properties;
- (2) Evaluate the chemical and physical integrity of the materials; and
- (3) Study the interactions between the prepared filter materials and other pollutants contained in ADWs (i.e., estrogens).

### **3. Materials and Method**

The work of this proposed study is divided into three tasks. In summary, the first task focuses on preparing and characterizing the pervious filter materials. At least three sets of P-type (i.e., materials selectively adsorb P-nutrients) and N-type (i.e., materials adsorbed nitrate and/or other N-nutrients) are prepared. In the second task, a series of column experiments are setup to (1) evaluate the adsorption efficiency and capacity of the selected pervious materials with a simulated ADW and (2) study the interactions between estrogens and filtration materials. In addition, the physical and chemical integrities of the pervious filter material during and after service are evaluated. The release of metals and metaloids (e.g., mercury, arsenic, selenium, thallium, and boron), as well as sulfate, from the filter materials during filtration are monitored. In addition, surface characterization techniques, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), are applied to investigate the transformations of mineral composition and surface morphology before and after the filtration materials are exhausted.

#### *Pervious Filter Material Preparation and Characterization*

Coal combustion by-products (i.e., fly ash and stabilized FGD materials) and bauxite leaching residue (i.e., red mud) are used in the preparation of the nutrient-selective pervious filtration materials (Figure 1). Two different types of pervious filtration materials (i.e., P- and N-types) are prepared using a method modified from Cheng et al.<sup>10</sup> and Jin<sup>11</sup>. Class F fly ash and sulfite-rich stabilized FGD material provided by coal combustion power plants located in eastern Ohio are used to prepare the phosphorous-capture (P-type) filtration materials. Quick lime

(Carmeus USA, Pittsburg, PA), CaO, is added to provide required alkalinity. The nitrogen-capture materials are prepared from red mud, fly ash, and stabilized FGD material. No quick lime is used in the preparation of N-type filter materials. The bauxite red mud provided by a bauxite processing plant located at southeast Texas is oven-dried before use. In one batch, manganese oxide (MnO<sub>2</sub>) is also added in the preparation of N-type material. Woodchip is used in the preparation of both N and P-type filter mixtures to modify the hydraulic properties. The prepared mixtures are then cured in a humidity chamber.

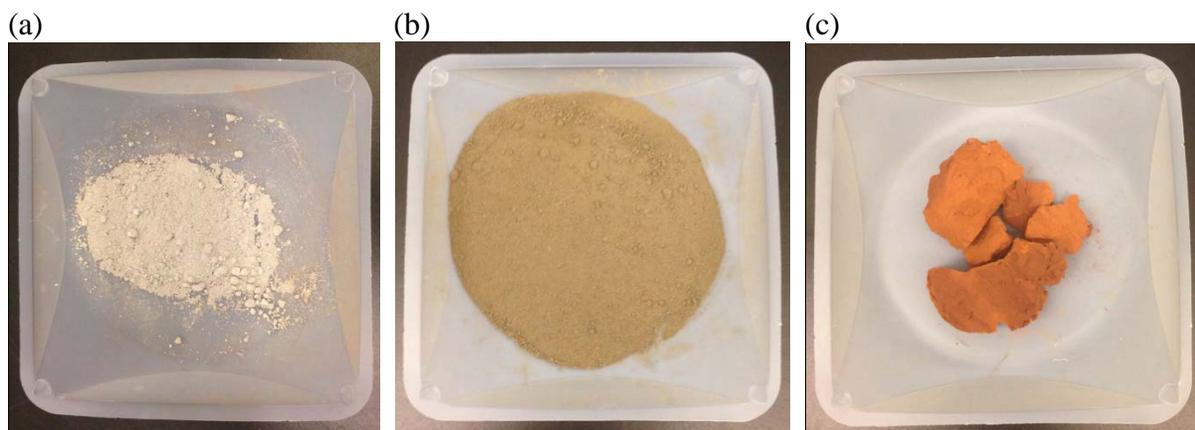


Figure 1. (a) Stabilized FGD material, (b) fly ash, and (c) bauxite red mud used in the preparation of pervious filtration materials.

The cured filter materials are tested for their chemical (i.e., elemental and mineral compositions), physical (density and surface morphology), and engineering (i.e., permeability (k) and/or hydroconductivity (K)) properties as per standard testing protocols. Details on the chemical and physical characterizations of the filter materials are described in the “*Physical and Chemical properties Integrity Evaluation*” section.

#### *Bench-Scale Column Test*

A series of column tests are carried out to measure the adsorption capacity and efficiency of prepared pervious materials for P- and N-nutrients with a simulated ADW. In addition to the prepared filter materials, two reference columns, packed separately with granular activated carbon (GAC) and top soil from the OSU’s Waterman Farm Complex, are also included in the column study. A control column, i.e., without packing medium, is included to evaluate the adsorption of nutrients and compounds on the experimental apparatus.

The setup of the column test is illustrated in Figure 2. The ADW used in the column test is synthesized based on formula listed in Table 1. In addition to the constituents listed in the table, one estrogen, e.g., estrone (E1) or 17 $\alpha$ -Estradiol (17 $\alpha$ -E2), commonly found in dairy wastewater<sup>12</sup> is added in selected experimental batches. A peristaltic pump delivers the synthetic ADW to the inlet of a series of two vertically-oriented columns at a constant feed rate (Figure 2). The ADW sequentially passes through the column containing P-type filter material (P-type column) and then the N-Type column. For a given set of filter materials, the column test is carried out under a saturation condition demonstrated in Figure 2.

Table 1. Composition of synthetic dairy wastewater used in this study

Component	Amount (mg/L)
Urea	115.7
NH <sub>4</sub> Cl	250.0
Na <sub>2</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	385.7
KHCO <sub>3</sub>	257.1
NaHCO <sub>3</sub>	668.6
MgSO <sub>4</sub> ·7H <sub>2</sub> O	257.1
FeSO <sub>4</sub> ·7H <sub>2</sub> O	10.3
MnSO <sub>4</sub> ·H <sub>2</sub> O	10.3
CaCl <sub>2</sub> ·6H <sub>2</sub> O	15.4

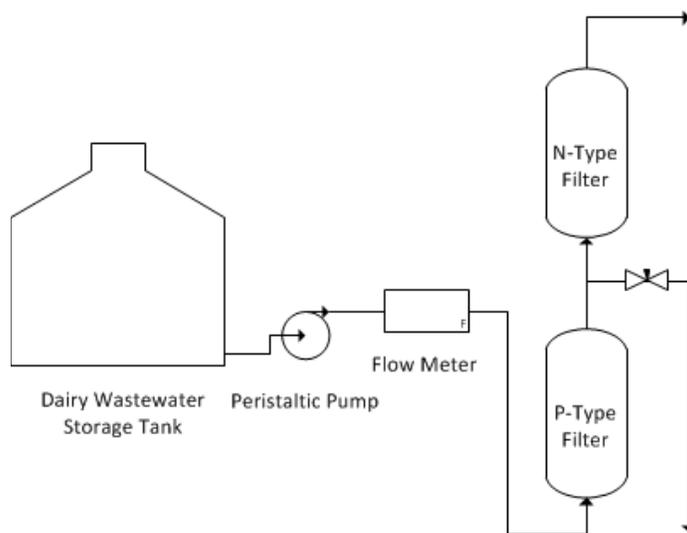


Figure 2. Setup of bench-scale column test

Effluent samples are collected periodically from the outlets of P-type and N-type columns for a list of chemical analyses shown in Table 2. After collection, sample is immediately separated into four sub-samples. The first sub-sample is for pH, conductivity, and redox potential measurements. In the selected batches when estrogen is included in the synthetic ADW, an aliquot of the first subsample is filtered with 1.2µm glass fiber and concentrated by solid-phase extraction for estrogen analysis. Any compounds remained on the sample collection bottle or filter is desorbed by rinsing the bottle and filter with methanol. The concentrated sample is analyzed using a high-performance reverse-phase liquid chromatography tandem electrospray ionization mass spectrometry (HPLC/MS/MS). Deuterated internal standards is added to the samples to correct the interferences caused by the matrix of the sample.

The second sub-sample is filtered and analyzed for alkalinity, total dissolved solids, Cl<sup>-</sup>, SO<sub>4</sub><sup>-2</sup>, PO<sub>4</sub><sup>-3</sup>, total Kjeldahl nitrogen, ammonia, and NO<sub>3</sub><sup>-</sup>. The third sub-sample is preserved with 5% HNO<sub>3</sub> and analyzed for “total” elements in the solution. The final sub-sample is filtered through a 0.45-µm syringe filter and preserved with 5% HNO<sub>3</sub> before being analyzed for “dissolved” elements.

Table 2. List of monitoring parameters and respective analytical methods for aqueous samples

Subsample	Parameter	Detection Methods	Instruments	Locations
Subsample I	Conductivity	AWWA Sec. 2510	Thermo Orion 1234	<i>in-situ</i>
	pH		Thermo Orion 1234	<i>in-situ</i>
	Redox Potential		Thermo Orion 1234	<i>in-situ</i>
	Estrogen <sup>c</sup>	HPLC/MS/MS	Micromass Q-TOF II	CCIC <sup>b</sup>
Subsample II	Alkalinity	AWWA Sec. 2310	-	CEGE EER Lab/ OARDC STAR Lab
	Total dissolved solid	AWWA Sec. 2540	-	
	Chloride (Cl)	AWWA Sec. 4110C	Dionex 2100	
	Sulfate (SO <sub>4</sub> <sup>-2</sup> )	AWWA Sec. 4110C	Dionex 2100	
	Phosphate(PO <sub>4</sub> <sup>-3</sup> )	AWWA Sec. 4110C	Dionex 2100	
	Nitrate (NO <sub>3</sub> <sup>-</sup> )	AWWA Sec. 4110C	Dionex 2100	
	Ammonia (NH <sub>4</sub> <sup>+</sup> )	AWWA Sec. 4110C	Dionex 2100	
Total Kjeldahl Method	AWWA Sec. 4500 N <sub>org</sub>	-		
Subsample III/ Subsample IV	Mercury (Hg)	CVAFS	Varian CVAAs,	
	Selected Elements <sup>a</sup>	AWWA Sec. 3120B	Varian VISTA-AX	
	Arsenic (As)/ Thallium(Tl)	AWWA Sec. 3120B	Varian GFAAs, Varian 880Z	
	Selenium (Se)	AWWA Sec. 3120B	Varian GFAAs, Varian 880Z	

<sup>a</sup> Aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), phosphorous (P), sodium (Na), silver (Ag), zinc (Zn).

<sup>b</sup> Campus Chemical Instrument Center at The Ohio State University

<sup>c</sup> On selected experimental batches

### *Chemical and Physical Integrity Evaluations*

The exhausted filter materials are preserved using liquid nitrogen and freeze-dried before being analyzed for the mineral and chemical compositions, surface morphology, and forms of adsorbed phosphorus by the methods listed in Table 35. The mineral compositions and morphology of the selected N- and P- type filters materials before and after service are characterized using X-ray diffraction (XRD) and scanning electronic microscopy (SEM), respectively. A Bruker D8 Advance X-ray diffractometer or equivalent is used to identify the mineral composition. The mineral patterns in the diffractograms are matched using the DIFFRACplus EVA software with ICDD Power Diffraction File (PDF2+) database. The complete elemental composition analysis is measured with the assistance of the digestion procedure described in EPA method 3052. A reference coal fly ash, 1633b, provided by the National Institute of Standards and Technology (NIST), is included for analytical quality control. A list of the analyses performed on the materials can be seen in Table 4.

The release potential of trace elements from filter materials before and after service will also be characterized. Standard protocols, i.e., EPA Standard Method 1311, Toxicity Leaching Characteristic Procedure (TCLP), the EPA Standard Method 1312, Synthetic Precipitation Leaching Procedure (SPLP), are used.

Table 3. Physical, mineral, and chemical analyses for selected pervious filter materials

	Method	Instrument	Location
Permeability	ASTM D4525-08		CEGE Soil Lab
Hydraulic Conductivity	ASTM D7100-06		
Morphology	Scanning Electron microscopy	Hitachi S-3000 SEM	OSU Nanotech West Lab
Mineral Composition	X-ray Diffraction	Bruker D8 Advance X-ray diffractometer	SENR Soil Lab <sup>c</sup>
Selected Elements <sup>a</sup>	ASTM D-6357	Milestone Microwave Digestor/ Varian VISTA-AX	CEGE EER Lab <sup>b</sup>
Mercury	ASTM D-6414	Varian CVAAs, Varian 880Z	CEGE EER Lab
Selenium	ASTM D-4606	Varian CVAAs, Varian 880Z	CEGE EER Lab
Arsenic, Thallium	ASTM D-3683	Varian GFAAs, Varian 880Z	CEGE EER Lab

<sup>a</sup> aluminum (Al), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), phosphorous (P), sodium (Na), sulfur (S), and zinc (Zn).

<sup>b</sup> Environmental Engineering Research Laboratory at Department of Civil, Environmental, and Geodetic Engineering of The Ohio State University

<sup>c</sup> Soil Lab at School of Environment and Natural Resources of The Ohio State University

#### 4. Current Progress and Tasks to be completed

##### *Characterizations of Industrial By-products*

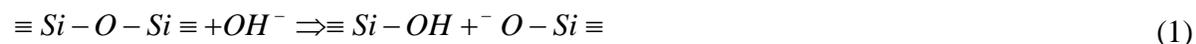
The chemical compositions of fly ash, stabilized FGD material, and bauxite red mud are first characterized and the results are summarized in Table 4. As shown in the table, calcium (Ca) and sulfur (S) are the two most abundant elements in the stabilized FGD material, which is associated with the presence of hanebachite ( $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ ), portlandite ( $\text{Ca}(\text{OH})_2$ ), and enttringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ) in the material. The X-ray diffractogram and mineral composition of stabilized FGD material can be seen in Figure 3. Iron (Fe), aluminum (Al), sulfur (S), and silicon (Si) are the major elements in fly ash. Based on XRD analysis, the fly ash used in this study is comprised of amorphous glass, aluminum silicates (e.g., mullite), and iron oxides (hematite, magnetite, and maghemite). Bauxite red mud is consisted of Al, Fe, and Ca. The X-ray diffractograms of fly ash and red mud are not shown.

By properly coalescing fly ash, stabilized FGD material, and red mud under high alkaline environment, fly ash acts as an inorganic polymer binder to enchain active ingredients through a geopolymerization process. After being alkali-activated, the Si-O-Si or Al-O-Si bonds in fly ash and stabilized FGD material are disassociated and subsequently form network-like crystalline and/or amorphous alkaline aluminosilicates with structural framework similar to zeolite<sup>13</sup>. In a previous project, it has been demonstrated that a geotextile material derived from the geopolymerization process with a mixture of fly ash and stabilized FGD material, has effective phosphorus sorption capability by forming Ca- and Fe-precipitates<sup>10,14,15</sup>. However, the fly ash/stabilized FGD material mixture did not show observable effect on nitrate mitigation<sup>10</sup>.

The addition of bauxite red mud is to enhance the nitrogen-nutrients adsorption capability of the fly ash/FGD mixture. Bauxite red mud contains minerals, e.g., iron (III) (hydr)oxides and hydrous aluminum oxides, that have high affinities for nitrate<sup>16</sup>. As a result, the material has been shown to be an effective nutrient sorbent<sup>17</sup>. Cengeloglu et al<sup>17</sup> used original and acid-treated bauxite red mud to remove nitrate from aqueous solution and reported 70% and over 90% of removal, respectively. They found the alkaline property of bauxite red mud hindered the adsorption performance.

In this study, bauxite red mud is used as the sole alkalinity source in the geopolymerization process, which might promote the nitrate adsorption capacity. During geopolymerization, the  $\text{OH}^-$  ions from bauxite red mud is consumed (eq. 1) and redistribute the electron density around the silicon atom in fly ash, which weaken the strength of Si-O-Si bond<sup>18</sup>

and progress the polymerization process. The reaction neutralizes the negative surface charge of red mud particles, and therefore, might promote the nitrate sorption.



*Preparation of P- and N-type pervious filtration*

A series of P- and N-type pervious filtration materials have been prepared based on the formulas listed in Tables 5 and 6. Currently, the prepared materials are undergoing a 21-day curing process. The images of two selected prepared materials can be seen in Figure 4. The hydraulic property of the filtration materials are adjusted by the addition of woodchip. Two different sizes of woodchip, i.e., <2.3mm and 2.3-3.6mm, are used. The addition of woodchip creates larger capillary routes for water to pass through. During the geopolymerization process, active ingredients are coated on the surface of woodchip, which allows the nutrients in ADW to react with the active ingredients while passing through the void space.

Table 4. Chemical compositions of fly ash, stabilized FGD material and bauxite red mud used in this study

		Fly Ash	Stabilized FGD material	Red Mud
Phosphorus	P	531	177	1054
Potassium	K	2986	1307	310
Calcium	Ca	9836	172906	33055
Magnesium	Mg	1528	10026	227
sulfur	S	11827	85746	2867
Aluminum	Al	27050	9705	62817
Boron	B	531	313	<3
Copper	Cu	42	<0.4	<0.8
Iron	Fe	59824	18855	240960
Manganese	Mn	85	73	139
Molybdenum	Mo	22	<13	<0.5
Sodium	Na	18851	5296	32412
Zinc	Zn	109	40	22
Arsenic	As	143	36	28
Barium	Ba	177	137	61
Beryllium	Be	<0.18	<0.11	<0.18
Cadmium	Cd	2	6	5
Cobalt	Co	23	4	15
Chromium	Cr	74	25	1397
Lithium	Li	167	106	55
Nickel	Ni	48	7	6
Lead	Pb	28	8	46
Antimony	Sb	<1.5	17	<1.5
Selenium	Se	20	18	1
Silicon	Si	4771	1481	184
Strontium	Sr	229	212	117
Thallium	Tl	129	38	871
Vanadium	V	2	<1.1	<0.6
Mercury	Hg	NA	0.318	NA

NA: Not Available  
Unit: mg/kg

Table 5. Formulas of Prepared P-type Filtration Materials

	P-Control	P-type I	P-type II	P-type III
Fly Ash	10.0	10.0	10.0	10.0
Stabilized FGD material	6.0	6.0	6.0	6.0
Quick Lime (CaO)	1.2	1.2	1.2	1.2
Deionized Water	10.5	10.5	10.5	10.5
Wood Chip (<2.3 mm)	0	2.5	5.0	0
Wood Chip (2.3-3.6 mm)	0	0	0	2.5

Unit: g

Table 6. Formulas of Prepared N-type Filtration Materials

	N-Control	N-type I	N-type II	N-type III
Fly Ash	10.0	10.0	10.0	10.0
Stabilized FGD material	6.0	6.0	6.0	6.0
Red Mud (dried weight)	8	8	8	8
Deionized Water	10.5	10.5	10.5	10.5
Wood Chip (<2.3 mm)	0	2.5	5.0	2.5
MnO <sub>2</sub>	0	0	0	2.0

Unit: g

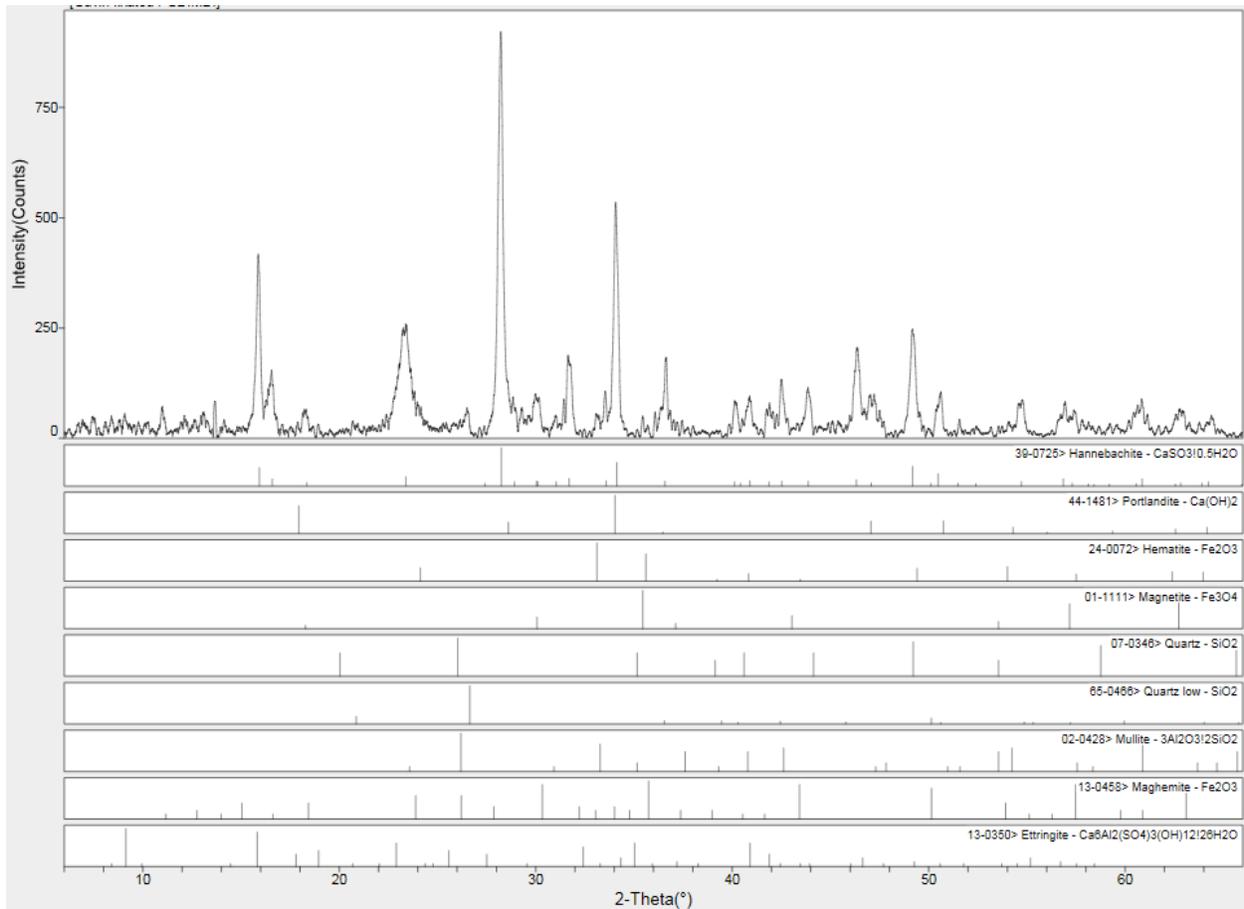


Figure 3. Mineral composition of stabilized FGD material

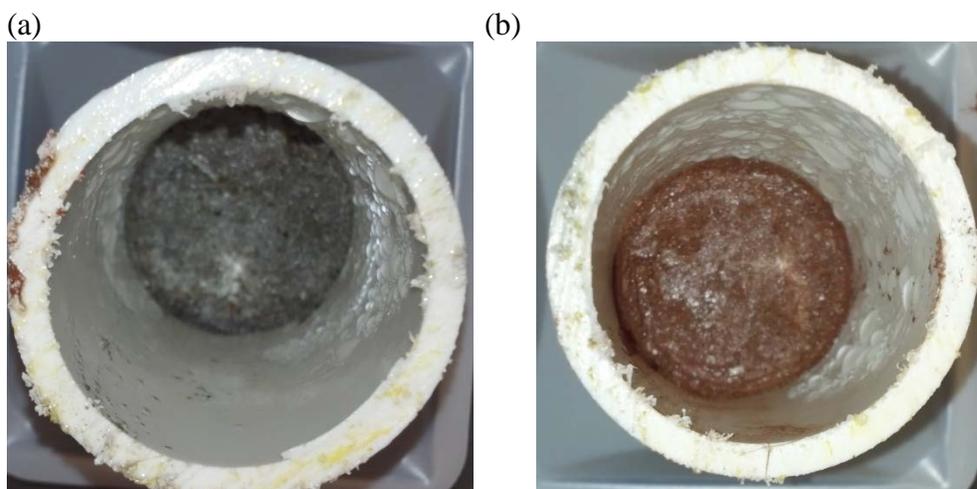


Figure 4. Prepared Pervious filtration materials. (a) P-type and (b) N-type.

These two types (i.e., P- and N-types) of pervious materials are expected to have selective sorption capacity, which can be used to sequentially separate and recover soluble phosphorous and nitrogen in agricultural drainage waters. In practice, two different pervious filter materials can be used in series. The dissolved phosphorous is expected to be selectively retained in the first pervious material (P-type) containing only fly ash and FGD material while allowing nitrate to pass through. Nitrate is captured in the second pervious material (N-Type) containing bauxite red mud, fly ash, and stabilized FGD material.

#### *Adsorption Capacities*

The nutrient adsorption capacities of P- and N-type materials were evaluated using the materials prepared from the formulas listed in Tables 5 and 6 for the P-Control and N-Control materials. For either type of the material, the adsorption experiment was carried out by adding six different amounts of the prepared solid, ranging from 0 to 1 gram, into six separate 125-mL HDPE bottles. Each bottle contains 100mL of either 250 mg/L of phosphate or 100 mg/L of nitrate solution. The bottles were then mixing by a tumbler for 24 hours at a rotating speed of 18 rpm. After mixing, the solution collected from each bottle was filtrated with 0.45mm filter and analyzed for  $\text{NO}_3^-$  or  $\text{PO}_4^{3-}$ .

The equilibrium concentrations of phosphate and nitrate in the solution after mixing as a function of material dosage are shown in Figure 5. As shown in the figure, over 97% of phosphate was removed by the P-type material with a solid-to liquid (L/S) ratio of 100. With the same L/S ratio, nearly 4% of nitrate was adsorbed by the N-type material.

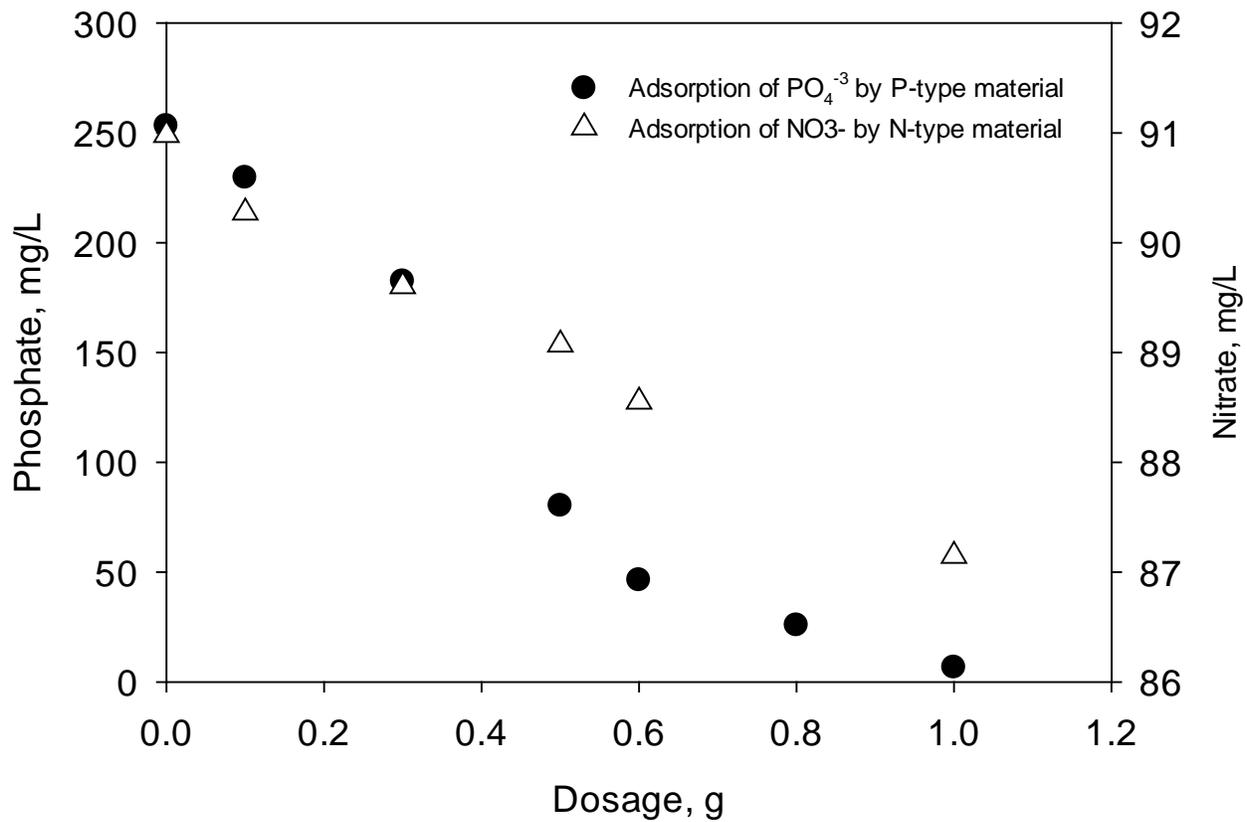


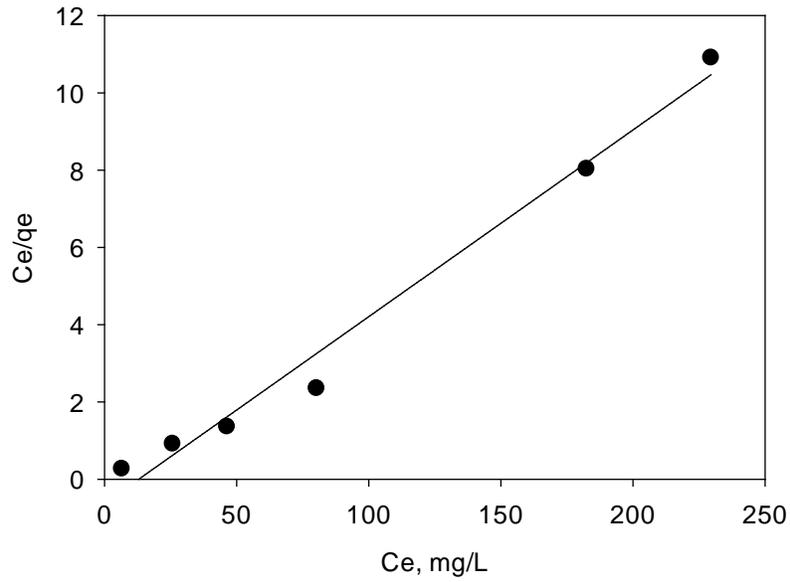
Figure 5. The equilibrium concentrations of phosphate and nitrate in the solution as a function of material dosage

The adsorption isotherms of phosphate on P-type material and nitrate on N-type material are illustrated in Figure 6. As shown in the figure, the adsorption isotherms of phosphate and nitrate can be expressed as Langmuir isotherm. The Langmuir isotherm equation is written as

$$\frac{C_e}{q_e} = \frac{1}{K \cdot Q_a^0} + \frac{C_e}{Q_a^0} \quad \text{Eq. 1}$$

where  $q_e$  is mass of material adsorbed (at equilibrium) per mass of adsorbent;  $Q_a^0$  represents the maximum adsorption capacity (monolayer coverage);  $C_e$  is the equilibrium concentration in solution when amount adsorbed equals  $q_e$ ;  $K$  is constant (L/mg).

(a)



(b)

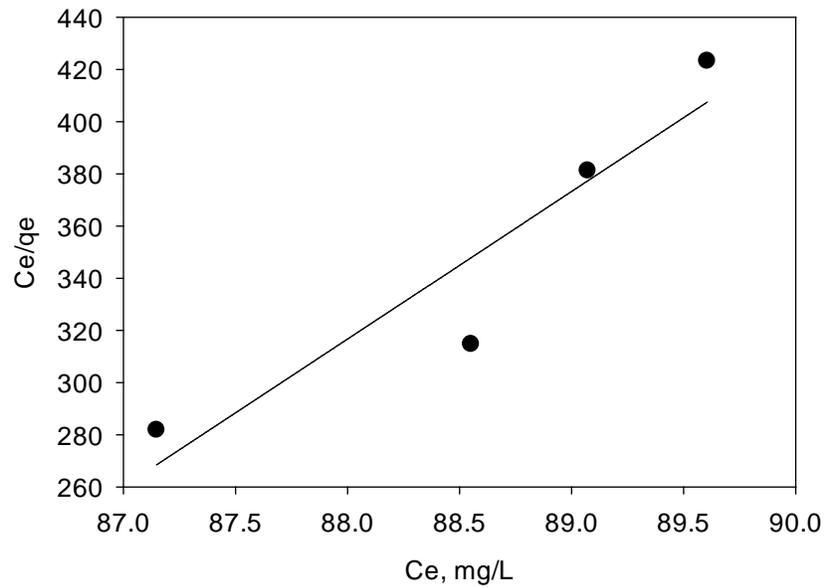


Figure 6. Langmuir isotherms for (a) phosphate and (b) nitrate

It is estimated that the maximum phosphate adsorption capacity of P-type material is 20.7 mg/g. For the N-type material, the adsorption capacity was approximately 0.18 mg/g, which is much less than the expected adsorption capacity.

## *Column Test*

### Close-loop Column System

Two series of bench-scale column tests were carried out using P-type and/or N-type columns in a close-loop mode to investigate the removal of nitrate and phosphate with extended contact time. The flow rate was kept at  $1.13 \pm 0.17$  mL/sec for both series. A simplified agriculturally degraded solution prepared with  $\text{NaH}_2\text{PO}_4$  and  $\text{NaNO}_3$  was used. In the first series, the solution was first introduced into P-type column and then N-type column. In the second series, only N-type column was used. A collection schedule was then setup to collect a series of eluent fractions based on pre-scheduled time interval. During each sampling interval, eluents were collected from the inlet and outlet of the first column, as well as the outlet of the second column in the first series, for nitrate and phosphate analyses.

The temporal trends of nitrate and phosphate at the inlet of the first column can be seen in Figure 7, which represent the concentrations in the storage tank. It was found that the concentration of nitrate in the first series decreased over 68.5% (from the original 47.1 mg/L to 14.8 mg/L) after 30 hours of circulation. In the second series, a similar removal efficiency (60.1%) was observed during the first 26 hours when only N-type column was used. However, the concentration of nitrate decreased to a level lower than the detection limit after 146 hours of circulation. In the case of phosphate, over 95% of the phosphate in the solution was removed within 30 hours of circulation in both close-loop series.

Results observed from the two close-loop series of column tests demonstrate that the pervious filter materials prepared in this study can effectively decrease the concentrations of nitrate and phosphate. Although the concentrations of both nitrate and phosphate showed a decreasing trend throughout the testing period in both testing series, for a given sampling interval, no significant changes were observed between the samples collected before and after the columns. It suggests that the time for the solution to travel through the lengths of these columns was not long enough to show any changes.

The decreases of nitration concentration observed in both column tests were unlikely due to adsorption. Results obtained from the adsorption isotherm experiment suggest that the adsorption of nitrate on the N-type material is very limited. Other mechanisms, such as biological reduction, might have involved in nitrate removal. Also, it seems the addition of red mud did not have significant effect on the reduction of nitration concentration.

### Flow through Column System

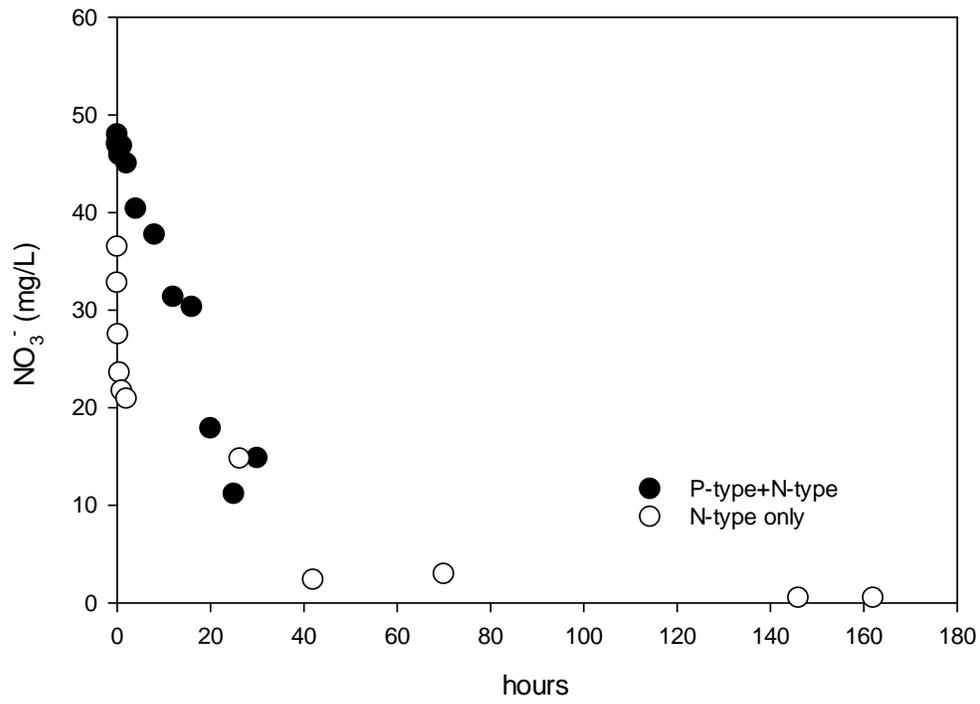
A flow-through column test was setup to further investigate the removal of nitrate and phosphate under the condition that is similar to real application. Only the P-type material was used in the test. The material was packed into a 2.5 ft long acrylic column with a diameter of 6 inches. The flow rate of the simulated agriculturally degraded solution, prepared from the same formula used in the close-loop column test, was controlled at 0.46 mL/min. As a result, the retention time of the solution in the column was maintained at 20 hours.

Results obtained from the test can be seen in Figure 8. As shown in the figure, over 77% of nitrate removal was achieved short after one pore volume passing through the column, which increased to 98% after approximately 168 hours. Compared to the results obtained from the close-loop system, which is also shown in Figure 8, the temporal trends of nitrate removal are very similar between the two systems.

In the case of phosphate, over 99% of removal was achieved after about 560 hours or 28 pore volumes, which increased from the 82.5% observed after about one pore volume. The removal of phosphate kept increasing as more solution passing through the column. It suggests that the adsorption of phosphate was likely controlled by the release of sulfate and the complexation of phosphate on the pore surface of the pervious material. As more solution passing through the column, more sulfate was released from the matrix of the pervious material, which allowed more phosphate to be retained within the pervious material.

Results obtained from the flow through column test confirmed the potential of using the pervious material derived from stabilized FGD material (P-type) to remove both nitrate and phosphate from agriculturally degraded solution.

(a)



(b)

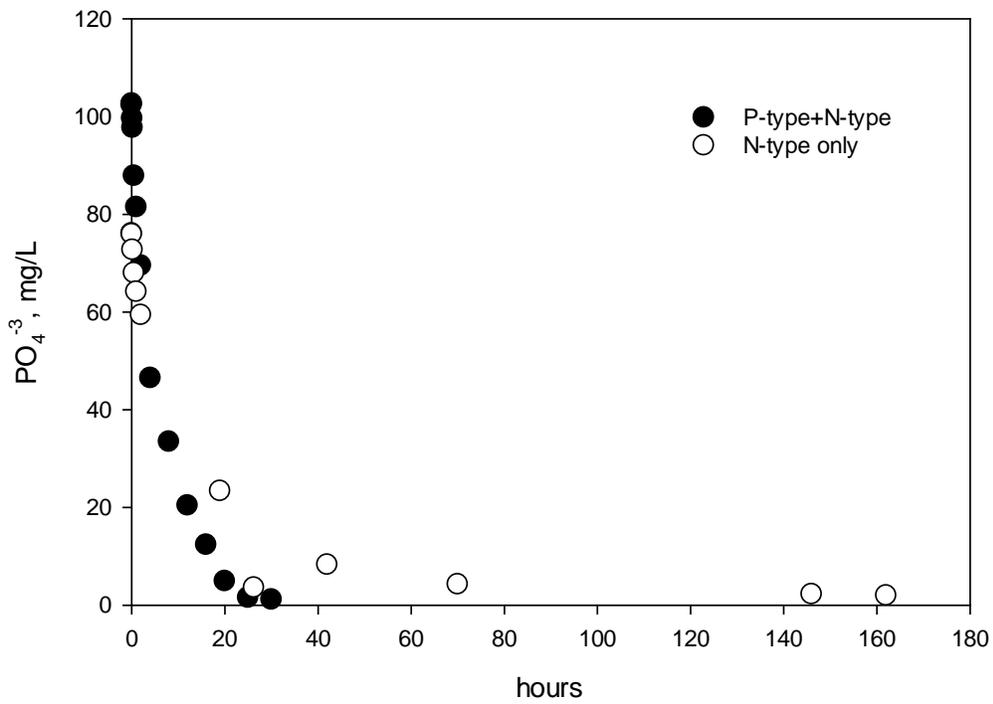
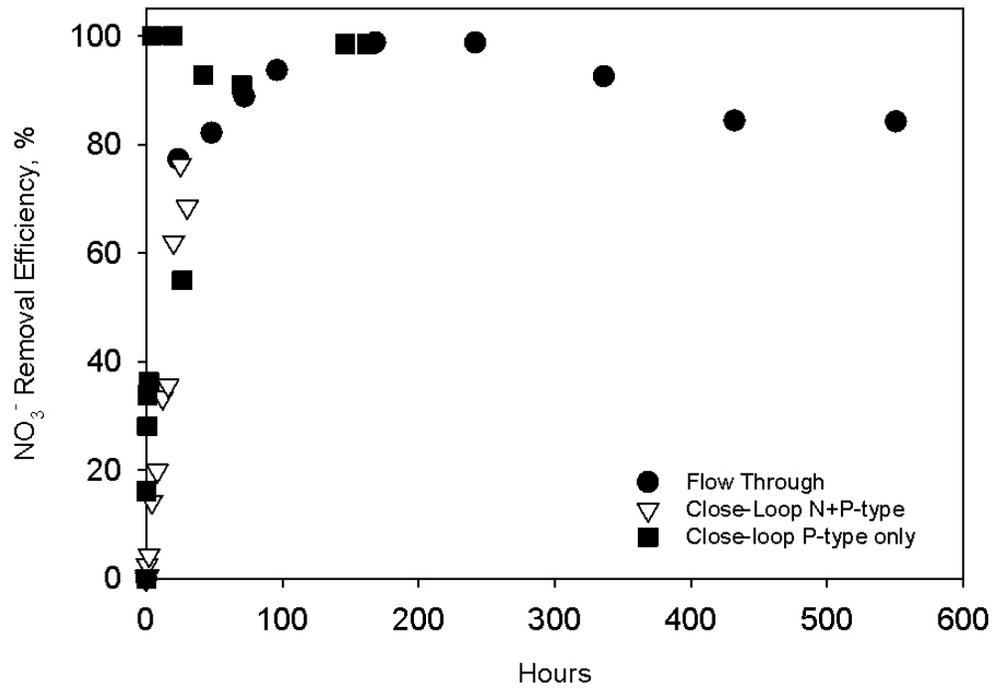


Figure 7. Temporal Trend of nitrate and phosphate in the close-loop column system

(a)



(b)

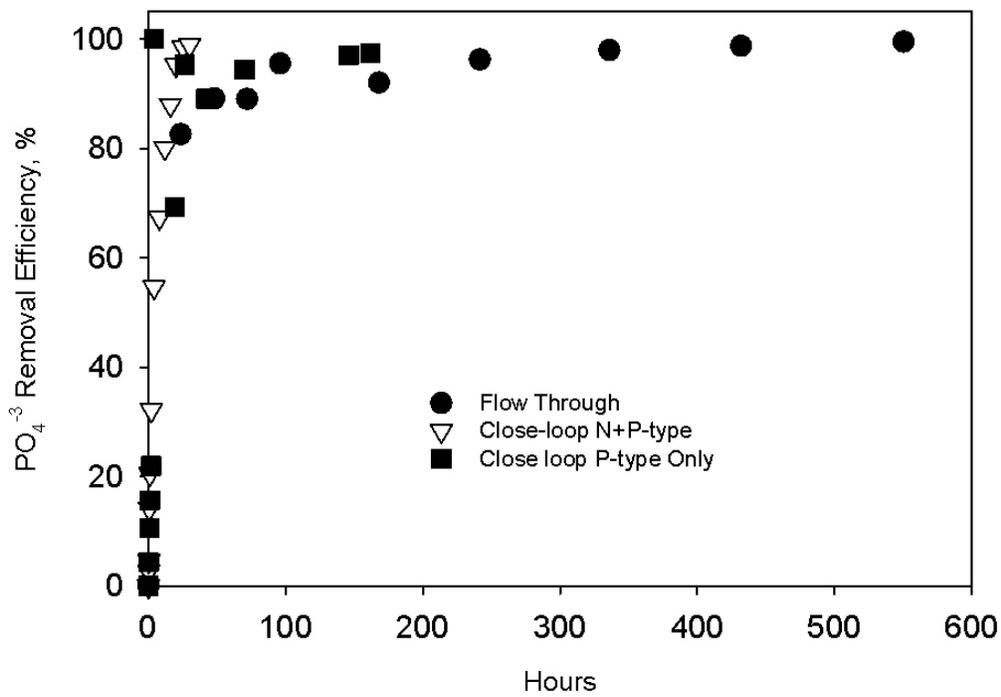


Figure 8. Removal efficiency of (a) nitrate and (b) phosphate using the P-type pervious material with a flow through column

### *Tasks to be completed*

The bench scale column test described in the “*Materials and Methods*” section will be continued. In addition, the mechanisms involved in the removal of N- and P-nutrients will be investigated. The integrities of physical and chemical properties of the pervious materials after adsorption will also be evaluated.

Despite the great potential for the proposed filtration application, the major concern of reutilizing these by-products is the release of trace elements contained in the materials after being contacted with water. Cheng *et al.*<sup>22</sup> investigated the water quality impacts associated with using stabilized FGD material as a low permeability liner for a swine manure storage pond. Based on five-year worth of field monitoring data, the concentrations of arsenic (As), boron (B), chromium (Cr), copper (Cu), and zinc (Zn) were consistently found lower in the water passing through the liner than the water collected from the pond. Other trace elements, such as Cd, Se, and Hg were often below the analytical detection limits. Ruyter *et al.*<sup>19</sup> investigated the red mud accident occurred on October 4<sup>th</sup> 2010 in Ajka, Hungary by testing the plant toxicity and trace element availability with mixtures of red mud and non-contaminated soil. They observed the concentrations of trace elements in the leachate of red mud were either non-detectable or less than 20µg/L. In addition, Peters and Basta<sup>18</sup> added bauxite red mud directly to soil to reduce the bioavailable phosphorus. No excessive soil pH and increases of soil salinity, extractable Al, or heavy metals in soils were found in their study. Based on available field data, the application of coal combustion by-products and bauxite red mud has not been suggested to post adverse impacts on the environments.

However, to comprehend the overall benefits of reusing these by-products, it is vital to understand the leaching properties of the prepared pervious materials under different application scenarios.

### **Expected Outcomes and Significances**

The outcome of this study is expected to provide:

- (1) Initial feasibility evaluation of a potential beneficial utilization for by-products produced from coal combustion and aluminum production processes
- (2) Insights regarding the interaction between nutrients and an agricultural emerging pollutant (i.e., estrogen) of FA zeolite-like material and the properties of biopolymers, and

- (3) Results to be transferred in forms of peer-reviewed publications and conferences, and be based upon in preparing competitive proposal for external funding.

The advantage of using selective sorption materials in the filtration approach is the potential to recycle and reutilize nutrients and industrial by-products, which promotes agricultural production to be in accord with the principles of sustainability. FGD gypsum and stabilized FGD material have shown to improve the yield of crops by providing necessary elements (e.g., calcium), changing soil physical properties, and increasing water infiltration and storage when they are applied as soil amendments<sup>20,21</sup>. Hylander et al.<sup>22</sup>, used different filter materials (i.e. limestone, Polonite®, and sand) to capture soluble phosphorus and evaluated the subsequent suitability for plant production. They observed some of recycled phosphorus achieved 76% of the yield increased by commercially available P-fertilizer. As demand for food increases, which results in more land to be used for agricultural purpose and a requirement for increased crop yields, the fertilizer demand have been projected to increase faster than world population<sup>23</sup>. With foreseeable increase in demand and depletion in reserve, use of recycled nutrients rather than a raw material is important step toward sustainable agricultural development. Currently, the majority of phosphate rock from mining goes into artificial fertilizer production<sup>24</sup>. It estimates that sources of high-grade phosphate ore deposits could disappear within the next 100 years at current use rates<sup>25</sup>.

## 5. References

- <sup>1</sup> Alexander, R. B., Smith, R. A., Schwarz, G.E., Boyer, E.W., Nolan, J.V., Brakebill, J.W. (2008) Differences in phosphorous and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. *Environ. Sci. Technol.*, 42, 822-830.
- <sup>2</sup> Mueller, D.K., Helsel, D.R., Nutrients in the Nation's Waters--Too Much of a Good Thing?. U.S. Geological Survey Circular 1136, <http://pubs.usgs.gov/circ/circ1136/circ1136.html#PUBS>, accessed 2/4/2011.
- <sup>3</sup> Smith, V.H., Tilman, G.D., Nekola, J.C. (1999) Eutrophication: impacts of excess nutrient inouts on freshwater, marine, and terrestrial ecosystems, *Environ. Poll.*, 100, 179-796.
- <sup>4</sup> Smil, V. *Enriching the Earth: Fritz Haber, Carl Bosch, and the Transformation of World Food*. The MIT Press, 2001, Cambridge, U.K.
- <sup>5</sup> Sharpley A, Foy B, Withers P (2000) Practical and innovative measures for the control of agricultural phosphorus losses to water: An overview. *J. Environ. Qual.*, 29, 1-9.
- <sup>6</sup> Kleinman P.J.A., Sharpley, A.N., Buda, A. R., McDowell, R.W., Allen, A.L. (2011) Soil controls of phosphorus in runoff: Management barriers and opportunities. *Can. J. Soil Sci.* 91, 329-338.

- <sup>7</sup> Sharpley A., Kleinman, P., and Weld J. (2010) Assessment of best management practices to minimize the runoff of manure-borne phosphorous in the United States, *New Zealand J. Agric. Res.*, 47, 461-477.
- <sup>8</sup> Sonzogni, W.C., Chapra, S.G., Armstrong, D.E., Logan, L.T. (1982) Bioavailability of phosphorus inputs to lakes. *J. Environ. Qual.*, 11, 555-563.
- <sup>9</sup> King, k.W., McDonald, J., Moore, J.F., Agrawal, S.G., Fischer, E.N., Balogh, J.C. (2010) Nutrient and pesticide removal from laboratory-simulated tile drainage discharge, *Trans. ASABE*, 53, 769-777.
- <sup>10</sup> Cheng, C.-M., Tu, W., Behrad, Z., Tarunjit B., Wolfe, W., Walker, H. (2007) Beneficial Reuse of FGD Material in the Construction of Low Permeability Liners: Impacts on Inorganic Water Quality Constituents, *J. Environ. Eng.*, 133, 523-531.
- <sup>11</sup> Jin, N. fly ash Applicability in Pervious Concrete, Master Thesis, The Ohio State University, Columbus, OH 2010.
- <sup>12</sup> Gall, H. E., Sassman S.A., Lee, L.S., and Jafvert, C.T., Hormone discharges from a Midwest tile-drained agroecosystem receiving animal wastes. *Environ. Sci. Tech.*, 2011, 45, 8755-8764.
- <sup>13</sup> Buchwald A., Dombrowski, k., and Weil, M. Influence of geopolymer binder composition on conversion reactions at thermal treatment, in *Developments in porous, Biological and Geopolymer Ceramics: A collection of Papers Presented at the 31<sup>st</sup> international conference on advanced Ceramics and Composites*, eds. Brito, M., Case, E., Kriven, W.M., Ceramic Engineering and Science Proceedings Volume 28. 257-271. Florida 2007,
- <sup>14</sup> Allred, B. (2010) Laboratory batch test evaluation of five filter materials for removal of nutrients and pesticides from drainage waters. *Transactions of the ASABE*, 53, 39-54.
- <sup>15</sup> Bryant, R.B., Buda A.R., Kkeinman, P.J.A., Church, C.D., Saporite, L.S., Folmar, G.J., Bose, S., Allen, A. (2012) Using fluegas desulfurization gypsum to remove dissolved phosphorus from agricultural drainage waters. *J. Environ. Qual.* 41, 664-671.
- <sup>16</sup> Yao, W., Millero, F.J. (1996) Adsorption of phosphate on manganese dioxide in seawater, *Environ. Sci. Technol*, 30, 536-541.
- <sup>17</sup> Cengeloglu, Y., Tor, A., Ersoz, M., Arslan, G. (2006) Removal of nitrate from aqueous solution by using red mud. *Sep. Purif. Technol*, 51, 374-378.
- <sup>18</sup> Duxson P, Lukey G.C., Separovic F. van Deventer J.S.J., (2005) Effect of alkali cations on aluminium incorporation in geopolymeric gels, *Ind. Eng. Chem. Res.*, 44, 832-839.
- <sup>19</sup> Ruters, S., Merten, J., Vassilieva, E., Dehandschutter, B., Poffijn, A., Smolders, E. (2010) The red mud accident in Ajka (Hungary): plant toxicity and trace metal bioavailability in red mud contaminated soil. *Environ. Sci. Technol.*, 45, 1616–1622.
- <sup>20</sup> Chen L., Dick W., Nelson S., (2001) Flue Gas Desulfurization by-product additions to acid soil: Alfalfa productivity and environmental quality, *Environ. Poll.*, 114, 161-168.
- <sup>21</sup> Punshon T., Adriano D.C., Weber, J.T. (2001) Effect of flue gas desulfurization residue on plant establishment and soil and leachate quality, *J. Environ. Qual.*, 30, 1071-1080.
- <sup>22</sup> Hylander, L.D., Kietlinska, A., Renman, G., Siman, G. (2006) Phosphorus retention in filter materials for wastewater treatment and its subsequent suitability for plant production. *Biores. Technol.*, 97, 914-921.
- <sup>23</sup> Haar, A. The Reuse of Phosphorus. Eureau Position Paper EU2-04-SL09, 2005; [http://eureau.org/sites/eureau.org/files/documents/2005.02.21\\_recovery\\_of\\_phosphorus\\_from\\_sludge.pdf](http://eureau.org/sites/eureau.org/files/documents/2005.02.21_recovery_of_phosphorus_from_sludge.pdf). Accessed 10/6/2012.

- <sup>24</sup> Jasinski S.M., Phosphate rock, 2006 Minerals Yearbook. United States Geological Survey, 2007, [http://minerals.usgs.gov/minerals/pubs/commodity/phosphate\\_rock/myb1-2006-phosp.pdf](http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/myb1-2006-phosp.pdf), accessed 10/2/2012.
- <sup>25</sup> Christen, K. (2007) Closing the phosphorus loop, *Environ. Sci. Technol.*, 41, 2078.

# Baseline measurements of methane emissions from rivers and lake waters in the proposed site of the OSU hydrofracking research station

## Basic Information

<b>Title:</b>	Baseline measurements of methane emissions from rivers and lake waters in the proposed site of the OSU hydrofracking research station
<b>Project Number:</b>	2015OH4800
<b>Start Date:</b>	6/1/2015
<b>End Date:</b>	5/30/2017
<b>Funding Source:</b>	Other
<b>Congressional District:</b>	3rd
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Surface Water, Climatological Processes, Wetlands
<b>Descriptors:</b>	Membrane separations; water treatment; biomimetic
<b>Principal Investigators:</b>	Gil Bohrer

## Publications

There are no publications.

## **Baseline measurements of methane emissions from rivers and lake waters in the proposed site of the OSU hydrofracking research station**

PI Gil Bohrer, Associate Professor, OSU

Progress Report 2016-2017

### **Abstract**

The goal of this project is to provide baseline measurements of methane emissions from the site of future fracking operation in Noble County, Ohio. We leverage on the Ohio State University NETL grant that provides the site, access and opportunity to conduct measurements before and during all stages of the fracking and production processes. We will combine eddy covariance and chamber measurements of the methane flux. Deployment of the observation setup months before drilling operations start will allow establishment of a baseline for the natural emissions of methane in and around the drill site. Originally, the NETL project was planned to be conducted in the OSU Eastern Extension Station in Noble County, and frack in agricultural land. However, the planned activity for the NETL project and the fracking site was changed and the potential new locations are all farther from OSU campus and in forested land. This project leverages on an NSF grant to provide base-line measurements for a future fracking site, which was awarded to PI Gil Bohrer. Specifically the funds from Ohio WRC were requested to supplement travel (to the farther site) and materials (taller tower is needed in forested landscape) that were not accounted for in the NSF grant, which was proposed for the original fracking site.

### **Methodology**

- 1) The establishment of an OSU fracking research site in Piedmont Lake by the NETL and the OSU USEEL center has failed and an OSU site will not exist. Our project was leveraging on that site, and therefore, we were forced to re-locate the flux tower for measurements of methane emissions, and the location of the baseline measurements.
- 2) A location for a 20 m tall flux tower was identified, and a contract with the land owner was signed. The location is downwind a planned well pad locations near Morgantown West Virginia. The tower is in the center of a 50x50 m<sup>2</sup> grassy field surrounded by trees. The tower is relatively tall to allow a wide footprint area and to get clear measurements over the surrounding trees.
- 3) Ongoing measurements of meteorological conditions (air temperature, pressure and humidity, wind, precipitation and incoming radiation) and methane and CO<sub>2</sub> fluxes using eddy-flux will be conducted continuously at the West Virginia site from a tower that we plan to construct in 5-6/2017 and will continue throughout this project. This tower was funded by NSF.
- 4) A campaign for chamber measurements of the fluxes from the river near the tower and fracking site, and from the grassland surrounding the tower took place in May 2017. We will repeat chamber measurements several more times until October 2017.

### **Major Activity**

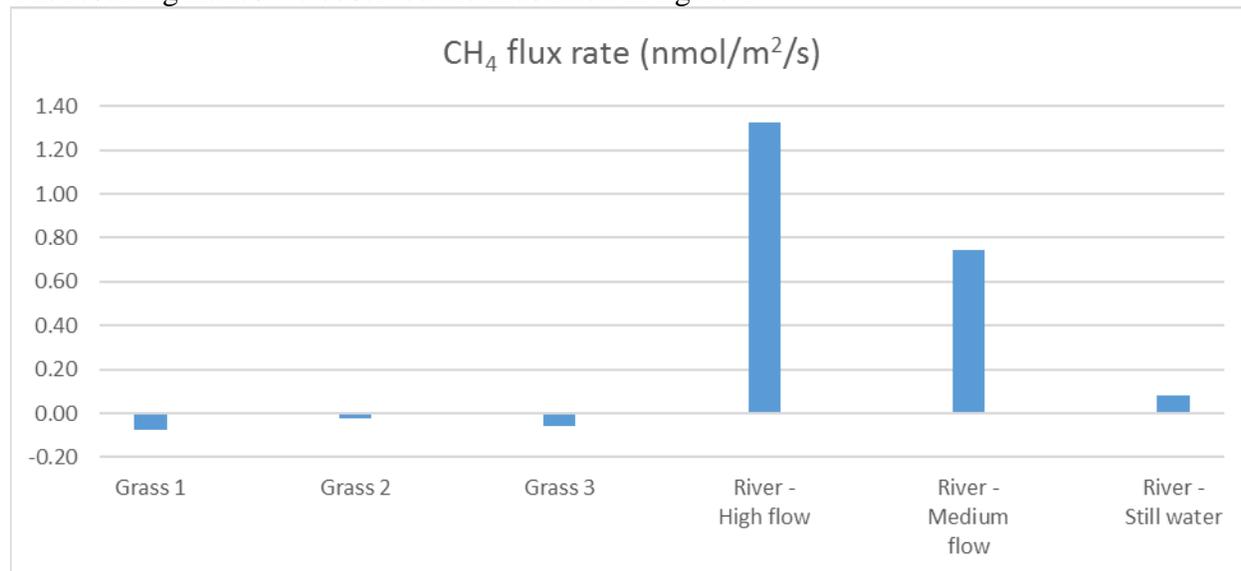
Unfortunately, the NETL project has failed to secure a study site and activities in the USEEL Will not be possible. Therefore, it was impossible for us to start our fieldwork to date. A 1-year

no-cost extension for the project was requested and approved. We have secured an alternative field site in collaboration with Prof. Derek Johnson in West Virginia University. The site is near Morgantown WV, on private land, near a fracking pad. Fracking activity is scheduled to start later this summer. This project provide an additional components of chamber measurements in a larger NSF-funded project that will fund the construction of a flux tower and the flux analysis activity. A subcontract from the NSF funding was signed with WVU and field work at the new site is scheduled to start within the coming weeks. Tower construction is now underway. The flux tower instrumentations including all sensors, datalogger, and wireless model were calibrated, tested and assembled in our laboratory, awaiting deployment in the field as soon as the tower in constructed. The tower will be instrumented and go online mid-June.

A chamber measurement campaign took place in May 2017. We measured bassline methane fluxes from the field surrounding the tower, and from the near-by river. At each patch type (field, river) duplicate chamber measurements were taken at 3 locations.

### Findings

The resulting fluxes we observed are illustrated in figure 1.



**Figure 1. Methane fluxes from grass field and river near flux tower location and fracking site**

The grass field produces no methane, and some very low rate of methane oxidation occur in the soil. This is important for the interpretation of the measurements from the flux tower, as it indicates that observations will represent remote sources of methane and are not influenced by baseline emissions at the local field around the tower. As expected, some methane emission occurred from the river. Any wet ecosystem typically produces some methane. Nonetheless, the emissions from the river were very low. For example, they are about 2 orders of magnitude lower than emissions we typically observe in natural wetlands.

### Significance

The project will provide baseline measurements of methane emissions from natural and agricultural aquatic ecosystems around the proposed locations of a hydrofracking site. These observations will allow developing an empirical model for the natural methane emissions from

the water system at the site and will allow determining whether these emissions increase due to diffused methane release into the ground water after the drilling operations started.

Local emissions from natural sources near the tower may mask any remote emission in the tower footprint. The chamber measurements of the river and field allow us to know that local emissions are not expected and that the tower observations should not be corrected to account for those.

# Effectiveness of Data Buoys as Early Warning Systems for cHABs (cyanobacterial Harmful Algal Blooms) in Lake Erie

## Basic Information

<b>Title:</b>	Effectiveness of Data Buoys as Early Warning Systems for cHABs (cyanobacterial Harmful Algal Blooms) in Lake Erie
<b>Project Number:</b>	2016OH484B
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	2/28/2018
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	OH-003 & OH-015
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Surface Water, Water Quality, Methods
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Justin Chaffin, Douglas L Kane

## Publications

1. Chaffin, J. "Effectiveness of data buoys for sampling cyanobacterial harmful algal blooms in Lake Erie", Event name: Ohio Academy of Science Annual Meeting, Size of audience: 20, Date: 4/16/2016, Type of presentation: Oral
2. Chaffin, J. "Let's Hear It for the Buoys?- Accuracy of data buoys for monitoring cyanobacterial blooms in Lake Erie" Event name: Great Lakes HABS Collaboratory Webinar, Size of audience: 50, Date: 6/2/2016
3. Chaffin, J. (2016) "Accuracy of Data Buoys for Monitoring Cyanobacterial Blooms in Lake Erie" International Association on Great Lakes Research Conference, Guelph, Canada, Size of audience: 500, Date: 6/6/2016, Oral Presentation
4. Chaffin, J. "Accuracy of data buoys for tracking cyanobacterial blooms in Lake Erie" Lake Erie Millennium Network, Size of audience: 125, Date: 2/21/2017, Type of presentation: Oral

## Ohio WRC Project Progress Report

“Effectiveness of Data Buoys as Early Warning Systems for cHABs (cyanobacterial Harmful Algal Blooms) in Lake Erie”

By:

Justin D. Chaffin  
Stone Laboratory  
Ohio State University and Ohio Sea Grant

And

Douglas D. Kane  
Defiance College

### **1. Progress Report**

#### *Problem and Research Objectives*

Toxic cyanobacterial harmful algal blooms (cHABs) are a global problem due to excessive anthropogenic nutrient inputs and a warming climate (Paerl and Huisman, 2008; Smith, 2003). These blooms have the potential to produce toxic compounds (“cyanotoxins”) that pose threats to human health because cHABs often occur in surface waters that are sources for drinking water. When water treatment fails to remove cyanotoxins from the water and a cyanotoxin is detected at dangerous levels post-treatment, a drinking water advisory is issued warning the public not to drink their tap water. A recent infamous example of a do not drink advisory due to cyanotoxins occurred in Toledo, Ohio during early August 2014 when the cyanotoxin microcystin was detected at concentrations that exceeded the safe drinking criterion (Bullerjahn et al., 2016). This event left nearly a half million people without safe drinking water for nearly 3 days. Another example occurred in Wuxi, China during when more than 2 million people were left without safe drinking water for 7 days (Qin et al., 2010).

The ultimate goal is to prevent cHABs from forming in lakes and rivers by decreasing influx of nutrients from the watershed. However, trends in climate and agricultural practices suggest that cHABs will become more common in the future (Michalak et al., 2013; Paerl and Huisman, 2008). Thus, eliminating cHABs will take time and the risk of cyanotoxins in water will be present for the near future. In the meantime, we will have to deal with cHABs and rely on the water treatment plants for providing safe drinking water. In order to aid the water plant operators in removing cyanotoxins from water, real-time estimates of cHAB biomass near the intake pipes will help the operators to adjust treatment accordingly. Moreover, the real-time information on cHAB biomass could be used to notify lake managers, tourists, and the general public when cHABs are causing water quality problems. The early detection of cHABs creates the opportunity to minimize the health risks and negative economic impacts by warning people before cHABs are actually a problem (Jochens et al., 2010), and also lets people know when a cHAB is not causing a problem in a given area of the lake or time.

Cyanobacterial blooms are an annual summer occurrence in Lake Erie (Bridgeman et al., 2013; Stumpf et al., 2012), and the lake serves as a drinking water source for millions of people. Several buoys with water quality sensors are deployed each summer in western Lake Erie to monitor water quality, including cyanobacterial biomass, total algal biomass, and water clarity. Some buoys are located near water intakes for treatment plants and are supposed to function as early warning systems for the plant operators. The buoys collect information every 15 minutes and can send alerts via email and/or text message that cHAB biomass exceeds a certain level.

However, there are several potential issues with sensors attached to buoys. First, the sensors do not measure algal or cyanobacterial biomass but measure surrogates for biomass. The sensors measure chlorophyll (chl) and phycocyanin (PC) fluorescence, which is assumed to be proportional to chl and PC concentration, which is used as a surrogate for total phytoplankton and cyanobacterial biomass, respectively. The first problem is the assumption that chl or PC concentration is proportional to algal or cyanobacterial biomass. Algae and cyanobacteria can alter their chl and PC content (pigment mass per cell) in response to light conditions (MacIntyre et al., 2002). For example, Lake Erie *Microcystis* doubled its chl content and PC content increased 6 times during the summer of 2008 in response to low light conditions in the lake (Chaffin et al., 2012). The second problem is the use of fluorescence to measure chl concentration. Fluorescence from algae is dependent on physiological state. Fluorescence per cell will increase under stressful conditions, such as low nutrient concentration and high light intensities (Campbell et al., 1998). This could lead to an underestimation or overestimation of cyanobacterial biomass. Thus, these data buoys are taking measurements of fluorescence without ground-truthing the sensor data with biomass data from water samples. Knowledge of how well these sensors accurately measure cyanobacteria biomass will further aid water treatment plant operators in adjusting treatment to match cyanobacteria biomass. The second potential issue with sensors is instrument drift. The sensors are deployed year-around or just during summer (April-November) and the sensors are only calibrated just a few times a year (< 5 times). It is possible that the sensors lose calibration throughout deployment and give inaccurate data. Thirdly, and associated with long-term deployment, is biofouling from algae and *Dreissena* mussels (Fig. 1). The densely packed mussels around the sensors would likely reduce water exchange around the sensors.

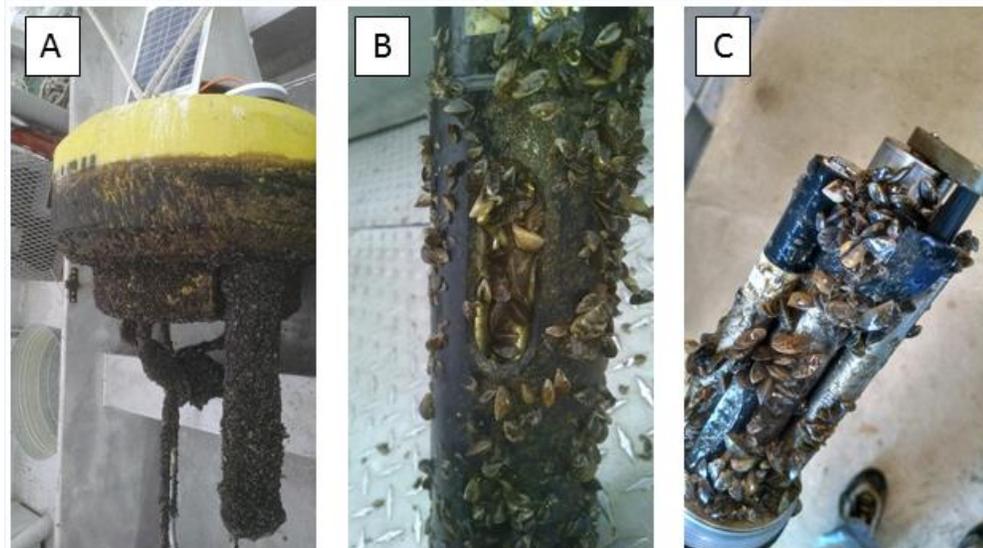


Figure 1. Images of biofouling by filamentous green algae and *Dreissena* mussels on the Sandusky buoy (A), on the YSI sonde (B), and on the YSI sensors (C).

The sensors attached to data buoys are located just below the surface of the water (~0.6 to 1 meter); however, water treatment plant intake pipes are near the bottom of the lake in water that is greater than 6 meters in depth. Thus, there is a potential disconnect between water quality data measured at the surface and water quality being drawn into the plant. Moreover, the different buoyancy regulation strategies of the different cyanobacteria in Lake Erie can further exacerbate that disconnect. For example, *Microcystis* is positively buoyant allowing it to accumulate near the surface in calm waters, whereas, *Planktothrix* is neutrally-to-negatively buoyant and will position itself in the center of the water column or sink to the bottom (Konopka et al., 1987; Reynolds et al., 1987). Thus, a data buoy may overestimate cyanobacteria abundance during a *Microcystis* bloom and underestimate cyanobacteria abundance during a *Planktothrix* bloom. This could result in a plant operator to over-treat (which wastes treatment chemicals and money) or under-treat (which could result in microcystins in tap water) the lake water. *Microcystis* and *Planktothrix* are known microcystins producers and bloom in waters that serve as source water for several large Ohio shoreline cities such as Toledo and Sandusky, respectively.

Wind speed can also impact how water treatment plant operators interpret buoy data. The lake is calm during low wind weather allowing cyanobacteria to position themselves at desired light levels (i.e. *Microcystis* near the surface and *Planktothrix* lower in the water column). High wind speeds create turbulent mixing of the water column and overpowers the buoyancy regulation of cyanobacteria resulting in cyanobacteria to be spread evenly from surface to lake bottom. A potential issue in water treatment can arise when a calm day is followed by a windy day. For example, a buoy measures high cyanobacteria biomass due to *Microcystis* at the surface one day, but then high winds the following day mix the bloom throughout the water column. The buoy data will show *less* cyanobacteria biomass but the intake is actually drawing in *more* cyanobacteria biomass because the wind mixed the bloom throughout the water column and down to the intake pipe.

The overall objective of this project is to determine the effectiveness of data buoys to serve as early warning systems of cHABs for drinking water treatment plant treatment operators.

Specific objectives include 1) to determine how well buoy sensor data for total algae biomass, cyanobacterial biomass, and water clarity correlate with water sample measurements and 2) to determine vertical position of cyanobacteria throughout the water column in relation to buoy cyanobacteria and wind speed data.

### *Methodology*

#### Buoy location and sonde calibration:

Two data buoys were the subject of this study. The Stone Lab buoy is deployed about 500 meters northwest of Gibraltar Island and the Sandusky buoy is deployed 100 meters from the City of Sandusky lake side drinking water intake. The Stone Lab buoy was equipped with an YSI 6600v2 multiprobe sonde during 2015 and an YSI EXO2 sonde during 2016. The Sandusky buoy had an EXO2 sonde both years. Sondes were calibrated for relative fluorescence units (RFU) for chl *a* and PC (surrogates for total algal and cyanobacterial biomass, respectively) and calibrated for nephelometric turbidity units (NTU) for water clarity (according to YSI instructions) prior to deployment with the same calibrants at the same time along with approximately 20 other sondes at the University of Toledo's Lake Erie Center. The Stone Lab sonde was calibrated and cleaned twice throughout deployment whereas the Sandusky sonde was not cleaned or calibrated until buoy retrieval.

#### Water sample collection:

Water samples were collected adjacent to the buoys to determine correlation between buoy sensor data and water sample data. The Stone Lab buoy was visited several times a week throughout deployment with small john boats and the boats would tie up to the buoy. A total of 125 samples were collected next to the Stone Lab buoy in 2015 and 2016. The Sandusky buoy was visit 8 times during summer aboard the *RV Erie Monitor* and the vessel would anchor within 20 meters of the buoy. A total of 16 samples were collected near the Sandusky buoy. To determine if the buoy sonde data correlated with surface water quality data a 0-2 meter intergraded tube sampler was used to collect surface water. The 0-2 meter sampler was used because it would sample the 'average' conditions experienced by the buoys' sonde as the buoy bobs up and down with waves (the sonde is between 0.7 and 1.0 meters depth). Water from the sampler was dispensed into a clean 5-gallon bucket and then poured into 1) two 2-L dark bottles for chl *a*, PC, total suspended solids (TSS) concentrations, and algal group-specific chl *a*, 2) 500-mL glass jar and preserved with Lugol's solution for analysis of phytoplankton identification and quantification, 3) 40-mL amber glass vial for total microcystins concentration, 4) two 250-mL bottles for total and total nitrogen and phosphorus concentrations, and 5) 0.45  $\mu\text{m}$  filtered water into a 60-mL polycarbonate bottle for dissolved nitrogen and phosphorus concentrations. All bottles were held on ice during transportation to the laboratory. Secchi disk depth was also measured.

On a subset of dates water samples were collected at every meter throughout the water column to determine phytoplankton vertical position. Water was collected with a Van Dorn bottle and poured into 250-mL polycarbonate bottles. Water was analyzed for algal group-specific chl *a* concentration.

#### Water sample analysis methods:

Chlorophyll *a*: Water from the 2-L bottle was filtered through GF/F filters (47 mm diameter, 0.7  $\mu\text{m}$  pore size) noting the volume filtered. Filters will be stored on silica gel at -20°C until analysis. Chlorophyll *a* was extracted with dimethyl sulfoxide and quantified with spectrophotometry, following (Golnick et al., 2016).

Algal group-specific chl *a*: ~30 mL from the dark 2-L bottle (collected 0 to 2 m) or 250-mL bottle (collected from discrete 1-m intervals) was read on a FluoroProbe benchtop reader for cyanobacteria-specific chl *a*. The FluoroProbe is a fluorometric device that uses chlorophyll and accessory pigment fluorescence to partition total chlorophyll *a* among four functional phytoplankton groups (green algae, cyanobacteria, diatoms, and cryptophytes).

Phycocyanin: Water was filtered on GF/F as listed for chlorophyll. Phycocyanin was extracted in a sodium phosphate buffer with sonication and quantified by fluorometry, following Chaffin et al. (2012).

Total suspended solids and non-volatile suspended solids (TSS&NVSS): TSS&NVSS were determined following Standard Method 2540 D and E. Water was filtered on pre-combusted, pre-weighed GF/F filters. Filter with plankton was dried at 103°C overnight and reweighed to determine TSS. Filters were then combusted at 550°C for 1 hour. Filters were weighed again to determine NVSS.

Phytoplankton: Phytoplankton was quantified with a FlowCam under 40x, 100x, and 200x. FlowCam is a fluid imaging device that captures images of particles (i.e. plankton) as they flow through the object lens carried in a medium (i.e. lake water). FlowCAM has been shown to provide very similar results to traditional phytoplankton counts using light microscopy with the Utermohl method (Álvarez et al., 2014). FlowCam software has an image recognition system to aid the user in sorting of phytoplankton and records 31 parameters for each particle, including length, diameter, and area which are used for calculating biomass. 8000 images were collected for each sample.

Total Microcystins: Microcystins were quantified following Ohio EPA Total (Extracellular and Intracellular) Microcystins - ADDA by ELISA Analytical Methodology (Version 2.0, December 2014). Microcystins were lysed from cells using three freeze-thaw cycles and then cellular debris removed by filtration using GMF filters. Abraxis enzyme-linked immunosorbent assay (ELISA) was used for quantification.

Phosphorus, nitrogen, silicate: Phosphorus (P), nitrogen (N), and silicate (Si) were quantified via wet chemistry on a SEAL QuAAtro flow-through nutrient analyzer. The following EPA methods were used for total P, total Kjeldahl N, nitrate, nitrite, ammonium, and dissolved reactive P (respectively) 365.1, 351.2, 353.2, 354.1, 350.1, and 365.1. Water was filtered within 5 minutes of collection for dissolved nutrient parameters.

#### Buoy data analysis:

Data from the 2 buoys was downloaded from WQDataLive website. The buoys recorded data every 15 minutes. Water sample data was compared to the buoy data on 3 time scales: 1) the single data point closest to the time that the water sample was collected, 2) the average of five buoy data points one hour prior to water sample collection (for example, if water sample was collected at 11:00 the buoy measurements at 10:00, 10:15, 10:30, 10:45, and 11:00 were averaged), and 3) averaged for 4 hours prior to water sample. Linear regression was used to compare water sample data to the buoy data.

In addition, buoy cyanobacteria data was compared with cyanobacteria-specific chl *a* data at discrete 1-m intervals (0-5 m) to determine how cyanobacteria biomass detected by the buoy compares to cyanobacteria biomass throughout the water column at different depths.

Finally, in order to determine what may account for agreement/disagreement in buoy vs. every-meter cyanobacteria data, we used linear regressions to determine whether wind speed (as a surrogate for mixing) was negatively correlated with (sub)surface accumulations of cyanobacteria. Data were obtained from NOAA's National Buoy Data Center (<http://www.ndbc.noaa.gov>) using South Bass Island site for Gibraltar buoy and Marblehead site for Sandusky buoy analyses. We initially proposed to use the buoys' weather station wind data for this project, but we had to find alternate wind data source due to malfunctions to both buoys' weather stations during summer 2016.

### *Principal Findings and Results*

Both the buoy and water samples at Stone Lab suggested that there was a large difference in cyanobacterial biomass between the summers 2015 and 2016 (Fig. 2 top). The larger 2015 bloom was first detected in late July by both the buoy and water samples, and highest biomasses were recorded during August at 57.6 µg/L of cyanobacteria-chl *a* and at 95.1 RFU. In contrast, the cyanobacterial bloom of 2016 was just above detectable levels for both the buoy and water samples and peaked at 2.3 µg/L of cyanobacteria-chl *a* and at 0.7 RFU.

At the Sandusky buoy, 2015, in general, had higher cyanobacterial biomasses than 2016. Cyanobacteria were detected by both the buoy and water sample throughout deployment in both summers.

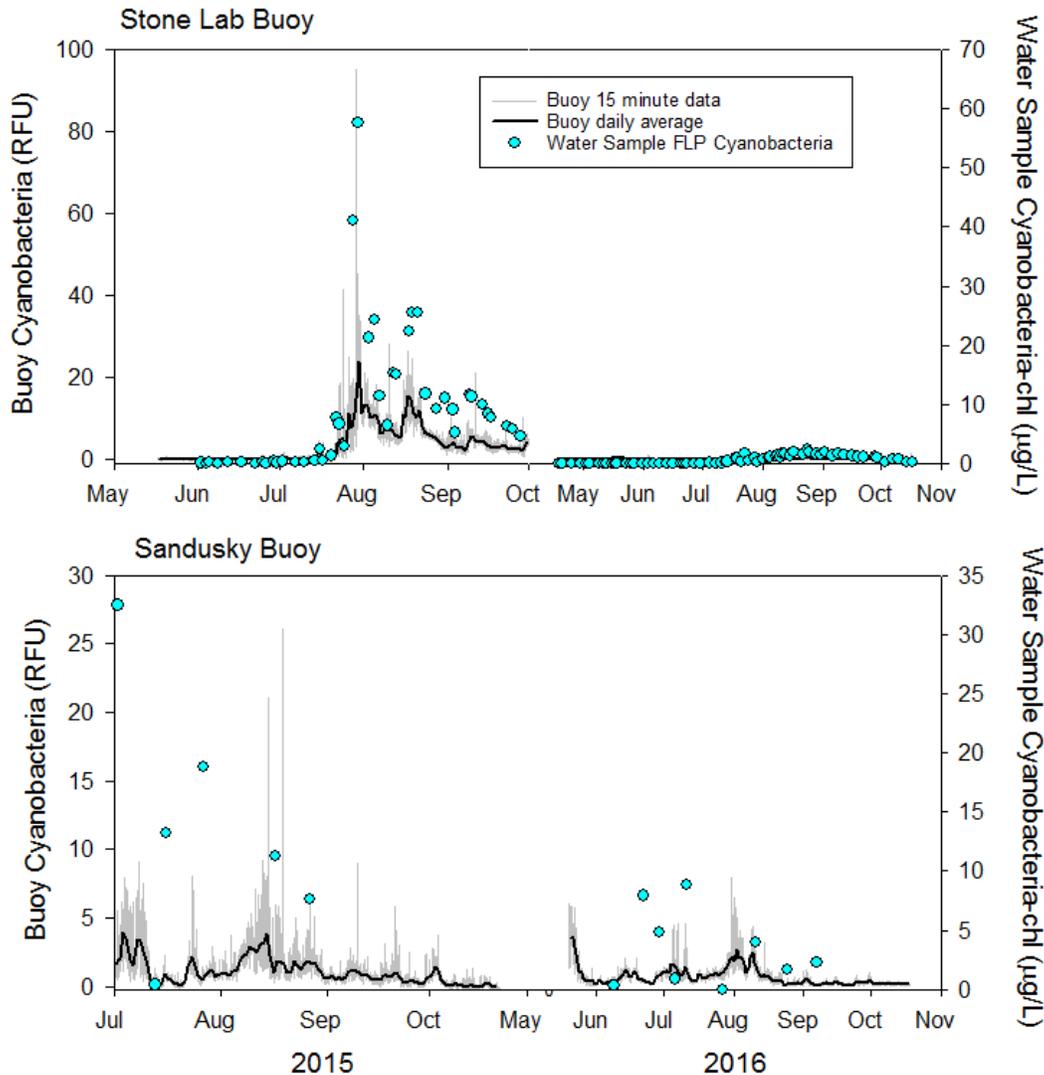


Figure 2. Cyanobacterial biomass at the Stone Lab (top) and Sandusky (bottom) buoys measured by the buoys' sonde (lines) and in water samples collected adjacent of the buoy (circles).

There was a very strong linear relationship ( $R^2 = 0.96$ ) between the Stone Lab buoy cyanobacteria RFU data and water sample cyanobacteria-chl *a* concentration; however, the trend was driven by the 2015 data (Fig. 3 top). There was no significant relationship between Sandusky buoy cyanobacteria and water sample data.

Different relationships were found between the Stone Lab buoy and water sample chl *a* data for 2015 and 2016. Water sample chl *a* concentrations were greater in 2015 whereas the buoy chl *a* RFU were greater in 2016. Additionally, the relationship between the buoy and water samples was weak ( $R^2 < 0.5$ ). At the Sandusky buoy, on the 2015 data has a significant relationship between buoy and water sample chl *a* data.

Buoy NTU and water sample TSS had similar, strong ( $R^2 > 0.80$ ) relationships in 2015 and 2016 at the Stone Lab buoy. There was no relationship between buoy NTU and water sample TSS at the Sandusky buoy.

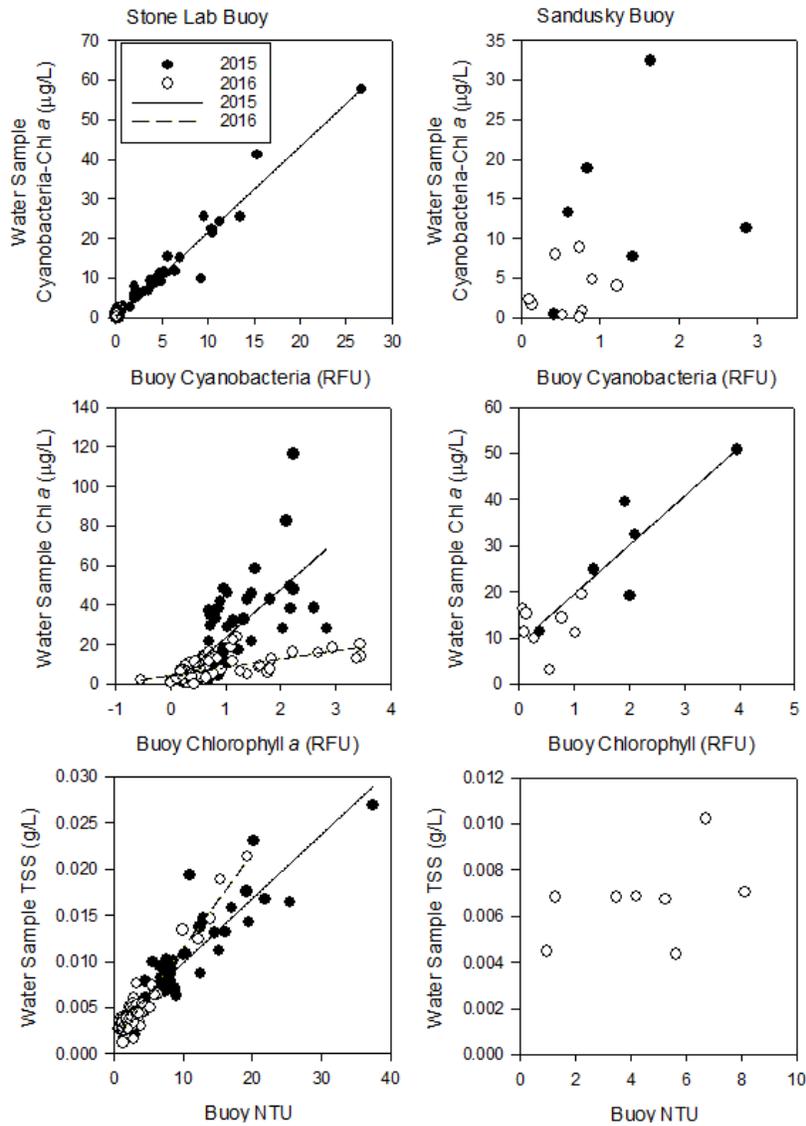


Figure 3. The relationship between buoy sonde data (x-axis) and water sample data (y-axis) for the Stone Lab (left) and Sandusky (right) buoys for measurements of cyanobacterial biomass (top), total algae (middle) and water clarity (bottom). Solid circles are 2015 and open circles are 2016. Only significant ( $P < 0.05$ ) regressions are shown.

Measurements of cyanobacterial biomass between the buoy and every meter throughout the water (FluoroProbe data) generally agreed for the Gibraltar buoy but there were deviations at higher cyanobacterial biomasses. However, there was no agreement at the Sandusky buoy. Further, agreement was better at lower concentrations than higher concentrations (Figure 4).

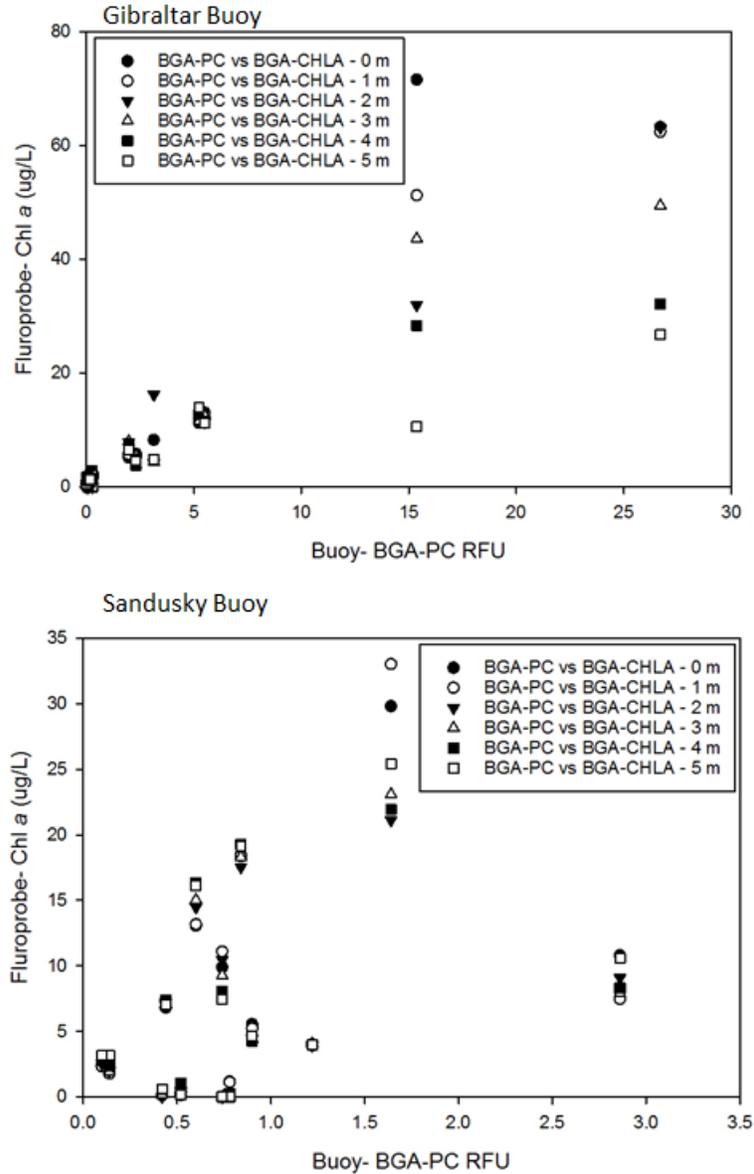
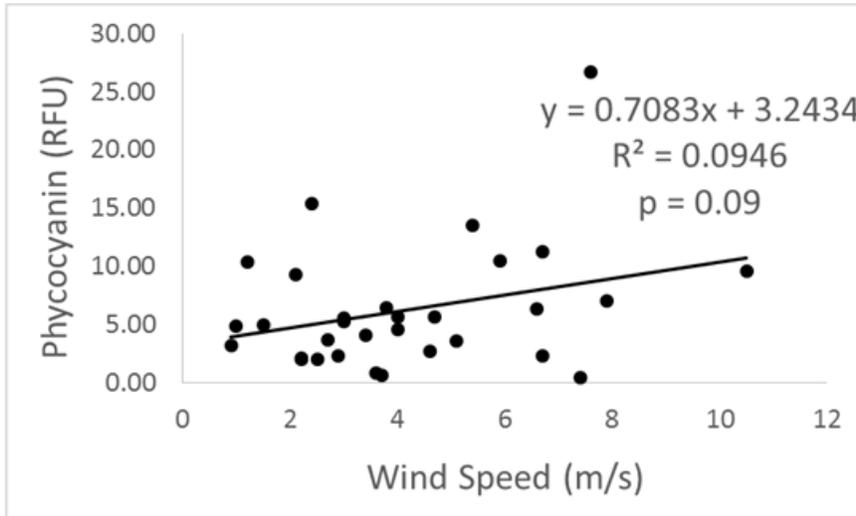


Figure 4. The relationship between cyanobacterial biomass buoy sonde data (Phycocyanin RFU; x-axis) and cyanobacterial biomass at discrete 1-m depth intervals (0-5 m) (FluoroProbe chl a; y-axis) for the Stone Lab (top) and Sandusky (bottom) Note that the x-axis of the top graph is approximately 10x that of the bottom graph.

Wind speed did not correlate (negatively) with buoy cyanobacterial biomass (RFU) at either buoy during 2015 and 2016.

Gibraltar Buoy



Sandusky Buoy

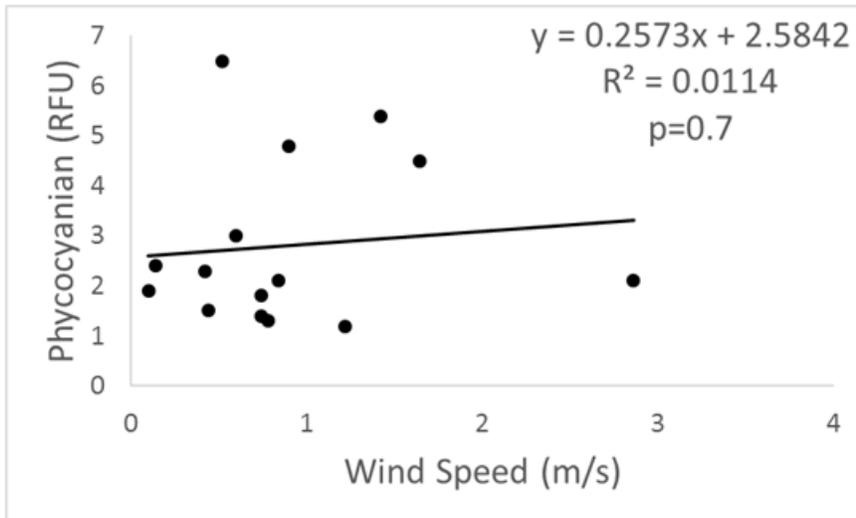


Figure 5. The relationship between wind speed (x-axis) and contemporaneous buoy sonde data (y-axis) and at nearby weather stations (x-axis) for the Gibraltar (top) and Sandusky (bottom) buoys. Note that the Gibraltar Buoy graph only shows 2015 data, as there was often near 0 RFUs in 2016 at this site.

### Finding Significance

1. The Stone Lab buoy was a good predictor of water sample cyanobacteria-chl *a* and water clarity (as TSS); however, the buoy was not a good predictor of total algal chl *a*. These results should give confidence to users of buoy data (water treatment plant operators, lake

managers, public) that buoy cyanobacteria RFU and NTU are adequate surrogates for cHABs and water clarity, and that their decisions based off buoy data are correct.

2. The Sandusky buoy data and water sample data had little to no correlation. This was likely due to the long-term deployment and fouling by *Dreissena* mussels and filamentous green algae.
3. Measurements of cyanobacterial biomass between the buoy and at every meter (with the FluoroProbe) generally agreed for the Gibraltar buoy but there were deviations at higher biomass; however, there was no agreement at the Sandusky buoy. We hypothesized also that this is also the case during well-mixed conditions compared to during more stratified conditions, although our initial analysis using wind as a proxy for mixing does not support that more mixing (higher wind speeds) leads to less near surface (1-m) accumulation of cyanobacteria. More surface (0 m) collected data and perhaps more complex surrogates for mixing are needed to further this analysis.

### *Plans for 2017*

We received an extension for this project because the cyanobacterial bloom in 2016 was very small (see Fig. 2). The Stone Lab buoy was deployed in early April 2017 and we have already begun sampling next to the buoy. Beginning July 2017 we will resume the every-meter discrete sample to measure cyanobacterial biomass throughout the water column and compare that to the buoy data.

A more in depth data analysis of wind data will be conducted. During the 2015 summer, there was a highly significant relationship between Stone Lab buoy RFU and water sample cyanobacteria-chl *a*. Because of this relationship we can convert the buoy RFU to FluoroProbe Cyano-Chla (because of high  $r^2$  value). We will then determine the residuals between buoy-converted-FluoroProbe-Cyanobacteria-chla compares to discrete FluoroProbe measurements and then compare those residuals to wind speed.

Additionally, preserved phytoplankton samples collected from the Stone Lab buoy during the 2015 bloom are analyzed for cyanobacteria identification and biovolume measurements.

Finally, there were large differences in cyanobacteria RFU at the Stone Lab buoy between 2015 and 2016, and the water samples supported that difference in RFUs. However, two different sonde models were used (2015 had a YSI 6600v2, 2016 had a YSI EXO2). Therefore, to determine if the different models measure cyanobacteria differently, we will deploy a YSI 6600v2 next to the Stone Lab buoy July through September.

### *References*

- Álvarez, E., Moyano, M., López-Urrutia, Á., Nogueira, E., Scharek, R., 2014. Routine determination of plankton community composition and size structure: a comparison between FlowCAM and light microscopy. *J. Plankton Res.* 36, 170–184.  
doi:10.1093/plankt/fbt069
- Bridgeman, T.B., Chaffin, J.D., Filbrun, J.E., 2013. A novel method for tracking western Lake Erie Microcystis blooms, 2002–2011. *J. Gt. Lakes Res.* 39, 83–89.
- Bullerjahn, G.S., McKay, R.M., Davis, T.W., Baker, D.B., Boyer, G.L., D'Anglada, L.V., Doucette, G.J., Ho, J.C., Irwin, E.G., Kling, C.L., Kudela, R.M., Kurmayer, R., Michalak, A.M., Ortiz, J.D., Otten, T.G., Paerl, H.W., Qin, B., Sohngen, B.L., Stumpf, R.P., Visser,

- P.M., Wilhelm, S.W., 2016. Global solutions to regional problems: collecting global expertise to address the problem of harmful cyanobacterial blooms. A Lake Erie case study. *Harmful Algae* 54, 223–238. doi:10.1016/j.hal.2016.01.003
- Campbell, D., Hurry, V., Clarke, A.K., Gustafsson, P., Oquist, G., 1998. Chlorophyll fluorescence analysis of cyanobacterial photosynthesis and acclimation. *Microbiol. Mol. Biol. Rev.* 62, 667–683.
- Chaffin, J.D., Bridgeman, T.B., Heckathorn, S.A., Krause, A.E., others, 2012. Role of suspended sediments and mixing in reducing photoinhibition in the bloom-forming cyanobacterium *Microcystis*. *J. Water Resour. Prot.* 4, 1029.
- Golnick, P.C., Chaffin, J.D., Bridgeman, T.B., Zellner, B.C., Simons, V.E., 2016. A comparison of water sampling and analytical methods in western Lake Erie. *J. Gt. Lakes Res.* 42, 965–971. doi:10.1016/j.jglr.2016.07.031
- Jochens, A.E., Malone, T.C., Stumpf, R.P., Hickey, B.M., Carter, M., Morrison, R., Dyble, J., Jones, B., Trainer, V.L., 2010. Integrated Ocean Observing System in Support of Forecasting Harmful Algal Blooms. *Mar. Technol. Soc. J.* 44, 99–121. doi:10.4031/MTSJ.44.6.16
- Konopka, A.E., Kromkamp, J., Mur, L.R., 1987. Regulation of gas vesicle content and buoyancy in light- or phosphate-limited cultures of *Aphanizomenon flos-aquae*(Cyanophyta). *J. Phycol.* 23, 70–78.
- MacIntyre, H.L., Kana, T.M., Anning, T., Geider, R.J., 2002. Photoacclimation of photosynthesis irradiance response curves and photosynthetic pigments in microalgae and cyanobacteria. *J. Phycol.* 38, 17–38.
- Michalak, A.M., Anderson, E.J., Beletsky, D., Boland, S., Bosch, N.S., Bridgeman, T.B., Chaffin, J.D., Cho, K., Confesor, R., Daloğlu, I., DePinto, J.V., Evans, M.A., Fahnenstiel, G.L., He, L., Ho, J.C., Jenkins, L., Johengen, T.H., Kuo, K.C., LaPorte, E., Liu, X., McWilliams, M.R., Moore, M.R., Posselt, D.J., Richards, R.P., Scavia, D., Steiner, A.L., Verhamme, E., Wright, D.M., Zagorski, M.A., 2013. Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proc. Natl. Acad. Sci.* 110, 6448–6452. doi:10.1073/pnas.1216006110
- Paerl, H.W., Huisman, J., 2008. Blooms Like It Hot. *Science* 320, 57–58. doi:10.1126/science.1155398
- Qin, B., Zhu, G., Gao, G., Zhang, Y., Li, W., Paerl, H.W., Carmichael, W.W., 2010. A drinking water crisis in Lake Taihu, China: linkage to climatic variability and lake management. *Environ. Manage.* 45, 105–112. doi:10.1007/s00267-009-9393-6
- Reynolds, C.S., Oliver, R.L., Walsby, A.E., 1987. Cyanobacterial dominance: The role of buoyancy regulation in dynamic lake environments. *N. Z. J. Mar. Freshw. Res.* 21, 379–390.
- Smith, V.H., 2003. Eutrophication of freshwater and coastal marine ecosystems a global problem. *Environ. Sci. Pollut. Res.* 10, 126–139. doi:10.1065/espr2002.12.142
- Stumpf, R.P., Wynne, T.T., Baker, D.B., Fahnenstiel, G.L., 2012. Interannual variability of cyanobacterial blooms in Lake Erie. *PLoS One* 7, e42444.

## Trace metal limitation of biofilm growth and metabolism: potential consequences for storage of nutrients in headwater streams

### Basic Information

<b>Title:</b>	Trace metal limitation of biofilm growth and metabolism: potential consequences for storage of nutrients in headwater streams
<b>Project Number:</b>	2016OH490B
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	2/28/2018
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	OH-013
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Nutrients, Ecology
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	David Costello

### Publications

There are no publications.

## **Trace metal limitation of biofilm growth and metabolism: potential consequences for storage of nutrients in headwater streams**

David Costello  
Kent State University  
Progress report submitted to Ohio Water Resources Center  
May 2017

### **Problem and Research Objectives**

The increased frequency and extent of harmful algal blooms (HABs) has sparked the need for greater knowledge about the physical factors that are involved in bloom formation and toxin production. Water quality, and in particular nutrient availability, has been a major focus of researchers' attempts to understand the mechanisms of HABs. Although primary producers require at least 20 different elements (Schlesinger and Bernhardt 2013), the vast majority of what is known about nutrient limitation in aquatic ecosystems focuses on just two elements: nitrogen (N) and phosphorus (P) (Hecky and Kilham 1988, Elser et al. 2007). In freshwater lakes and large rivers, the metals required for metabolic processes (e.g., iron (Fe), zinc (Zn), molybdenum (Mo)) can be measured at concentrations known to limit growth of marine algae (e.g., Nriagu et al. 1996, Shiller 1997). This study attempts to address the unknown importance of limiting concentrations of trace metals on primary production in small streams draining into Lake Erie.

Abiotic and biotic processes in streams can retain, transform, and remove nutrients effectively (Peterson et al. 2001). Biofilms—the consortium of algae, bacteria, and fungi that cover the streambed (Lock et al. 1984)—remove N and P from the water column to fuel their growth (Arango et al. 2008, Sobota et al. 2012). Assimilation of N and P by biofilms can lessen stream nutrient loads and convert inorganic nutrients like nitrate ( $\text{NO}_3^-$ ) and phosphate ( $\text{PO}_4^{3-}$ ) to less bioavailable organic forms (Bronk et al. 1994, Johnson et al. 2009). Although biofilms are composed of microscopic organisms, algal-dominated mid- and low-order stream reaches can have biofilms at high biomass that drive in-stream nutrient processes and store ecologically relevant amounts of N and P (Vannote et al. 1980, Arango et al. 2008, Bernot et al. 2010). However, saturation of in-stream nutrient processing is common in streams draining urban and agricultural landscapes as biofilm growth (and related processing) is limited by resources other than N and P (Bernot and Dodds 2005, Arango et al. 2008, Johnson et al. 2009). I hypothesize that low trace metal concentrations in eutrophic streams limit biofilm growth, contribute to saturation of nutrient removal processes, and limit biofilm storage of N and P. To test this broad hypothesis, I ask two research questions:

- Q1: Are trace metals at in tributaries to Lake Erie at concentrations that may limit primary production?
- Q2: When supplemented with trace metals, does primary production and nutrient storage increase?

### **Methodology**

#### *Trace metal and nutrient concentrations in tributaries to Lake Erie*

In summer 2016, trace metal and nutrient concentrations were measured in small to mid-order streams in the Lake Erie watershed. Smaller streams were targeted for sampling because

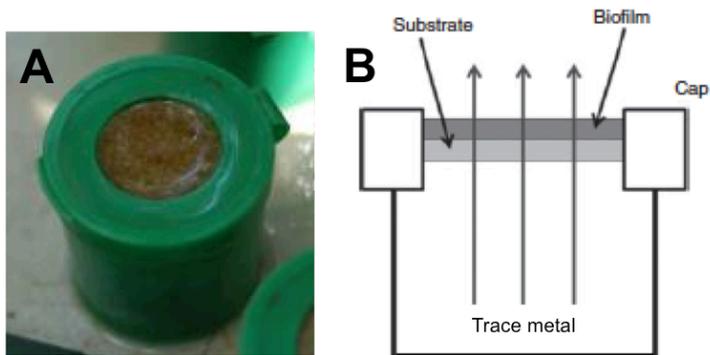
previous studies have demonstrated that streams of this size are both more abundant on the landscape and provide the majority of nutrient processing and storage in a watershed (Vannote et al. 1980, Bernot et al. 2010). Water chemistry was monitored from spring to late summer to coincide with the periods of peak nutrient delivery and seasonal HAB formation in Lake Erie.

In collaboration with the National Center for Water Quality Research (NCWQR) at Heidelberg University, surface water samples from five Lake Erie tributaries were shipped to Kent State University for trace metal analysis. Tributaries sampled were Rock and Honey Creeks (Sandusky watershed), Lost Creek (Maumee watershed), Portage Creek, and River Raisin. Surface water samples were collected at least daily by ISCO refrigerated samplers and samplers were emptied by NCWQR staff weekly. To minimize the effects of sample holding time on metal concentrations, only the most recently collected surface water sample (i.e., <24 h since collection) was selected for metals analysis. Water samples were filtered (0.45  $\mu\text{m}$ ), acidified to pH <2 with  $\text{HNO}_3$ , and stored at room temperature until transport to Kent State University. Water samples were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) for a suite of essential trace metals (Fe, Zn, Cu, Mn, Mo, and Ni). The trace metal data was supplemented with nutrient chemistry data that NCWQR shares through the Tributary Loading Program (<https://www.heidelberg.edu/academics/research-and-centers/national-center-for-water-quality-research/tributary-data-download>).

Twenty-six headwater streams (1–3<sup>rd</sup> order) in the Cuyahoga and Chagrin River watersheds (both drain to Central Basin of Lake Erie) were sampled monthly from June–August 2016. Filtered (0.45  $\mu\text{m}$ ) and unfiltered surface water was collected from all headwater streams within a 72-h period. Filtered samples were analyzed for nitrate ( $\text{NO}_3^-$ ) by ion chromatography, soluble reactive phosphorus (SRP) by spectrophotometry (molybdate blue method), and trace metals (Fe, Zn, Cu, Mn, Mo, and Ni) by ICP-OES.

#### *Nutrient and trace metal limitation of primary producers*

Using data from the water chemistry survey of streams in the Central Basin watersheds, five streams with potential nutrient and/or trace metal limitation were identified: Brandywine Creek, Mill Creek, Breakneck Creek, Fish Creek and Cicada Creek. Nutrient and trace metal limitation was quantified using trace metal nutrient diffusing substrates (tNDS). Using this approach, the concentration of nutrient and/or trace metals are elevated in the small area around an attachment substrate (Fig. 1). If low nutrient or trace metal concentrations in the stream are limiting growth, then the biofilms growing on the substrate that supplies the limiting element should grow to a greater biomass. The tNDS were composed of a general growth agar amended with nutrients (N and P) and trace metals (Fe, Zn, Mo and Ni) and a fritted glass disk was placed on the surface of the agar to provide a substrate for biofilm attachment (Costello et al. 2016). Single element and multi-element mixtures were used



**Figure 1.** Photograph of a single tNDS colonized by biofilm (A) and a cross-sectional schematic of a tNDS.

to target specific mechanisms of limitation and co-limitation by nutrients and trace metals. Treatment combinations included: N only, P only, and Fe only to test for single element limitation, N-P-Fe and N-P-Fe-Mo-Ni-Zn to test for general co-limitation, Mo-P-Fe to test for co-limitation related to nitrification, Ni-P-Fe to test for co-limitation related to organic N acquisition, and N-Zn-Fe to test for co-limitation related to organic P cycling.

In September 2016, the tNDS (70 per stream) were secured to the bed of each stream with a Hobo light sensor and MiniDOT oxygen and temperature sensor to measure water column conditions. Filtered water samples were collected to measure ambient nutrient and trace metal concentrations at deployment and collection of the tNDS cups. After three weeks of incubation, the tNDS cups were collected and the fritted discs were removed from the agar and placed in a small chamber with stream water to quantify metabolism (GPP and ER) using the light-dark incubation method (Bott et al. 1997). Rates of nutrient assimilation (i.e.,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  uptake) were also calculated during chamber incubations (Steinman and Mulholland 2006, North et al. 2007). Biofilms and glass substrates were frozen prior to measuring biofilm chlorophyll *a* and biomass. Due to a large storm event during the incubation, some individual cups and entire treatments were lost from the stream or buried; these missing data have been excluded from all analyses. For the purposes of this report, we only present the results of algal biomass (i.e., chlorophyll *a*).

## **Principal Findings and Results**

### *Trace metal and nutrient concentrations in tributaries to Lake Erie*

Ambient nutrient and trace metal concentrations in tributaries to Lake Erie exhibited strong regional patterns (i.e., Western and Central Basin streams differed), but we observed potential trace metal limitation across all study streams. On average, streams draining into the Western Basin of Lake Erie had greater dissolved N and P concentrations than tributaries in the Central Basin watersheds (Table 1). However, Breakneck Creek and Mill Creek in the Cuyahoga River watershed had  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  concentrations that approached those observed in eutrophic Western Basin streams. In all study streams, dissolved Zn, Ni, and Mo were frequently at concentrations below our detection limits, which suggests that these trace metals may be near the physiological limits of algae (Table 1). Mo concentrations were higher in the Western Basin tributaries than in the Central Basin tributaries, in which Mo was never measured above our detection limits. Fe concentrations varied greatly between and within streams (Table 1). Lost Creek (Western Basin) and Brandywine Creek (Central Basin) had the highest average Fe concentrations (Table 1), but both of those streams had Fe concentrations measured below the potential limiting concentrations at some time during the summer (Table 1). River Raisin (Western Basin) and Cicada and Breakneck Creeks (Central Basin) had average Fe concentrations that were near or below potential limiting concentrations (Table 1). The concentrations of dissolved N and P were correlated (Pearson  $r = 0.34$ ,  $p < 0.001$ ), but ambient trace metals were not correlated to N or P (e.g., Fe and P: Pearson  $r = 0.15$ ,  $p = 0.08$ ). These data from tributaries to Lake Erie confirm national trends in water quality that suggest trace metals can be measured at concentrations known to limit or co-limit (with macronutrients) primary producer growth, and suggest that there is potential trace metal limitation in both Western and Central Basin watersheds.

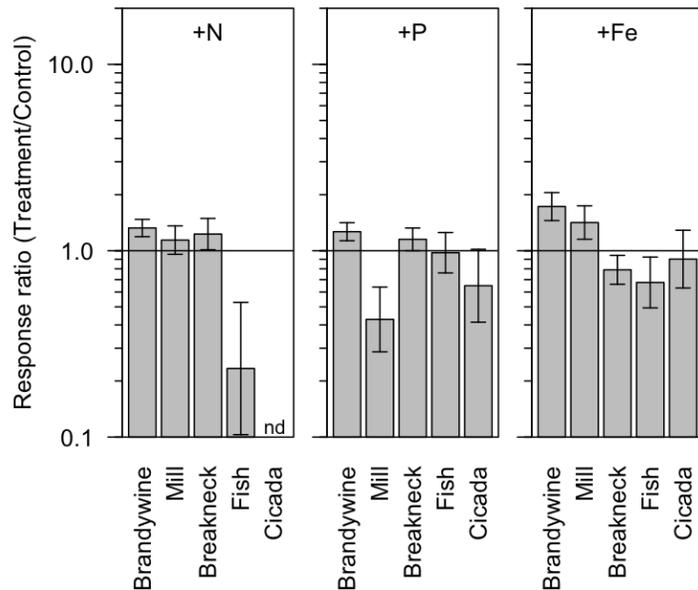
**Table 1.** Ambient nutrient chemistry of streams draining into Lake Erie. Twenty-six tributaries (1–3<sup>rd</sup> order) in the Central Basin (Cuyahoga and Chagrin River watersheds) were sampled from June–August 2016, and mean water quality is reported for the five streams in which nutrient limitation assays were completed. The range of concentrations for all 26 streams are also reported (in parentheses). Western Basin tributaries were sampled weekly from March–September 2016 (n=23–28) and values reported are means and ranges (in parentheses). Ambient trace metal concentrations that are predicted to cause growth limitation are provided for reference.

Stream	NO <sub>3</sub> <sup>-</sup> -N (µg/L)	PO <sub>4</sub> <sup>3-</sup> -P (µg/L)	Fe (µg/L)	Zn (µg/L)	Ni (µg/L)	Mo (µg/L)	Chlorophyll a (µg/cm <sup>2</sup> )
<i>Central Basin tributaries</i>							
Brandywine	138	17	26	< 2	< 5	< 5	65.8
Mill	587	82	17	< 2	< 5	< 5	21.6
Breakneck	3870	59	7.3	< 2	< 5	< 5	19.5
Fish	192	37	10	< 2	< 5	< 5	17.6
Cicada	87	19	1.3	< 2	< 5	< 5	9.0
26 streams	(33–3870)	(14–290)	(<1–45)	(<2–9)	(< 5)	(< 5)	
<i>Western Basin tributaries</i>							
Honey	2730 (260–9560) <sup>b</sup>	58 (12–152) <sup>b</sup>	29 (<1–166)	2 (<2–4)	< 5 (<5–6)	6 (<5–13)	
Lost	4220 (1520–9900)	29 (3–276)	35 (<1–167)	2 (<2–4)	< 5	5 (<5–10)	
Portage	3910 (250–9660)	91 (19–323)	19 (<1–145)	3 (<2–7)	< 5	7 (<5–15)	
Raisin	2970 (60–7900)	30 (6–66)	5.4 (<1–37)	4 (<2–23)	< 5 (<5–9)	< 5 (<5–8)	
Rock	1110 (<50–4280)	39 (9–105)	31 (<1–274)	4 (<2–41)	< 5	6 (<5–10)	
<i>Predicted limits<sup>a</sup></i>			4.4	0.5	0.6	0.03	

<sup>a</sup> Potential limiting concentrations are based on cellular quotas from marine algae (Moore et al. 2013) and measured inorganic carbon concentrations (130 mg/L). <sup>b</sup> NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> data from Western Basin tributaries is from the Heidelberg University Tributary Loading Program.

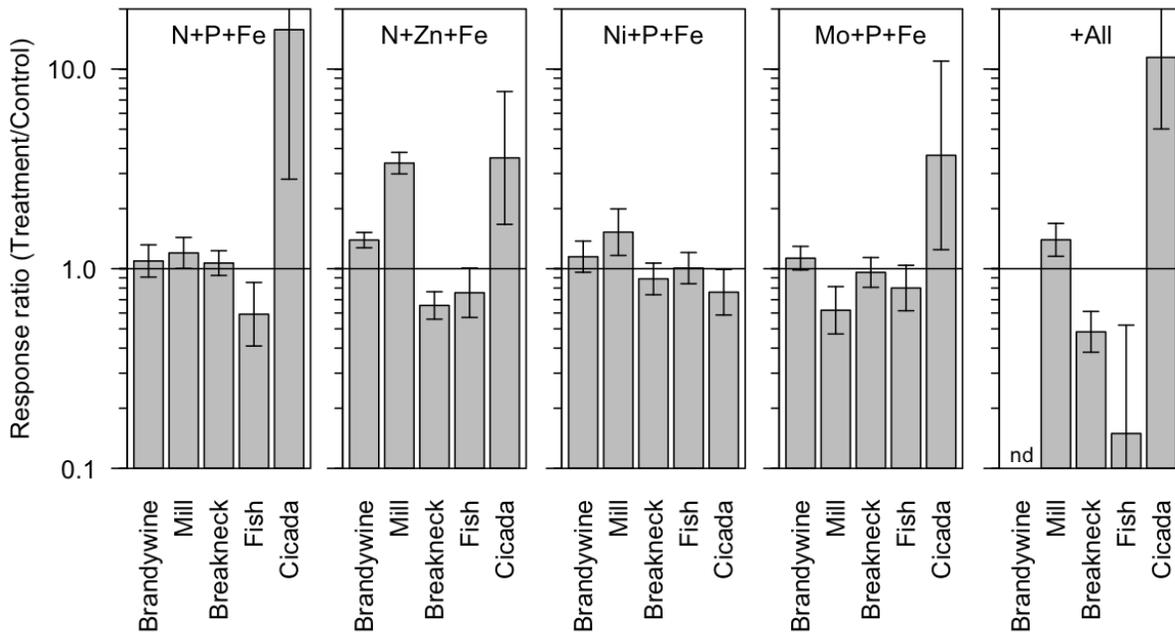
### Nutrient and trace metal limitation of primary producers

Nutrient additions performed in five streams in the Cuyahoga River watershed demonstrated that trace metals may be limiting algal growth, nutrient limitation differed between streams, and the differential response of algae to nutrient amendments was related to ambient nutrient concentrations. Single element additions (Fig. 2) had less of an effect on stimulating algal biomass when compared to multi-element treatments (Fig. 3). This supports cross-ecosystem studies that found co-limitation of primary producer growth is more common



**Figure 2.** Response of primary producer biomass in five streams to single element additions of essential nutrients (N, P, or Fe). Response ratios > 1 indicate greater biomass with nutrient amendment relative to controls and ratios < 1 had lower biomass on nutrient-amended treatment relative to controls. Error bars indicate standard errors. nd = no data.

that limitation by a single nutrient (Francoeur 2001, Elser et al. 2007). N and P only stimulated algal biomass in Brandywine Creek only, and Fe stimulated growth in Brandywine and Mill Creeks (Fig. 2). This suggests that although single nutrient limitation is less common than multi-element co-limitation, it is just as likely for a trace metal alone to be limiting as a macronutrient like N or P.



**Figure 3.** Response of primary producer biomass in five streams to multi-element additions of potentially limiting nutrients. Response ratios >1 indicate greater biomass with nutrient amendment relative to controls and ratios <1 had lower biomass on nutrient-amended treatment relative to controls. Error bars indicate standard errors. nd = no data.

For the multi-element treatments, there was evidence that three of our five student streams (Brandywine, Mill, and Cicada Creeks) all may have been co-limited by nutrients and trace metals (Fig. 3). Biofilms in Brandywine Creek exhibited stimulated growth when provided with N, Fe, and Zn together (Fig. 3 N+Zn+Fe). Zn is needed in the enzyme alkaline phosphatase, and if Zn stimulates growth, then biofilms in Brandywine may have been limited by their ability to access organic P. Biofilms in Mill Creek were co-limited by nutrients and trace metals, and growth was stimulated by Zn and Ni (Fig. 3 N+Zn+Fe and Ni+P+Fe). This also suggests greater growth when alleviating limitation to enzymes responsible for using organic P (Zn in alkaline phosphatase) and organic N (Ni in urease). Most striking was Cicada Creek, which did not respond to any of the single element additions but showed a ten-fold increase in biomass when provided with a mixture of N, P, and trace metals. Inorganic N and P in combination with trace metals caused the greatest stimulation of biomass (Fig. 3 N+P+Fe and +All), but the Ni+Zn+Fe and Mo+P+Fe treatments also caused a large increase in algal biomass. This suggests that biofilms in Cicada Creek can use organic P (Fig. 3 N+Zn+Fe) and  $N_2$  via nitrification (Fig. 3 Mo+P+Fe) as alternative nutrient sources when the appropriate trace metal is supplied. Results from both Breakneck Creek and Fish Creek indicated that these biofilms were likely not limited or co-limited by nutrients or trace metals and thus growth was limited by other factors (e.g., light, disturbance). All together, the magnitude of response from the Zn amended treatments

suggests that Zn-P co-limitation is common even in relatively nutrient rich streams. These data highlight the importance that P availability and P recycling play in driving primary production.

#### *Associated additional research*

In addition to the proposed research, an unfunded project was completed in the Central Basin tributaries. By gaining site access and visiting the 26 tributaries repeatedly through the summer, we could leverage this effort into a related undergraduate project (see Citations). In 18 of the 26 tributaries that spanned a rural–urban gradient, we placed organic substrates that differed in nitrogen content (cotton and silk strips representing low and high N, respectively) into the stream to measure rates of decomposition and microbial community composition. We found that rates of decomposition were correlated to ambient nitrate concentrations, which suggests that N availability plays an important role in decomposition. The taxonomic diversity of the microbial community was similar on the different organic materials but the composition of the community differed between substrates. These data suggest that nitrogen content in substrates and stream water is a critical driver of microbial decomposition in these diverse streams.

#### **Finding Significance**

This study addresses crucial knowledge gaps about how trace metals may limit algal production. The data show that limitation of primary production by trace metals can occur as frequently as limitation by macronutrients like N and P. Importantly, limitation by trace metals was observed in both nutrient-replete eutrophic streams and nutrient-poor oligotrophic streams. Excess nutrient inputs (mostly P) to Lake Erie have been linked to recurring seasonal planktonic HABs, and a massive amount of resources are being devoted to reducing P loading into the lake (IJC 2014). Small streams can be very efficient at slowing nutrient transport to downstream ecosystems by storing nutrients in biomass and potentially removing N and P through burial and nutrient transformations (Peterson et al. 2001, Bernot et al. 2010). This data show that trace metals (especially Zn) may be a pathway for promoting algal growth in streams, which can increase nutrient removal rates and ultimately reduce or delaying the export of macronutrients to Lake Erie. Given the extent of nutrient sources that drive HABs, management efforts that consider trace metals may be an important tool for addressing nutrient load reduction goals.

#### **References**

- Arango, C. P., J. L. Tank, L. T. Johnson, and S. K. Hamilton. 2008. Assimilatory uptake rather than nitrification and denitrification determines nitrogen removal patterns in streams of varying land use. *Limnology and Oceanography* 53:2558–2572.
- Bernot, M. J., and W. K. Dodds. 2005. Nitrogen retention, removal, and saturation in lotic ecosystems. *Ecosystems* 8:442–453.
- Bernot, M. J., D. J. Sobota, R. O. Hall, P. J. Mulholland, W. K. Dodds, J. R. Webster, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, S. V Gregory, N. B. Grimm, S. K. Hamilton, S. L. Johnson, W. H. McDowell, J. L. Meyer, B. J. Peterson, G. C. Poole, H. M. Valett, C. P. Arango, J. J. Beaulieu, A. J. Burgin, C. L. Crenshaw, A. M. Helton, L. T. Johnson, J. Merriam, B. R. Niederlehner, J. M. O'Brien, J. D. Potter, R. W. Sheibley, S. M. Thomas, and K. Wilson. 2010. Inter-regional comparison of land-use effects on stream metabolism. *Freshwater Biology* 55:1874–1890.
- Bott, T. L., J. T. Brock, A. Baattrup-Pederson, P. A. Chambers, W. K. Dodds, K. T. Himbeault, J. R. Lawrence, D. Planas, E. Snyder, and G. M. Wolfaardt. 1997. An evaluation of techniques for measuring periphyton metabolism in chambers. *Canadian Journal of*

- Fisheries and Aquatic Sciences* 725:715–725.
- Bronk, D. A., P. M. Glibert, and B. B. Ward. 1994. Nitrogen uptake, dissolved organic nitrogen release, and new production. *Science* 265:1843–1846.
- Costello, D. M., E. J. Rosi-Marshall, L. E. Shaw, M. R. Grace, and J. J. Kelly. 2016. A novel method to assess effects of chemical stressors on natural biofilm structure and function. *Freshwater Biology* 61:2129–2140.
- Elser, J. J., M. E. S. Bracken, E. E. Cleland, D. S. Gruner, W. S. Harpole, H. Hillebrand, J. T. Ngai, E. W. Seabloom, J. B. Shurin, and J. E. Smith. 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters* 10:1135–1142.
- Francoeur, S. 2001. Meta-analysis of lotic nutrient amendment experiments: detecting and quantifying subtle responses. *Journal of the North American Benthological Society* 20:358–368.
- Hecky, R. E., and P. Kilham. 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on the effects of enrichment. *Limnology and Oceanography* 33:796–822.
- [IJC] International Joint Commission. 2014. A balanced diet for Lake Erie: Reducing phosphorus loadings and harmful algal blooms.
- Johnson, L. T., J. L. Tank, and W. K. Dodds. 2009. The influence of land use on stream biofilm nutrient limitation across eight North American ecoregions. *Canadian Journal of Fisheries and Aquatic Sciences* 66:1081–1094.
- Lock, M. A., R. R. Wallace, J. W. Costerton, R. M. Ventuilo, and S. E. Chariton. 1984. River epilithon: toward a structural-functional model. *Oikos* 1:10–22.
- Moore, C. M., M. M. Mills, K. R. Arrigo, I. Berman-Frank, L. Bopp, P. W. Boyd, E. D. Galbraith, R. J. Geider, C. Guieu, S. L. Jaccard, T. D. Jickells, J. La Roche, T. M. Lenton, N. M. Mahowald, E. Maranon, I. Marinov, J. K. Moore, T. Nakatsuka, A. Oschlies, M. A. Saito, T. F. Thingstad, A. Tsuda, and O. Ulloa. 2013. Processes and patterns of oceanic nutrient limitation. *Nature Geoscience* 6:701–710.
- North, R. L., S. J. Guildford, R. E. H. Smith, S. M. Havens, and M. R. Twiss. 2007. Evidence for phosphorus, nitrogen, and iron colimitation of phytoplankton communities in Lake Erie. *Limnology and Oceanography* 52:315–328.
- Nriagu, J. O., G. Lawson, H. K. T. Wong, and V. Cheam. 1996. Dissolved trace metals in Lakes Superior, Erie, and Ontario. *Environmental Science and Technology* 30:178–187.
- Peterson, B. J., W. M. Wollheim, P. J. Mulholland, J. R. Webster, J. L. Meyer, J. L. Tank, E. Martí, W. B. Bowden, H. M. Valett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. Gregory, and D. D. Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. *Science* 292:86–90.
- Schlesinger, W. H., and E. S. Bernhardt. 2013. Biogeochemistry: An analysis of global change. 2nd edition. Academic Press, Boston, MA, USA.
- Shiller, A. M. 1997. Dissolved trace elements in the Mississippi River: Seasonal, interannual, and decadal variability. *Geochimica et Cosmochimica Acta* 61:4321–4330.
- Sobota, D. J., S. L. Johnson, S. V. Gregory, and L. R. Ashkenas. 2012. A stable isotope tracer study of the influences of adjacent land use and riparian condition on fates of nitrate in streams. *Ecosystems* 15:1–17.
- Steinman, A. D., and P. J. Mulholland. 2006. Phosphorus limitation, uptake, and turnover in benthic stream algae. Pages 187–212 *Methods in Stream Ecology*. 2nd edition.
- Vannote, R. L., G. W. Minshall, K. W. Cummins, K. W. Sedell Jr., and C. E. Cushing. 1980. River continuum concept. *Canadian Journal of Fisheries and Aquatic Sciences* 37:130–137.

# Prevention of harmful algal blooms through nutrient zero wastewater treatment using a vertical membrane bioreactor with food waste

## Basic Information

<b>Title:</b>	Prevention of harmful algal blooms through nutrient zero wastewater treatment using a vertical membrane bioreactor with food waste
<b>Project Number:</b>	2016OH4910
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	2/28/2017
<b>Funding Source:</b>	Other
<b>Congressional District:</b>	OH-001
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Wastewater, Nutrients, Treatment
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Soryong Chae, George Sorial

## Publications

1. Fangang Meng, Shaoqing Zhang, Yoontaek Oh, Zhongbo Zhou, Hang-Sik Shin, So-Ryong Chae. Fouling in membrane bioreactors: An updated review. *Water Research*, 114, 151-180, 2017 (<http://doi.org/10.1016/j.watres.2017.02.006>).
2. So-Ryong Chae. Advances and Challenges in Recycling of High Strength Organic Waste and Wastewater for Clean Water and Energy. The 252th ACS National Meeting and Exposition, Philadelphia, PA, August 21 – 25, 2016.

**Project title:** Prevention of harmful algal blooms through nutrient zero wastewater treatment using a vertical membrane bioreactor with food waste

**Project number:** 2016OH491B

**PI:** Soryong Chae, Ph.D., Assistant Professor, Department of Biomedical, Chemical, and Environmental Engineering, University of Cincinnati

**Co-PI:** George Sorial, Ph.D., Professor, Department of Biomedical, Chemical, and Environmental Engineering, University of Cincinnati

## 1. Problem and Research Objectives

Eutrophication is a key driver causing a number of pressing environmental problems including reductions in light penetration and increases in harmful algal blooms (HABs) [1]. The major factors affecting eutrophication are mineral nutrients such as nitrogen and phosphorus in municipal and industrial wastewater [2].

In Ohio's lakes and rivers, the key symptom of eutrophication is cyanobacterial blooms [3]. The increasing occurrence of HABs in fresh water due to eutrophication of surface water has become an emerging concern threatening human and environmental health because cyanobacteria, more commonly known as blue-green algae, can produce and release potent toxic compounds, known as cyanotoxins, in sources of drinking water supply [4-7].

In 1931, the first observations of adverse health effects from exposure to cyanotoxins were reported in Ohio, affecting thousands of people [8]. After that, HABs have been a major issue in Ohio. More recently (August 2014), Lake Erie encountered again a huge formation of blue-green algae producing harmful cyanotoxins. A stream of this algal bloom, which included high level of microcystins (MCs), has found its way to the Toledo's water treatment plant pipes. This required the city of Toledo to issue a "Do Not Use the Water" warning to about half million citizens [9].

In nutrient-sensitive estuaries, municipal and industrial water resource recovery facilities (WRRFs) are required to implement more advanced treatment methods in order to meet increasingly stringent effluent guidelines for nutrients. According to literature, biological nutrient removal (BNR) processes that incorporate coupled nitrification/denitrification have the potential to remove total nitrogen (TN) down to about 5 ~ 12 mg/L, in selected cases, down to 3 mg/L. The TN concentration in effluent is known as less than 10 mg/L at most inland municipal WRRFs.

In BNR processes, phosphorus removal efficiencies are very sensitive to both quantity and characteristics (especially biodegradability) of organic source as poly-P accumulating organisms (PAOs) and denitrifying microorganisms require organic matter for phosphorus release and denitrification [10]. According to the literature, approximately 5 ~ 10 mg and 8 mg of biochemical oxygen demand (BOD) are required to remove 1 mg of each nitrate nitrogen ( $\text{NO}_3\text{-N}$ ) and phosphorus, respectively [11, 12].

However, most municipal wastewater (MWW) in the U.S. has insufficient BOD content for effective nutrient removal [13]. For example, in a preliminary analysis, it was found that concentration of biodegradable organic matter in MWW entering the Mill Creek WRRF in Cincinnati (Ohio) is limited at 95.1 mg/L as BOD, but theoretically minimum 150.6 mg/L of BOD is required for complete removal of 25 mg/L TN and 3.2 mg/L TP (*data not shown*). To enhance BNR efficiency, it is necessary to provide external carbon sources such as methanol, ethanol, and acetic acid but it increases overall treatment costs of WRRFs.

On the other hand, over 250 million tons of wastes (35.2% paper, 12.1% yard trimmings, 11.7% food scraps, 11.3% plastics, 8.0% metals, etc.) generated each year in the United States. The top

two portions (*i.e.*, paper and yard waste) of the U.S. waste stream have been successfully diverted from landfills through recycling and composting efforts, with recovery rates of 50 percent and 62 percent, respectively. Piling in comparison, the food scrap recovery rate is less than 3% [14].

According to the Ohio Department of Natural Resources (ODNR), food waste (FW) comprises 15% of Ohio's valuable landfill space, but FWs negatively affect the domestic landfills because of their high leachate [15]. FW could be burned with other combustible domestic wastes for energy production. Production of dioxins is one of the main hazards associated with this process [16]. FW also can easily be reused as organic resources in the form of animal feed or compost. However, one problem associated with composting of organic-rich wastes is the production of odor (mainly ammonia) and large quantities of leachate [17]. Therefore, there is a *critical need* in developing engineering solutions for prevention of HABs and sustainable recycling of FW.

Due to the continuously increasing occurrence of HABs in Ohio's lakes and rivers and the inefficient or impractical technologies for the elimination of nutrients such as nitrogen and phosphorus, there is a critical need to develop an effective solution for a satisfactory removal of nutrients (especially phosphorus) from wastewater sources in order to achieve clean and safe drinking water supplies and protect human health.

The main objective of this project is to develop and optimize an engineering process for the efficient removal of nutrients from municipal wastewater (MWW). A bench-scale vertical membrane bioreactor (VMBR) was optimized for simultaneous removal of nitrogen and phosphorus with soluble organic compounds, which will be produced from FW using an ultrasound-assisted anaerobic fermenter for enhanced phosphorus removal. Through this project, we expect to have developed and optimized engineering solutions for the treatment of MWW and FW to prevent HABs.

## 2. Methodology

### 2.1 Anaerobic fermentation of food waste with ultrasound

The main component of FW is cellulosic organic compounds such as cellulose, lignin, hemicelluloses, and starch, while the remaining small parts are lipids, proteins, and inorganic [18]. In a preliminary test, FW (chemical oxygen demand, COD = 121.7 g/L) from campus dining halls at the University of Cincinnati (UC) was converted to CFW in an anaerobic fermenter operated at 35 °C and 12 hr hydraulic retention time (HRT) at pH 5~5.5. **Figure 1** shows a process flow diagram of the anaerobic fermentation system for production of condensate of FW (CFW).



**Figure 1.** Schematic diagram of an anaerobic fermentation process for production of CFW.

**Table 1** summarizes some of the key parameters associated with the CFW, which contains high concentration of VFAs (> 9,000 mg/L as COD) that is composed of 1.5% lactic acid, 80% acetic acid, 10% propionic acid, and 8.5% butyric acid, which could be effectively used as carbon

sources for nutrient removal in BNR processes. However, the conversion rate of the COD of FW to soluble COD in the CFW is very limited by 17.5% (= 21.3/121.7 x 100%) by the anaerobic fermenter, indicating there is great potential for optimization and upgrade of the anaerobic treatment.

**Table 1.** Characteristics of the CFW produced from an anaerobic fermenter.

Item	Typical concentration	Unit
Soluble COD	21,300	mg/L
Total solids (TS)	< 10	mg/L
Total nitrogen (TN)	103	mg/L
Total phosphorus (TP)	25	mg/L
VFAs as COD	9,100	mg/L

In this study, we applied an ultrasound to improve conversion efficiency of cellulosic organic compounds in FW into easily biodegradable organic substances (*i.e.*, VFAs or BOD). Ultrasonic irradiation (also known as “Sonication” or “Sonolysis”) causes cavitation phenomena leading to the production of free radicals. The phenomenon of cavitation could possibly contribute towards enhancement of the kinetics and yield of the reaction.

Ultrasonic waves produce cavitation bubbles in liquid solution. After several compression cycles, the cavitation bubbles collapse violently and adiabatically with extremely high temperature over 5000 °C and pressures of 500 atmospheres [19]. As a result, organic compounds present near bubble/water interface can undergo thermal decomposition, and/or secondary reactions take place between solute molecules and the reactive radicals such as H• and •OH. The formation of free radicals during ultrasonic irradiation can be explained from the following Eqs. (1) – (3) in the absence of oxygen [20] where “)))” refers to the application of ultrasound:



We hypothesize that the combination of ultrasound and anaerobic fermentation will achieve a higher reaction rate and a lower energy input for the destruction of organic compounds in FW than conventional anaerobic fermentation by (i) producing hydroxyl radicals and (ii) promoting decomposition of the reaction intermediate of recalcitrant organic compounds such as cellulose, lignin, and hemicelluloses in FW.

In this study, an ultrasound horn (20 kHz, 450 Digital Sonifier, Branson Ultrasonics, U.S.A) will be directly applied between the Step 3 and the Step 4 shown in **Figure 1** to increase conversion rate of organic compounds in FW to BOD. We evaluated ultrasound duration (*i.e.*, 0, 1, 2, 4, and 8 hr) on the conversion efficiency of total COD to SCOD and VFAs.

## 2.2 A bench-scale vertical membrane bioreactor

A bench-scale VMBR (treatment capacity = 10 L/day at HRT = 8 hr) with anoxic and oxic zones in one reactor was operated over 4 months with synthetic wastewater (**Table 2**). To improve nutrient removal efficiency of the bench-scale VMBR, the CFW that was produced from the anaerobic fermenter with 8 hr sonication, was added into influent in Run 2 and Run 3 (**Table 3**).

**Table 2.** Characteristic of synthetic wastewater.

Item	Chemical formula	Concentration (mg/L)
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	150 (as COD)
Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	30 (as N)
Potassium phosphate	KH <sub>2</sub> PO <sub>4</sub>	6 (as P)
Sodium bicarbonate	NaHCO <sub>3</sub>	200 (as CaCO <sub>3</sub> )
Calcium chloride	CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.50
Cobalt chloride	CoCl <sub>2</sub> ·6H <sub>2</sub> O	0.35
Cupric sulfate	Cu SO <sub>4</sub> ·5H <sub>2</sub> O	0.15
Ferric chloride anhydrous	FeCl <sub>3</sub>	0.80
Magnesium sulfate	Mg SO <sub>4</sub> ·7H <sub>2</sub> O	0.34
Manganese chloride	MnCl <sub>2</sub> ·4H <sub>2</sub> O	0.50
Sodium molybdate dihydrate	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	0.20
Yeast extract	-	10
Zinc sulfate	ZnSO <sub>4</sub> ·5H <sub>2</sub> O	0.55

**Table 3.** Operation conditions of the bench-scale VMBR.

Run	Period	Synthetic wastewater (v/v, %)	CFW with 8 hr sonication (v/v, %)	SCOD concentration in influent (mg/L)
1	1 ~ 60 days	100	0	150.0
2	61 ~ 90 days	99.5	0.5	377.8
3	91 ~ 125 days	99.0	1.0	605.5

### 2.3 Analysis of membrane fouling

To determine the effects of the CFW on changes in membrane resistance due to membrane fouling, the resistance-in-series model was used to analyze membrane fouling resistances with various CFW mixing ratios (**Table 3**), which describes the permeate flux - transmembrane pressure (TMP) relationship over the entire domain of pressure as described in the previous study [21]. Based on the model, the permeate flux on the applied TMP can be described by Darcy's law as Eq. (4):

$$J_v = \frac{1}{A} \frac{dV}{dt} = \frac{\Delta P}{\mu R_t} \quad (4)$$

where  $J_v$  is the permeate flux (m<sup>3</sup>/m<sup>2</sup>/s),  $V$  is the total volume of permeate (m<sup>3</sup>),  $A$  is the membrane area (m<sup>2</sup>),  $\Delta P$  is the TMP (Pa),  $\mu$  is the dynamic viscosity of permeate (Pa·s), and  $R_t$  is the total membrane resistance (m<sup>-1</sup>).

### 2.4 Characterization of food waste and wastewater

Concentrations of various ions such as NO<sub>2</sub>-N, NO<sub>3</sub>-N, and ortho-P were analyzed using ion chromatography (IC) (Dionex DX-120, U.S.A) after filtering with a 0.45 μm membrane filter (ADVANTEC MFS Inc., Dublin, CA, U.S.A). Temperature and pH were measured using temperature and pH electrodes connected with a pH meter (Orion Model 420A, Orion Research Inc., U.S.A). Concentrations of COD, BOD, total solid (TS), TN, and TP of both FW and CFW were measured according to *Standard Methods* [22]. All experiments of this study were performed at least three times. Analysis of variance (ANOVA) was applied for the statistical analysis and differences from controls was considered significant when  $p \leq 0.05$ .

### 3. Principal Findings and Results

#### 3.1 Changes in characteristics of the CFW by ultrasound

**Table 4** shows characteristics of CFW that was produced from the anaerobic fermenter. To improve the conversion of organic matter to SCOD, ultrasound has been used between the Step 3 and the Step 4 (**Figure 1**). As sonication time increased from 0 to 8 hr, concentrations of SCOD and VFA in the CFW increased by approximately 115% and 27%, respectively. From these results, it could be concluded that ultrasound was an efficient technology to convert organic matter in FW to soluble organic matter. However, it is required to optimize the anaerobic fermenter to increase production of VFA from the soluble organic matter.

**Table 4.** Effects of sonication on characteristics of the CFW.

Sonication time (hr)	SCOD concentration (mg/L)	VFA concentration (mg/L)	Change in SCOD	Change in VFA
0	21,300	9,100	-	-
1	22,100	9,236	+ 3.8%	+1.5
2	23,400	9,309	+9.9%	+2.3
4	36,600	10,283	+71.8%	+13.0
8	45,700	11,577	+114.5%	+27.2

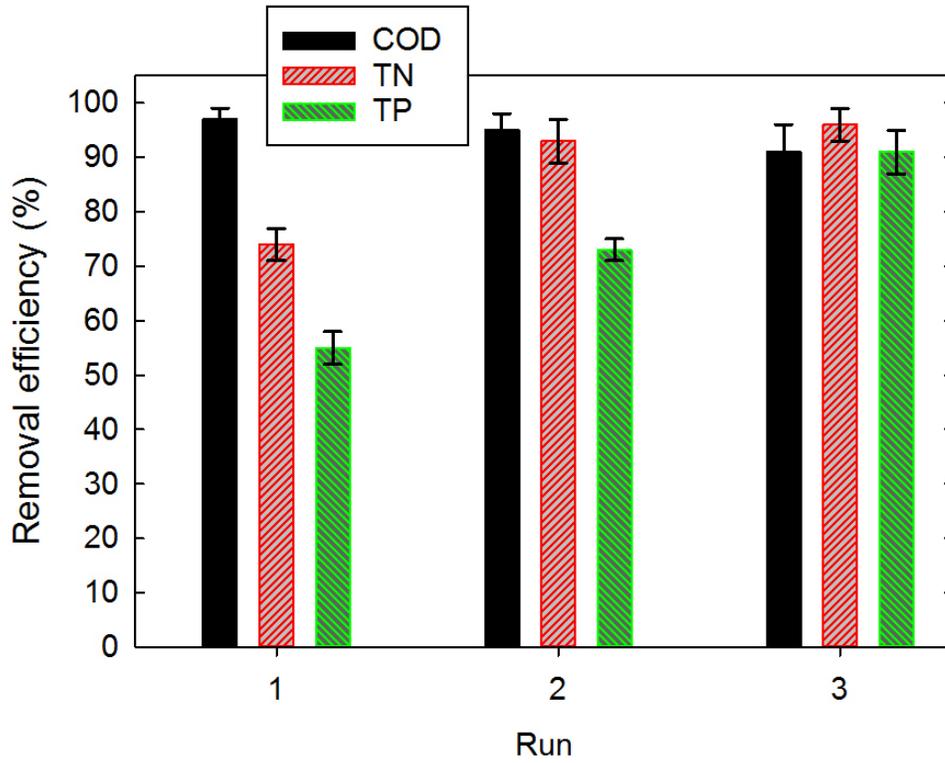
#### 3.2 Effects of the CFW on removal efficiency of nutrients and membrane fouling in a bench-scale VMBR

In BNR processes, nutrient removal efficiency highly depends on quantity and characteristics of organic source. However, most MWW contains a low carbon-to-nitrogen (C/N) ratio of less than 5 that is insufficient for nutrient removal. For example, 4.2 g COD/g N was required for total-nitrogen removal, including assimilation, when glucose is the carbon source [23]. Since a part of the COD in a combined nitrification–denitrification process was oxidized by oxygen, the COD/N requirement in practice was higher, with typical values lying in the range of 5 ~ 10 g COD/g N [23].

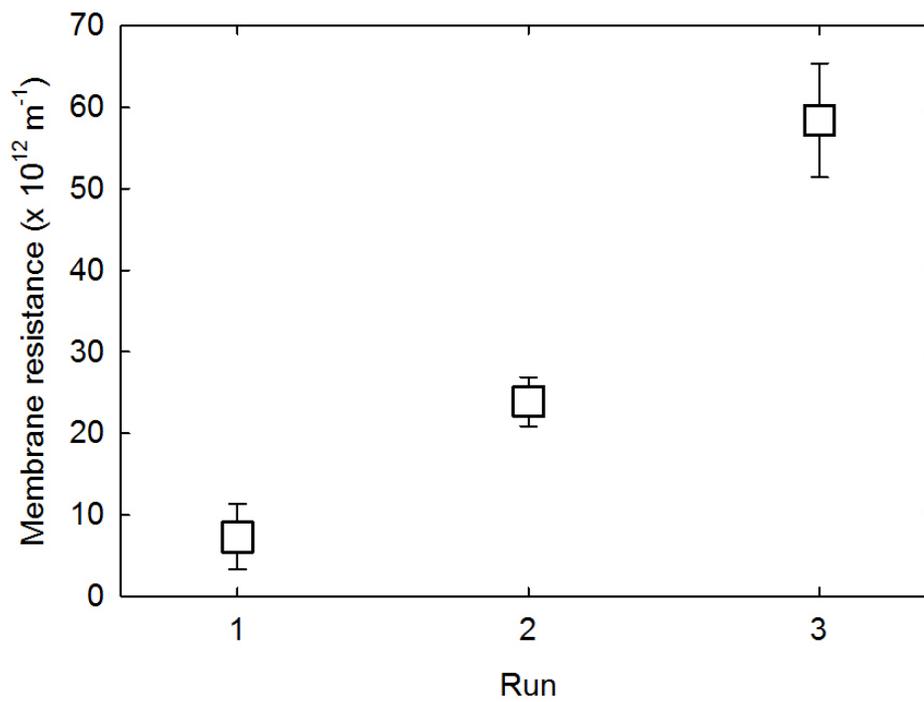
In our previous study, it was found that when the readily biodegradable COD was depleted, both denitrification and phosphorus removal rates significantly reduced [24]. In this situation, acetic acid and methanol are generally recommended as external carbon sources, but these increase operating cost and could decrease pH of the system [25].

In general, FW has relatively high COD content with high C/N ratio over 20, suggesting its potential for nutrient removal when mixed with influent. In this study, we aimed to improve removal efficiencies of nutrients in the VMBR by supplementing the CFW. As shown in **Figure 2**, typical removal efficiencies of nitrogen and phosphorus by the VMBR with synthetic wastewater were 74% and 55%, respectively. As the SCOD concentration increased from 150 to 605.5 mg/L by adding the CFW, removal efficiencies of nitrogen and phosphorus significantly increased up to 96% and 91%, respectively.

The VMBR showed good performance in removing nutrients from low organic-strength wastewater when the CFW was added as an external carbon source. However, the supplemented CFW increased COD concentration in the effluent (**Figure 2**) and also membrane resistance (**Figure 3**). Therefore, there is a critical need in optimizing the ultrasound and anaerobic fermenter for efficient production of VFAs from SCOD to improve BNR performance and to mitigate membrane fouling in MBR.



**Figure 2.** Changes in removal efficiencies of COD, TN and TP during the experimental period.



**Figure 3.** Changes in membrane resistance during the experimental period.

#### **4. Finding Significance**

HABs have a significant impact on drinking water quality, fish and animal habitat as well as ecosystem services. The need to reduce anthropogenic nutrient inputs to aquatic ecosystems in order to protect drinking-water supplies and to reduce eutrophication, including the proliferation of HABs and “dead zones” in coastal marine ecosystems has been widely recognized. BNR is one of the most cost-effective treatment technologies for nutrient removal from MWW. However, there is clear a gap in knowledge between the enhanced biological phosphorus removal (EBPR) mechanism and potential applications of renewable carbon sources such as FW for effective nutrient removal. In this study, we report that the VMBR showed good performance in removing nutrients (over 90%) with low organic-strength wastewater when the CFW, which was produced from an anaerobic fermenter with ultrasound, was added as an external carbon source.

The results provide a fundamental understanding of (i) the effects of ultrasound on the fate and conversion of recalcitrant organic compounds in FW, and (ii) the effects of organic matter originated from FW on the EBPR efficiency and membrane fouling in MBR. Such investigations are critical for the development of eco-friendly management of FW and the enhancement of biological phosphorus removal activity in BNR systems to protect watersheds in Ohio from HABs. Also, it will allow for development of novel engineering solutions for the production of easily degradable organic matter that will eventually increase nutrient removal efficiency in BNR systems and also reduce HABs’ risks to public health and the environment.

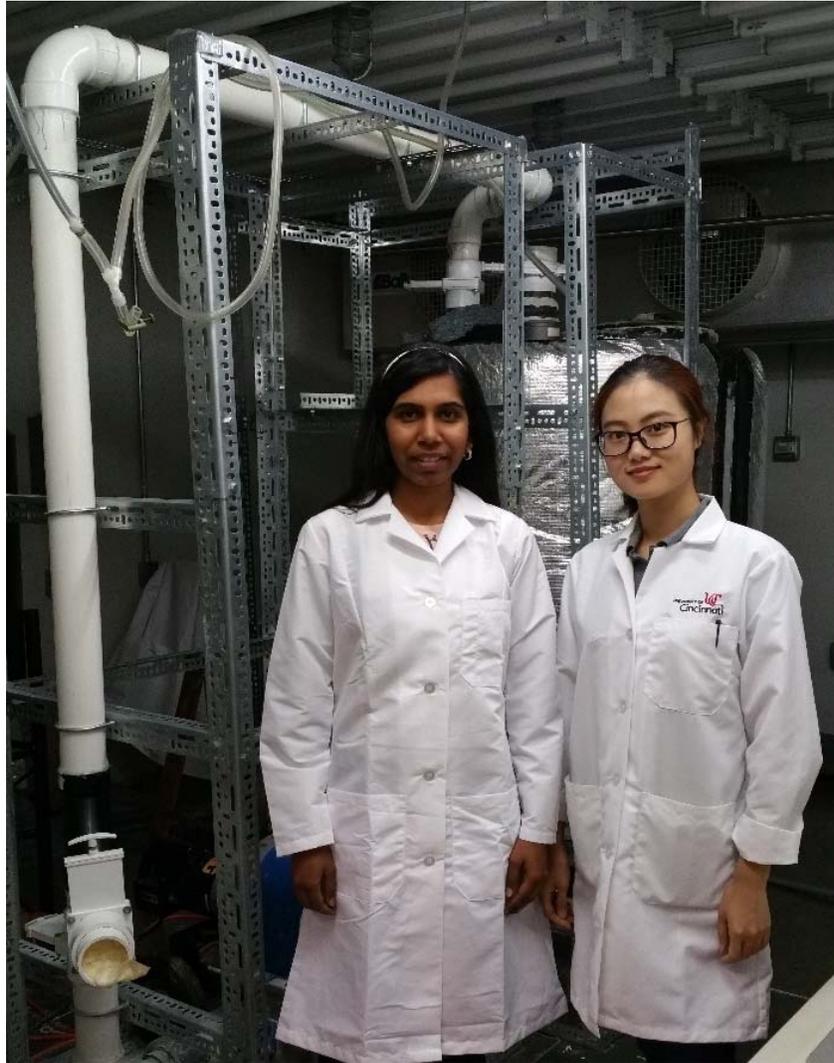
#### **5. Publication citations (all journal articles, proceedings and presentations at conferences)**

- 1) Fangang Meng, Shaoqing Zhang, Yoontaek Oh, Zhongbo Zhou, Hang-Sik Shin, So-Ryong Chae. Fouling in membrane bioreactors: An updated review. *Water Research*, 114, 151-180, 2017 (<http://doi.org/10.1016/j.watres.2017.02.006>).
- 2) So-Ryong Chae. Advances and Challenges in Recycling of High Strength Organic Waste and Wastewater for Clean Water and Energy. The 252th ACS National Meeting and Exposition, Philadelphia, PA, August 21 – 25, 2016.

## References

1. Mesfioui, R.; Love, N. G.; Bronk, D. A.; Mulholland, M. R.; Hatcher, P. G., Reactivity and chemical characterization of effluent organic nitrogen from wastewater treatment plants determined by Fourier transform ion cyclotron resonance mass spectrometry. *Water Res.*, 46(3), 622-634, 2012.
2. Correll, D. L., The Role of Phosphorus in the Eutrophication of Receiving Waters: A Review. *Journal of Environmental Quality*, 27(2), 261-266, 1998.
3. Schindler, D. W., Eutrophication and Recovery in Experimental Lakes: Implications for Lake Management. *Science*, 184(4139), 897-899, 1974.
4. Chorus, I.; Falconer, I. R.; Salas, H. J.; Bartram, J., Health risks caused by freshwater cyanobacteria in recreational waters. *J. Toxicol. Env. Health-Pt b-Crit. Rev.*, 3(4), 323-347, 2000.
5. Vasconcelos, V. M.; Sivonen, K.; Evans, W. R.; Carmichael, W. W.; Namikoshi, M., Hepatotoxic microcystin diversity in cyanobacterial blooms collected in Portuguese freshwaters. *Water Res.*, 30(10), 2377-2384, 1996.
6. Pitois, S.; Jackson, M. H.; Wood, B. J. B., Sources of the eutrophication problems associated with toxic algae: An overview. *J. Environ. Health*, 64(5), 25-32, 2001.
7. Kotak, B. G.; Lam, A. K. Y.; Prepas, E. E.; Kenefick, S. L.; Hrudey, S. E., VARIABILITY OF THE HEPATOTOXIN MICROCYSTIN-LR IN HYPEREUTROPHIC DRINKING-WATER LAKES. *J. Phycol.*, 31(2), 248-263, 1995.
8. Zaccaroni, A.; Scaravelli, D., Toxicity of Fresh Water Algal Toxins to Humans and Animals. In *Algal Toxins: Nature, Occurrence, Effect and Detection*, Evangelista, V.; Barsanti, L.; Frassanito, A.; Passarelli, V.; Gualtieri, P., Eds. Springer Netherlands: 2008; pp 45-89.
9. Frankel, T. C., The toxin that shut off Toledo's water? The feds don't make you test for it. (<http://www.washingtonpost.com/news/storyline/wp/2014/08/11/watching-toledos-toxic-water-troubles-with-a-wary-eye-and-few-regulations/>). *The Washington Post* 2014.
10. Smolders, G. J. F.; van der Meij, J.; van Loosdrecht, M. C. M.; Heijnen, J. J., Model of the anaerobic metabolism of the biological phosphorus removal process: Stoichiometry and pH influence. *Biotechnol. Bioeng.*, 43(6), 461-470, 1994.
11. Comeau, Y.; Hall, K. J.; Hancock, R. E. W.; Oldham, W. K., BIOCHEMICAL-MODEL FOR ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL. *Water Res.*, 20(12), 1511-1521, 1986.
12. Henze, M., CAPABILITIES OF BIOLOGICAL NITROGEN REMOVAL PROCESSES FROM WASTE-WATER. *Water Sci. Technol.*, 23(4-6), 669-679, 1991.
13. Villaverde, S., Recent developments on biological nutrient removal processes for wastewater treatment. *Re/Views in Environmental Science & Bio/Technology*, 3(2), 171-183, 2004.
14. Ohio-EPA, [http://wwwapp.epa.ohio.gov/ocapp/food\\_scrap/index.html](http://wwwapp.epa.ohio.gov/ocapp/food_scrap/index.html)

15. Misi, S. N.; Forster, C. F., Semi-Continuous Anaerobic Co-Digestion of Agro-Wastes. *Environmental Technology*, 23(4), 445-451, 2002.
16. Katami, T.; Yasuhara, A.; Shibamoto, T., Formation of Dioxins from Incineration of Foods Found in Domestic Garbage. *Environmental Science & Technology*, 38(4), 1062-1065, 2004.
17. Lin, C. S. K.; Pfaltzgraff, L. A.; Herrero-Davila, L.; Mubofu, E. B.; Abderrahim, S.; Clark, J. H.; Koutinas, A. A.; Kopsahelis, N.; Stamatelatou, K.; Dickson, F.; Thankappan, S.; Mohamed, Z.; Brocklesby, R.; Luque, R., Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective. *Energy & Environmental Science*, 6(2), 426-464, 2013.
18. ElMekawy, A.; Diels, L.; De Wever, H.; Pant, D., Valorization of Cereal Based Biorefinery Byproducts: Reality and Expectations. *Environmental Science & Technology*, 47(16), 9014-9027, 2013.
19. Suslick, K. S., Sonochemistry. *Science*, 247(4949), 1439-1445, 1990.
20. Beckett, M. A.; Hua, I., Elucidation of the 1,4-Dioxane Decomposition Pathway at Discrete Ultrasonic Frequencies. *Environmental Science & Technology*, 34(18), 3944-3953, 2000.
21. Chae, S. R.; Ahn, Y. T.; Kang, S. T.; Shin, H. S., Mitigated membrane fouling in a vertical submerged membrane bioreactor (VSMBR). *J. Membr. Sci.*, 280(1-2), 572-581, 2006.
22. APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, 18th ed. Washington, DC. 1992.
23. Henze, M., Capabilities of Biological Nitrogen Removal Processes from Wastewater. *Water Science and Technology*, 23(4-6), 669-679, 1991.
24. Chae, S.-R.; Jeong, H.-S.; Lim, J.-L.; Kang, S.-T.; Shin, H.-S.; Paik, B.-C.; Youn, J.-H., Behaviors of Intercellular Materials and Nutrients in Biological Nutrient Removal Process Supplied with Domestic Wastewater and Food Waste. *Water Environment Research*, 76(3), 272-279, 2004.
25. Grabińska-Loniewska, A., Biocenosis diversity and denitrification efficiency. *Water Research*, 25(12), 1575-1582, 1991.



A pilot-scale anaerobic fermenter, which was operated by Ms. Brindha Murugesan, M.S. student (left) and Ms. Jiong Gao, Ph.D. student (right) for production of soluble organic matter from food waste. By supplementing soluble organic matter into wastewater, nutrient removal efficiency of a membrane bioreactor significantly improved.

# Determining components for a phosphorus interceptor to reduce harmful algal blooms in the western Lake Erie basin

## Basic Information

<b>Title:</b>	Determining components for a phosphorus interceptor to reduce harmful algal blooms in the western Lake Erie basin
<b>Project Number:</b>	2016OH5000
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	2/28/2018
<b>Funding Source:</b>	Other
<b>Congressional District:</b>	OH-009
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Nutrients, Non Point Pollution, Agriculture
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Daryl F Dwyer

## Publication

1. Bartos, A., D. F. Dwyer, R. W. Jackwood. September 2016. Effectiveness of Natural and Industrial Byproducts to Adsorb Dissolved Phosphorus as a Water Quality Management Technique in the Maumee River Watershed". Presented as a poster at the University of Toledo Undergraduate Research Symposium, Toledo, OH.

**Title:** Determining Components for a Phosphorus Interceptor to Reduce Harmful Algal Blooms in the Western Lake Erie Basin

**Agency:** Water Resources Research Institute

**Program:** Ohio Water Resources Center

**PI:** Daryl Dwyer

## 1. Problem

Harmful algal blooms (HABs) have been observed annually in the western basin of Lake Erie and have increased in size and severity since 2003. *Microcystis aeruginosa* is the dominant species in HABs and produces a hepatotoxin, microcystin, that is harmful to human and environmental health. Elevated levels of microcystin were detected in Toledo's drinking water in August 2014 and caused the city to issue a "do not drink" advisory leaving approximately 500,000 citizens without drinkable tap water.

The occurrence and growth of HABs in Lake Erie is driven by a variety of factors including excessive nutrient transport to surface waters, climate change, and geomorphology of the lake. The presence of excess dissolved reactive phosphorus (DRP) is the primary cause for the growth of HABs. The Maumee River contributes approximately 50% of the phosphorus that reaches Lake Erie with an estimated 85% of the phosphorus derived from agricultural fertilizers and manures. The International Joint Commission set a goal of 40% reduction of phosphorus inputs to Lake Erie from the Maumee River as a potential means to significantly reduce the severity of HAB growth.

Phosphorus in surface water runoff is a combination of particulate and dissolved reactive phosphorus (DRP); whereas, phosphorus derived from tile drainage is almost entirely DRP. We set out to determine a means to capture DRP from tile drainage water that bypasses agricultural field strips. This study investigates the use of calcium-based phosphorus sorbent materials (PSMs) that are incorporated into what we refer to as "nutrient interceptors" with the goal of removing DRP from tile drainage water prior to the water entering drainage ditches and ultimately Lake Erie.

Research Objectives:

- (1) Laboratory studies will be used to determine the sorbent-rate, capacity and hydraulic retention time of selected PSMs for use within the nutrient interceptors.
- (2) The nutrient interceptors will be tested for removal of DRP from agricultural field drainage water during a rain event to quantify the reduction of DRP per volume water.

## 2. Methodology

Photos of the experimental set-ups are presented at the end of the written report. A number of PSMs were chosen according to their availability and calcium content and tested to determine the rate of sorption of DRP. Based on the rate of sorption, the most efficient PSM was selected for a laboratory study using flow-through columns and finally field-scale experiments with nutrient interceptors. The chosen PSMs were dried, spent lime obtained from a water treatment plant, limestone gravel, broken and sieved zebra mussel shells in three size fractions (small: < 850  $\mu\text{m}$ ; medium: between 850  $\mu\text{m}$  and 2 mm; large: >2mm), sand collected from the Stranahan arboretum, and lab-grade sand.

### *Phosphorus Sorption Rate*

Phosphorus sorption rate was measured by adding a PSM to a solution of DRP in an Erlenmeyer flask and shaking the sample for 24 hr with periodic measurements. Dried PSM (2 g) was added to 150 mL Erlenmeyer flasks. Each flask then received 30.0 mL of a matrix solution (0.5 mg P/L, 1.0 mg P/L, and 5.0 mg P/L) and placed on the shaker table and shaken at 120 rpm; a 1 mL sample was taken at 1 min, 10 min, 30 min, 60 min, 5 h, and 24 h time periods. The samples were placed in a centrifuge tube and centrifuged for 5 minutes or until the material was fully separated from the solution. The samples were then refrigerated until tested. All PSMs were treated with each matrix solution in triplicate. The samples were analyzed for the concentration of phosphorus using the ascorbic acid colorimetry assay.

### *Flow-through Column Experiments*

Spent lime exhibited the highest rate of phosphorus sorption and was the chosen PSM for flow-through column experiments. Laboratory grade sand was used as a comparative control. For the experiments, the spent lime (5 g) was mixed evenly with laboratory grade sand (95 g), presumably free of phosphorus. This mixture allowed the phosphorus solution to flow through the column unhindered. Six glass columns, 3.8 cm x 20 cm, were placed in a stand and individually connected to a peristaltic pump. The test material was packed into the columns; a phosphorus solution (1.0 mg/L) was pumped to the top of the column and allowed to flow through the PSM. A 45  $\mu\text{m}$  filter was placed at the bottom of each column to prevent passage of the sand or water treatment residuals out of the columns and into collection flasks. The phosphorus concentrations in the exiting water solutions were measured at thirty minutes intervals in 5 mL samples.

### Flow-through Nutrient Interceptors

The water treatment spent lime exhibited promising sorption capacity using the above controlled laboratory settings. Performance was therefore measured at a scale similar to that present for agriculture drain tile flow. A nutrient interceptor was constructed for this purpose using two 19 L open top buckets, two ½” bulkhead fittings, and a 5 micron industrial filter. Water treatment residuals and laboratory grade sand at a 1:6 volumetric ratio were mixed evenly as above and two kilograms of the mixture were placed into the interceptor. A 0.5-mg/L DRP solution was passed through the interceptor using a 1-meter head for 3.5 minutes; during this time, approximately 11 liters of phosphorus solution flowed through the interceptor at a rate of 3.14 liters/minute. Inflow and outflow samples of solution were taken every 30 seconds in a 10 mL test tube. In total, 8 samples were taken for both inflow and outflow, which were then assayed for phosphorus concentration.

## 2. Principal Findings and Significance

### Phosphorus Sorption Rate

For the majority of PSMs, phosphorus sorption increased over time and at a rate that increased with increasing concentrations within the solutions. The water treatment spent lime achieved maximum sorption within 1 minute of contact with solution. The results for two PSM is depicted in Figure 1: note that sorption with zebra mussel shells is comparatively slower; the spent lime has a faster sorption rate and reaches capacity in less than one minute.

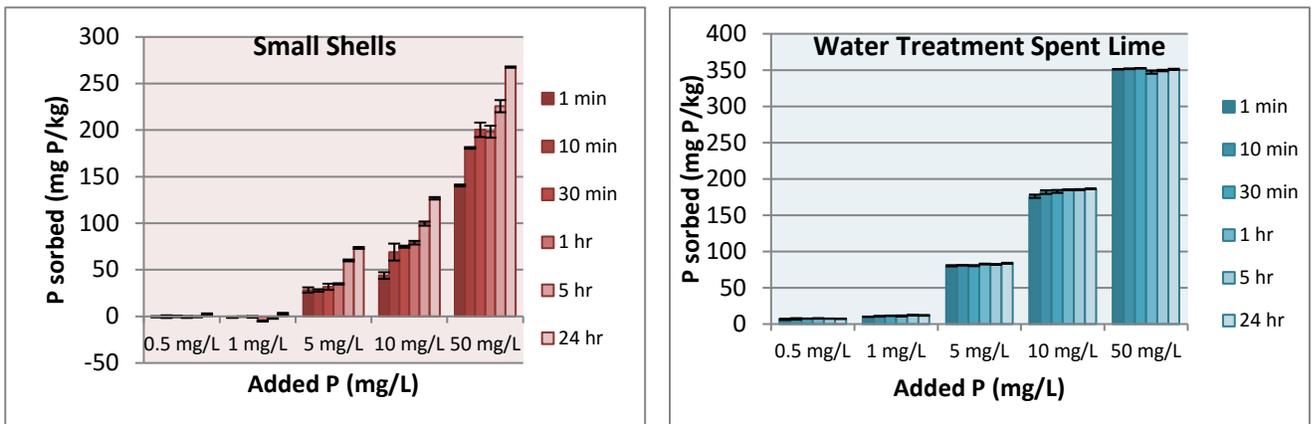


Figure 1. Phosphorus sorption (mg/kg) of small pulverized mussel shells (left) and water treatment spent lime (right) at various phosphorus concentrations and timeframes.

### Flow-through Columns

Water treatment spent lime was mixed with sand in a flow-through experiment to determine the sorption capacity of the spent lime. Figure 2 depicts a flow-through data set of phosphorus sorption as a 1.0 mg/L solution of phosphorus flows through a spent lime and sand mixture. Sorption of phosphorus reached a maximum at 0.4 to 0.5 mg P sorbed to 1 gram of PSM. These values for carrying capacity will be utilized to design full scale nutrient interceptors for agricultural drain tiles.

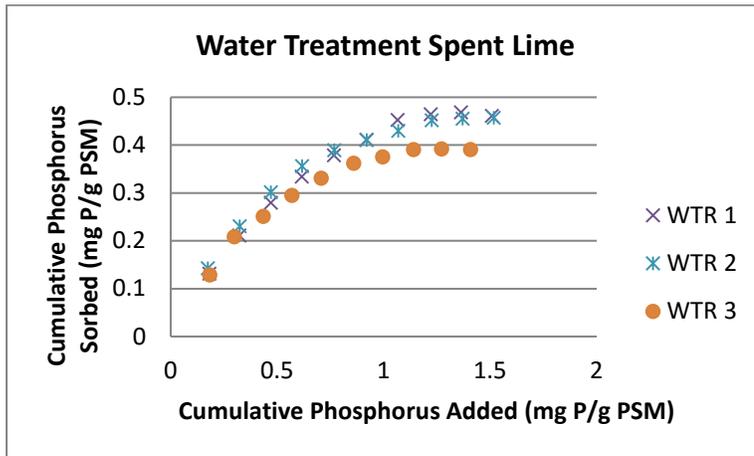


Figure 2. Sorption curve of spent lime in a flow-through experiment.

### Flow-through Nutrient Interceptors

To date, the nutrient interceptor has been designed, constructed, and tested. Data have been collected for a preliminary laboratory experiment to ensure that the system was structurally sound. To date, the nutrient interceptor was used to treat tile drainage water for a single replicate using a farm field in the City of Oregon, OH. Data have yet to be analyzed; we will continue to test the effectiveness of the nutrient interceptor in the coming weeks with additional replicates.

## Photos



\*Flow-through experimental setup



\*Flow-through experimental setup and PSM in columns



\*Sorption rate experimental setup/shaker table.

# Improved Estimates of Peak Water Demand in Buildings: Implications for Water-Energy Savings

## Basic Information

<b>Title:</b>	Improved Estimates of Peak Water Demand in Buildings: Implications for Water-Energy Savings
<b>Project Number:</b>	2016OH506O
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	12/31/2017
<b>Funding Source:</b>	Other
<b>Congressional District:</b>	1
<b>Research Category:</b>	Engineering
<b>Focus Category:</b>	Models, Water Supply, Conservation
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Steve Buchberger

## Publications

1. Omaghomi, T. and Buchberger, S. G. (February, 2017) Residential Water Demand Calculator Poster presentation in 2017 Graduate Student Expo & Poster Forum, Cincinnati, OH
2. Omaghomi, T. and Buchberger, S. G. (2017) Residential Water Demand Calculator Poster presentation in the 13th Annual OVALS Conference: Water Technology: The Wave of the Future, Cincinnati, OH

## Improved Estimates of Peak Water Demand in Buildings: Implications for Water-Energy Savings

Steven Buchberger and Toritseju Omaghomi  
University of Cincinnati

### Problem

Water use in buildings is a random process. Working for the National Bureau of Standards, Dr. Roy Hunter (1940) showed how the binomial probability distribution could be used to provide theoretically rigorous estimates of the 99th percentile for peak (hot and cold) water demand in buildings. Hunter's design curve has been incorporated into the Uniform Plumbing Code and adopted by water agencies across Ohio, throughout the US and around the world. Hunter's curve may soon be embedded into newly emerging digital Building Information Modeling (BIM) technologies for visualizing and designing buildings of the 21st century.

What then is the problem? Over the years, the performance of water fixtures and consumer demands for treated water have changed markedly. Today's emphasis on water efficient fixtures in net zero buildings is far removed from assumptions inherent in Hunter's original 1940 analysis. It is now widely recognized that Hunter's iconic design curve often significantly over-estimates peak demand for hot and cold indoor water (AWWA, 2004). This over-prediction does not signal a limitation in Hunter's theoretical method. Rather, it reflects incorrect application by zealous practitioners who have pushed the curve beyond its intended use. To compensate, ASHRAE and other professional organizations have generated a myriad of "modified" Hunter's curves to fix design discrepancies (Armstrong Hot Water Group, 2014). Unfortunately, this makeshift approach is inconsistent and subjective. Further, it does not provide a firm foundation for designing and constructing the next generation of smart high efficiency (water / energy) homes and buildings that will populate cities of the future.

According to the US Energy Information Administration (2015), energy consumption in the residential sector accounted for 22 percent of the total energy consumed in the US in 2014. Heating water is the most energy intensive process of the water-use cycle using up to 25 percent of the total energy consumed in residential buildings (Vieira *et al.* 2014; Siddiqi and Fletcher 2015). Yet there has been scant attention on the water-energy nexus in the residential sector. Home water use is linked inextricably to home energy use and vice versa. Premise plumbing is the epitome of the water-energy nexus on a local scale. Inaccurate design guidance for indoor water supply systems (i.e., premise plumbing) has far reaching consequences for

today's new generation of water conserving net zero energy buildings. As a result, obsolete water supply design guidelines produce over-sized plumbing systems and improperly-sized water meters, heaters and softeners. This, in turn, leads to a myriad of water – energy problems including: [ i ] inflated construction costs, [ ii ] inaccurate water monitoring and billing, [ iii ] wasted energy and lost water through inefficient water heating, and [ iv ] increased potential health hazards from risk of microbial contamination (*Legionella*) (ANSI/ASHRAE 2015). These issues can adversely impact owners, residents, and users of facilities throughout the public and private sectors. What is needed today is a 21st century version of the Hunter's curve for premise plumbing and an equivalent aid for residential energy consumption, especially as related to hot water use. Our research is a big step in this direction.

## **Research Objectives**

As outlined in the previous section, our primary objectives are twofold. First, we will develop and demonstrate a theoretically rigorous updated procedure for modeling and simulating realistic estimates of peak hot and cold water demands in a wide variety of end-use scenarios, but with special focus on the residential sector. Second, we will compare building energy consumption associated with hot water use for two cases. Case 1 will reflect current building water supply systems sized using the conventional Hunter's curve. Case 2 will be based on a building water supply system sized using the new water demand model. We expect the energy cost associated with hot water use for case 2 to be significantly lower than the corresponding energy cost for case 1.

## **Methodology**

### **Peak Water Demand**

Hunter viewed water fixtures as binary devices. They were either on or off, busy or idle. He recognized that the binomial probability model described the distribution of busy fixtures in a building. While developing his model, Hunter focused on large buildings and assumed peak periods with congested use; these conditions are not like peak water use in residential buildings. In our previous research, the peak hour probability of a busy fixture was investigated in residential homes with efficient fixtures. As shown in Table 1, the results reveal that individual fixtures are busy less than six percent (6%) of the time even during peak hour of use.

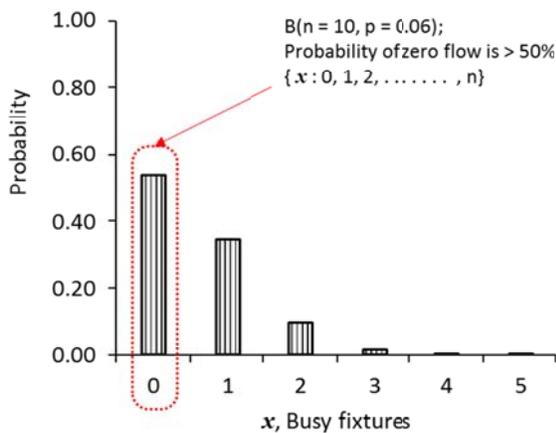
Table 1: Residential fixture  $p$ -values

Fixture	Bathtub	Clothes washer	Dishwasher	Faucet*	Shower	Water Closet
<b>p-value</b>	0.010	0.055	0.005	0.020	0.045	0.010

\* kitchen or bathroom sink

When low fixture  $p$ -values are applied to the binomial model to determine the number of busy fixtures in a residential building, there is a high probability of zero busy fixtures (i.e. no water flow). Unlike single family residential buildings, Hunter’s congested assumption effectively pulls the binomial distribution of busy fixtures away from the lower boundary zero. The presence of the probability of zero flow from idle fixtures lowers the expected demand flow and the design percentile using the binomial model. We have introduced the zero-truncated binomial distribution (ZTBD) to estimate demand conditioned on at least one busy fixture. Figure 1 illustrates the classical binomial distribution and the corresponding ZTBD. Since operation of premise plumbing implies running water, only the ZTBD is appropriate for design purposes.

a) Standard Binomial Distribution



b) Zero-truncated Binomial Distribution

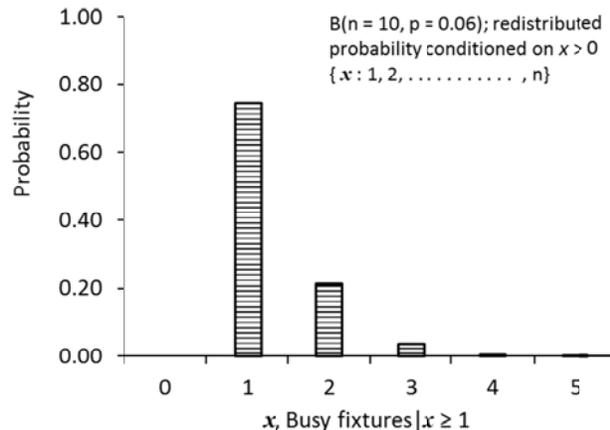


Figure 1: Probability distribution of busy fixtures in a group of  $n = 10$  fixtures, each with probability  $p = 0.06$  of being in use.

A demand model was developed using derived moments (mean and variance) of the ZTBD to estimate the 99<sup>th</sup> percentile peak demand flow ( $Q_{0.99}$ ). Equation [1] gives peak demand for small buildings with high probability of zero flow ( $P_0$ ) using the ZTBD. As  $P_0$  approaches 0, Equation [1] transitions to Equation [2]. Equation [2] was developed by Wistort in 1994. Wistort’s model is relevant for conditions similar to Hunter’s congested peak water demand.

$$Q_{0.99} = \frac{1}{1-P_0} \left[ \sum_{k=1}^K n_k p_k q_k + (z_{0.99}) \sqrt{\left[ (1-P_0) \sum_{k=1}^K n_k p_k (1-p_k) q_k^2 \right] - P_0 \left( \sum_{k=1}^K n_k p_k q_k \right)^2} \right] \quad [1]$$

$$Q_{0.99} = \sum_{k=1}^K n_k p_k q_k + (z_{0.99}) \sqrt{\sum_{k=1}^K n_k p_k (1-p_k) q_k^2} \quad [2]$$

The parameters  $n$ ,  $p$ ,  $q$  must be estimated to use Equation [1] or [2]. The fixture count  $n$  is a physical feature that can easily be measured, while the parameter  $q$  can be obtained from the fixture manufacturer. The probability that a fixture is busy,  $p$  can only be estimated from water use survey. The fixture  $p$ -values in Table 1 were calculated from the International Association of Plumbing and Mechanical Officials (IAPMO) data set. The index  $k$  represents different types of fixtures (i.e. shower, faucet etc.) while  $z_{0.99}$  is the 99<sup>th</sup> percentile from the standard normal distribution.

### **Water-Energy Nexus**

The suggested methods to estimate peak water demand result in lower peak water demand compared to demand estimated using Hunter’s curve for the same number of fixtures. In most cases, lower peak water demand flows require a reduced pipe size. The energy savings from reduced pipe size can be quantified by tracking the frequency of hot water use at different fixtures in a building. Water trapped in the hot water line cools between uses. Estimates of how much cooled water must be flushed from the supply pipe before hot water arrives at a fixture needs to be determined.

PRPsym will be used in conjunction with EPANET to simulate demand for a specified residential water distribution system representing case 1 and case 2. The PRPsym code simulates stochastic indoor water use at fixtures on a 1 second interval. PRPsym parameters (demand intensity and pulse duration) for different fixtures will be estimated from the IAPMO data set. EPANET’s first-order decay option will be used to simulate the cooling of water between uses. The amount of water flushed depends on pipe size and frequency of hot water use due to estimated demand (in PRPsym). Results for the same hot water use pattern for cases 1 and 2 will be compared to estimate energy savings.

To illustrate, consider the early morning shower in a typical single family home. Suppose the supply line from the hot water heater to the bathroom shower is not insulated and has been idle overnight. Because the hot water supply has cooled to ambient room temperature, the user will run the hot water line to flush the cool water until hot water arrives. At a minimum, the amount of water wasted corresponds to the volume of water in the hot

supply line between the water heater and the shower. Depending on the plumbing configuration, this can amount to several gallons of treated and heated water. Similarly, the amount of energy wasted corresponds to the energy needed to heat the total volume of water in the supply line from ambient room temperature to the set point of the hot water heater.

### Principal Findings and Results

The Water Demand Calculator (WDC) was developed to facilitate use of Equations 1 and 2 for estimating peak flows in buildings. The WDC is a simple intuitive user interface that runs in Microsoft Excel (see Figure 2). The user supplies information to columns B (number of fixtures) and D (fixture flow rate) and runs the calculator (macro). The WDC returns the appropriate estimate of demand flow as shown in the green cell of Figure 2.

	[A] FIXTURE	[B] ENTER NUMBER OF FIXTURES	[C] PROBABILITY OF USE (%)	[D] ENTER FIXTURE FLOW RATE (GPM)	[E] MAXIMUM RECOMMENDED FIXTURE FLOW RATE (GPM)
1	Bar Sink	0	2.0	1.5	1.5
2	Bathtub	0	1.0	5.5	5.5
3	Bidet	0	1.0	2.0	2.0
4	Clothes Washer	1	5.5	3.5	3.5
5	Combination Bath/Shower	2	5.5	5.5	5.5
6	Dishwasher	1	0.5	1.3	1.3
7	Kitchen Faucet	1	2.0	2.2	2.2
8	Laundry Faucet	0	2.0	2.0	2.0
9	Lavatory Faucet	4	2.0	1.5	1.5
10	Shower, per head	1	4.5	2.0	2.0
11	Water Closet, 1.28 GPF Gravity Tank	3	1.0	3.0	3.0
12	Other Fixture 1	0	0.0	0.0	6.0
13	Other Fixture 2	0	0.0	0.0	6.0
14	Other Fixture 3	0	0.0	0.0	6.0

Total Number of Fixtures      13

99th PERCENTILE DEMAND FLOW = **11.0** GPM           

Figure 2: Residential Water Demand Calculator

### Significance

This project is a blend of peak water demand, incorporating water use habits to estimate design flows for designing a water distribution system. Quantifying the energy savings from appropriate pipe sizes, and residential hot water demand patterns will highlight the benefits of sizing a distribution system properly. The overriding positive outcome of this project is provision of safe sustainable efficient premise plumbing to encourage water conservation and energy savings in modern building systems.

## References

ANSI/ASHRAE Standard -188. (2015). "Legionellosis: Risk Management for Building Water Systems." *ASHRAE*: <https://www.ashrae.org/>,

Armstrong Hot Water Group: ASHRAE Modified Hunter Curve - Flow Charts; pages 12 – 15 <https://www.armstronginternational.com/files/products/wheaters/pdf/sizing%20chart.pdf> accessed June 2014

AWWA. (2004). *Sizing Water Service Lines and Meters: Manual of Water Supply Practices (M22)*. American Water Works Association, Denver, CO.

Hunter, R. B. (1940). "Methods of Estimating Loads on Plumbing Systems." *Rep. No. BMS65*, US National Bureau of Standards, Washington DC.

Omaghomi, T., and Buchberger, S. (2014). "Estimating Water Demands in Buildings." *Procedia Engineering*, 89(0), 1013-1022.

Siddiqi, A., and Fletcher, S. (2015). "Energy Intensity of Water End-Uses." *Curr Sustainable Renewable Energy Rep*, 2(1), 25-31.

U.S. EPA WaterSense Program. (2014). "Guide for Efficient Hot Water Delivery Systems." *Rep. No. Version 1.2*, EPA, accessed October 08 2015 at [http://www3.epa.gov/watersense/docs/hw\\_distribution\\_guide.pdf](http://www3.epa.gov/watersense/docs/hw_distribution_guide.pdf).

U.S. Energy Information Administration. (2015). "Monthly Energy Review - June 2015." *Rep. No. DOE/EIA-0035(2015/06)*, U.S. Energy Information Administration, 214 p, accessed: June 30, 2015 at <http://www.eia.gov/totalenergy/data/monthly/>.

Vieira, A. S., Beal, C. D., and Stewart, R. A. (2014). "Residential water heaters in Brisbane, Australia: Thinking beyond technology selection to enhance energy efficiency and level of service." *Energy Build.*, 82(0), 222-236.

Wistort, R. A. (1995). "A new look at determining water demands in building: ASPE direct analytic method." *Technical Proceedings; ASPE 1994 Convention*, American Society of Plumbing Engineers, Kansas City, MO, 17-34.

## Baseline measurements of methane emissions from Piedmont Lake - current and future fracking area

### Basic Information

<b>Title:</b>	Baseline measurements of methane emissions from Piedmont Lake - current and future fracking area
<b>Project Number:</b>	2016OH507B
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	2/28/2018
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	3
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Climatological Processes, Non Point Pollution, Wetlands
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Gil Bohrer

### Publications

There are no publications.

# **Baseline measurements of methane emissions from Piedmont Lake - current and future fracking area**

Progress Report 2016-2017

PI Gil Bohrer

## **Abstract**

Methane is the second most important green-house gas (GHG). Methane is emitted from natural wetlands and lakes, and also from natural gas extraction and production operations. The large uncertainty surrounds both the quantity and mechanisms producing natural methane emissions from lakes and wetlands, and fugitive methane emissions during hydrofracking, compound in areas where fracking is conducted near and/or under lakes and wetlands. In such cases, there is a strong need for baseline observations of the natural emissions which will be used to distinguish those from additional emissions, if present, related to fracking.

The direct result of this project will be the development of a dataset of observations of baseline emissions from Piedmont Lake, OH, and an empirical model for the emission rates from the lake. Though the modelling approach is general and could be applied anywhere, we will use the depth of data at our field site in the 4H camp at the shore of Piedmont Lake, near future potential fracking sites. Some of the area around the lake was cleared for fracking activity, and production may start in the next few years.

## **Methodology**

- 1) The establishment of an OSU fracking research site in Piedmont Lake by the USEEL center has failed and an OSU site will not exist. Our project was leveraging on that site, and therefore, we were forced to locate a flux tower with measurements of methane emissions.
- 2) A 20 m tall flux tower will be located downwind a planned well pad locations near Morgantown West Virginia. The tower is relatively tall to allow a wide footprint area.
- 3) Ongoing measurements of meteorological conditions (air temperature, pressure and humidity, wind, precipitation and incoming radiation) and methane and CO<sub>2</sub> fluxes using eddy-flux will be conducted continuously at the West Virginia site from a tower that we plan to construct in 5-6/2017 and will continue throughout this project. This tower was funded by NSF.
- 4) A campaign for chamber measurements of the fluxes from the river near the tower and fracking site will start in May 2017 and continue monthly until October 2017.
- 5) We will use a model developed in our group to combine chamber with EC flux measurements to determine a continuous time series of lake emissions.
- 6) We will numerically construct an Automated Neural Network-based empirical model (ANN) of natural baseline methane emission rates from the fracking site and its surrounding environment.

## **Major Activity**

Unfortunately, the NETL project has failed to secure a study site and activities in the USEEL Will not be possible. Therefore, it was impossible for us to start our fieldwork to date. A 1-year no-cost extension for the project was requested and approved. We have secured an alternative

field site in collaboration with Prof. Derek Johnson in West Virginia University. The site is near Morgantown WV, on private land, near a fracking pad. Fracking activity is scheduled to start later this summer. This project provide an additional components of chamber measurements in a larger NSF-funded project that will fund the construction of a flux tower and the flux analysis activity. A subcontract from the NSF funding was signed with WVU and field work at the new site is scheduled to start within the coming weeks. We have attended a site-scoping trip in February 2017, and designed the tower location, structure and construction. We have been coordinating the tower construction planning through teleconference with Derek Johnson in WVU. We have ordered all the required equipment and supplies to conduct the project. We have secured an agreement with the Olentangy River Wetland Research Center for access to the GCMS for analyzing the chamber observations and in the process of preparing the needed supplies for the chamber measurement campaign (sterilizing and evacuating vials). The tower have been delivered to WVU and is awaiting on-site for construction. The flux tower instrumentations including all sensors, datalogger, and wireless model were calibrated, tested and assembled in our laboratory, awaiting deployment in the field as soon as the tower in constructed.

### **Findings**

None to date

### **Significance**

The project will provide baseline measurements of methane emissions from natural and agricultural aquatic ecosystems around the proposed locations of a hydrofracking site. These observations will allow developing an empirical model for the natural methane emissions from the water system at the site and will allow determining whether these emissions increase due to diffused methane release into the ground water after the drilling operations started.

# Co-Optimizing Enhanced Water Recovery and CO2 Sequestration in Ohio

## Basic Information

<b>Title:</b>	Co-Optimizing Enhanced Water Recovery and CO2 Sequestration in Ohio
<b>Project Number:</b>	2016OH508B
<b>Start Date:</b>	3/1/2016
<b>End Date:</b>	2/28/2017
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	03
<b>Research Category:</b>	Engineering
<b>Focus Category:</b>	Water Use, Hydrology, Treatment
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Jeffrey M Bielicki

## Publications

1. Hunter, K., and Bielicki, J. "The Production of Water from Saline Aquifers through Carbon Dioxide Capture and Storage Operations." CO2 II: Summit Technology and Opportunities. Albuquerque, New Mexico. April 10-14, 2016. Poster presentation.
2. Hunter, K., and Bielicki, J. "Optimizing Water Extraction and Carbon Dioxide Storage in Saline Aquifers." WaterSmart Innovations Conference. Las Vegas, Nevada. October 5-7, 2016. Poster presentation.
3. Hunter, K., Bielicki, J., Middleton, R., Stauffer, P., Pawar, R., Harp, D., and Martinez, D. "Integrated CO2 Storage and Brine Extraction." GHGT-13 Conference. Lausanne, Switzerland. November 14-16, 2016. Conference paper and oral presentation.
4. Hunter, K., Bielicki, J., Middleton, R., Stauffer, P., Pawar, R., Harp, D., Martinez, D., Sullivan Graham, J., and Chu, S. "Offsetting Water Requirements and Stress with Enhanced Water Recovery and CO2 Storage." Mickey Leland Energy Fellowship Program Technical Forum. Pittsburg, Pennsylvania. August 7-12, 2016. Oral presentation.

# Final Report: Co-Optimizing Enhanced Water Recovery and CO<sub>2</sub> Sequestration

**Jeffrey M. Bielicki<sup>a,b,c</sup>, Kelsey A. Hunter<sup>b</sup>**

<sup>a</sup>Department of Civil, Environmental, and Geodetic Engineering, The Ohio State University

<sup>b</sup>The John Glenn College of Public Affairs, The Ohio State University

<sup>c</sup>Environmental Science Graduate Program, The Ohio State University

## Table of Contents

<b>1</b>	<b>Summary</b> .....	<b>3</b>
<b>2</b>	<b>Problem and research objectives</b> .....	<b>4</b>
2.1	Present and emerging stressors of the energy water nexus .....	4
2.2	CO <sub>2</sub> enhanced water recovery (CO <sub>2</sub> -EWR).....	5
<b>3</b>	<b>Subsurface modeling of CO<sub>2</sub>-EWR</b> .....	<b>6</b>
3.1	Methodology .....	6
3.2	Principle findings .....	8
<b>4</b>	<b>Generalized reservoir equation</b> .....	<b>11</b>
4.1	Methodology .....	11
<b>5</b>	<b>Optimization format</b> .....	<b>13</b>
5.1	Methodology .....	13
5.2	CO <sub>2</sub> -EWR operational costs and the water treatment model .....	16
<b>6</b>	<b>Significance</b> .....	<b>17</b>
<b>7</b>	<b>Publication Citations</b> .....	<b>18</b>
<b>8</b>	<b>Number of Students Supported by the Project</b> .....	<b>18</b>
<b>9</b>	<b>Professional Placement of Graduates</b> .....	<b>19</b>
<b>10</b>	<b>Awards or Achievements</b> .....	<b>19</b>
<b>11</b>	<b>Additional Funding</b> .....	<b>19</b>
<b>12</b>	<b>References</b> .....	<b>19</b>

## 1 Summary

The nexus between water and energy is one of the major challenges for present societies. Emerging constraints on the electricity sector to limit carbon dioxide emissions while reducing the freshwater used during the cooling process demonstrates the intrinsic link in the production and use of modern energy. For example, the emission reduction technology of carbon dioxide (CO<sub>2</sub>) capture and storage (CCS), where CO<sub>2</sub> is captured from power plants and injected into deep saline aquifers for storage, can cut CO<sub>2</sub> emissions released to the atmosphere, but increase water demand due to the CO<sub>2</sub> capture process. This would increase the overall demand of water for energy production. The simultaneous extraction and treatment of brine, during CO<sub>2</sub> injection into deep saline aquifers, could provide a usable water source. The use of CO<sub>2</sub> to provide a marketable commodity, treated brine in this case, transitions CCS to CCUS, where the “U” refers to the utilization. This process is also known as CO<sub>2</sub> Enhanced Water Recovery (CO<sub>2</sub>-EWR). The overall objective of this research is to improve our understanding of how CO<sub>2</sub>-EWR can be co-optimized and the relationships between CO<sub>2</sub> sequestration, water extraction, and costs. These relationships result in tradeoffs between the amount of CO<sub>2</sub> injected into the storage formation and the amount of brine removed, reservoir pressure build up or relief due to injection and extraction, increased storage at the expense of brine treatment costs, and dependence on the value of water and CO<sub>2</sub> emissions through a future CO<sub>2</sub> tax or cap-and-trade mechanism.

The research is comprised of three major parts. After learning of the limitations in the CO<sub>2</sub> Predicting Engineered Natural Systems (CO<sub>2</sub>-PENS) and the CO<sub>2</sub>-PENS Water Treatment (WTM) models that we planned to implement, we shifted to using a finite element heat and mass transfer (FEHM) code developed by Los Alamos National Laboratory (LANL) to model a saline aquifer with CO<sub>2</sub>-EWR. A preexisting mesh for the Rock Springs Uplift (RSU) in Wyoming was used to understand the intricate nature of subsurface pressure management through the injection of CO<sub>2</sub> and extraction of brine. The second part of this research is currently in progress and will use the results of the detailed reservoir model to parameterize a generalized equation, based on the Theis groundwater pumping equation, that

incorporates tradeoffs observed in the reservoir models. This equation will be applied to reservoirs without the need for in-depth subsurface flow modeling, specifically targeting Ohio saline aquifers. The final component of this research will consist of a cost-minimization optimization that will use the parameters of the reservoir model and set costs to the injection and storage of CO<sub>2</sub> as well as the production and treatment of brine from the existing saline aquifer. The goal is to implement this research in the Ohio in order to determine the viability of CO<sub>2</sub>-EWR within the state.

## **2 Problem and research objectives**

### **2.1 Present and emerging stressors of the energy water nexus**

The state of Ohio historically has substantial water resources in both groundwater and surface water. Due to high water demand for various activities through manufacturing plants, agricultural irrigation, and thermoelectric power plants the state is moving towards a “Medium to High” or “High” water risk according to the World Resources Institute (WRI) Aqueduct Water Risk Atlas (WRI n.d.). Energy production through thermoelectric power plants is the highest consumer of freshwater and accounts for 77% of freshwater withdrawals in Ohio (Averyt et al. 2011). This freshwater is used to cool thermoelectric power plants and instills the connection between energy and water in Ohio. With the increase in hydraulic fracturing for unconventional hydrocarbon production, energy extraction is another challenge for water availability within the state. Water, typically from surface water sources, is used during the hydraulic fracturing process as water is injected under high pressure into tight shale seams to produce oil and natural gas. The byproduct of the production, flowback water, is highly contaminated (U.S. EPA 2016) and disposed in deep injection wells, treated in wastewater treatment facilities, or reused for subsequent on-site hydraulic fracturing.

Changing environmental conditions due to climate change is another challenge for Ohio’s water resources (Hartmann, D. L.; Tank, A. M. G. K; Rusticucci 2013). The Midwest is projected to endure more extreme

precipitation events, heat waves, and droughts in the future. This will further increase the impact of water resource availability and its connection to energy exploration and production. The increased demand and variability of water due to potential climate change impacts has already started to change the energy market. Combined changes in temperatures and drought resulted in instances where power plants have shut down because they lacked suitable cooling water (Rogers et al. 2013). These instances are increasing over time, resulting in the increased need to understand how to optimize the connection between water and energy.

One of the intersections between water and energy is the increased need to reduce CO<sub>2</sub> emissions, a principle driver of human-induced climate change (Melillo, Richmond, and Yohe 2014). The reduction of CO<sub>2</sub> emissions through improvements to heat rates will increase the water required for thermoelectric power plant cooling unless a new cooling system is implemented, but installing cooling systems to reduce water use and consumption furthers the level of CO<sub>2</sub> emissions released to the atmosphere (Zhang et al. 2014). As a result, the goal of a decreased carbon emission electricity sector will impact the water consumption per unit of electricity generated.

## **2.2 CO<sub>2</sub> enhanced water recovery (CO<sub>2</sub>-EWR)**

Emerging policies and regulations to limit harmful CO<sub>2</sub> emissions released during thermoelectric power production may increase the implementation of CO<sub>2</sub> capture and storage (CCS) operations. CCS captures CO<sub>2</sub> from thermoelectric power plant operations and injects the emissions into deep saline aquifers to store. The CO<sub>2</sub> capture process is water intensive resulting in an increased demand for water during energy production. The simultaneous extraction of brine during CO<sub>2</sub> injection is used to manage the pressure buildup of the aquifer and provide a new source of water. The extracted brine typically has high levels of total dissolved solids (TDS) and can be treated to provide a usable water source through CO<sub>2</sub>-EWR. The use of extracted brine makes it a marketable commodity and the process of CO<sub>2</sub>-EWR is part of the utilization in CO<sub>2</sub> capture, utilization and storage (CCUS). CO<sub>2</sub>-EWR could prove a new source of water in water stressed environments and limit the dependency of energy generation on the current

freshwater supplies. Therefore, the object of this research is to empirically assess how water stress engendered by water requirements of existing thermoelectric power plants in Ohio can be reduced while simultaneously reducing the amount of CO<sub>2</sub> emitted to the atmosphere from these power plants while understanding the tradeoffs associated with the combined operation.

### **3 Subsurface modeling of CO<sub>2</sub>-EWR**

#### **3.1 Methodology**

The initial strategy of subsurface reservoir modeling involved a reduced form model, CO<sub>2</sub>-Predicting Engineered Natural Systems (Stauffer et al. 2009). The model's capabilities tracked the CO<sub>2</sub> sequestration pathway starting at the CO<sub>2</sub> source and modeling the transport, injection, storage, and the release or leak of CO<sub>2</sub> from the storage reservoir. This model was unable to generate data that depicted the intricate nature and dynamic changes of pressure within the reservoir during CO<sub>2</sub> injection and brine extraction. The Finite Element Heat and Mass Transfer (FEHM) Code (<https://fehm.lanl.gov>), developed by Los Alamos National Laboratory (LANL), was used instead to model CO<sub>2</sub> and brine, injection, extraction, and flow within a deep, saline aquifer. The simulation uses the control volume finite element method (CVFE) to simulate multi-fluid, multi-phase heat and mass transfer (Zyvoloski 2009). This detailed subsurface flow equation provided more realistic results of multi-fluid flow behavior within a reservoir needed for this research.

A preexisting mesh for the Rock Springs Uplift (RSU) formation was used as the targeted formation for a series of subsurface model scenarios. The formation was characterized through extensive analysis on a test well and geophysical surveys (Surdam et al. 2013; Surdam and Jiao 2007) and has been the subject of numerous DOE-funded investigations specifically interested in using the formation in Wyoming (DEFE0002142, DE-FE0009202, DE-FE0026159, and DE-FE0023328). Through well log analysis, core data and 3D seismic surveys, a nominal heterogeneous permeability field was developed by LANL researchers using the Los Alamos Grid Toolbox (LaGriT) (<http://lagrit.lanl.gov>). We used the mesh

because it is still highly transferable to other subsurface flow models and will later be used to parameterize a more generalized equation that can be applied to a broader sample of saline aquifers, including Ohio reservoirs.

The RSU was a 50 by 35 square mile area and characterized as a doubly-plunging anticline formation (Surdam 2013; Surdam and Jiao 2007). The Pennsylvanian Weber Sandstone and Mississippian Madison Limestone layers were previously identified as potential CO<sub>2</sub> storage locations within the RSU. Neither the Weber or Madison formation layers were exposed in the RSU and the nearest surface outcrops were 50 to 100 miles from the margins of the structure while the flanks of the structure were nearly 15,000 feet or more below ground. The formation structure was an ideal fluid trapping formation. The Madison formation was the focus of this study. The cap for the formation consisted of 5,000 feet of low-permeability Cretaceous shale. The Wyoming Oil and Gas Fields Symposium Green River Basin in 1979 averaged the porosity of the Madison formation at approximately 10% with a salinity range from 50,000 to 80,000 ppm. The DOE FutureGen project specified that the Madison could accept approximately 8 billion tons of CO<sub>2</sub>.

The modeled mesh consisted of a 6 by 6 km top surface area with the Lower Madison formation at an approximate depth between 2.8 to 4.3 km. It was modeled as a sealed domain, which assumed boundaries are sealed, opposed to an open flow boundary which would have permitted movement of CO<sub>2</sub> or brine outside the boundaries of the mesh. The Lower Madison is the only formation with distinct porosities and permeabilities; all other formations were assigned porosities of 0.01 and permeabilities of  $1 \times 10^{-18} \text{m}^2$ , which designated them as cap-rock seals during CO<sub>2</sub> injection. The mesh coded a geothermal gradient of 25.5°C/km, average surface temperature of 4.4°C, and fracture gradient of 13.6 kPa/m. The CO<sub>2</sub> injector had an initial pressure of 37 MPa, which indicated a fracture pressure of approximately 90 MPa and an overpressure of 53 MPa.

Scenarios, using the FEHM code, were developed to study the impact of CO<sub>2</sub> injection and brine extraction within the Lower Madison formation. Each scenario involved CO<sub>2</sub> injection at the RSU#1

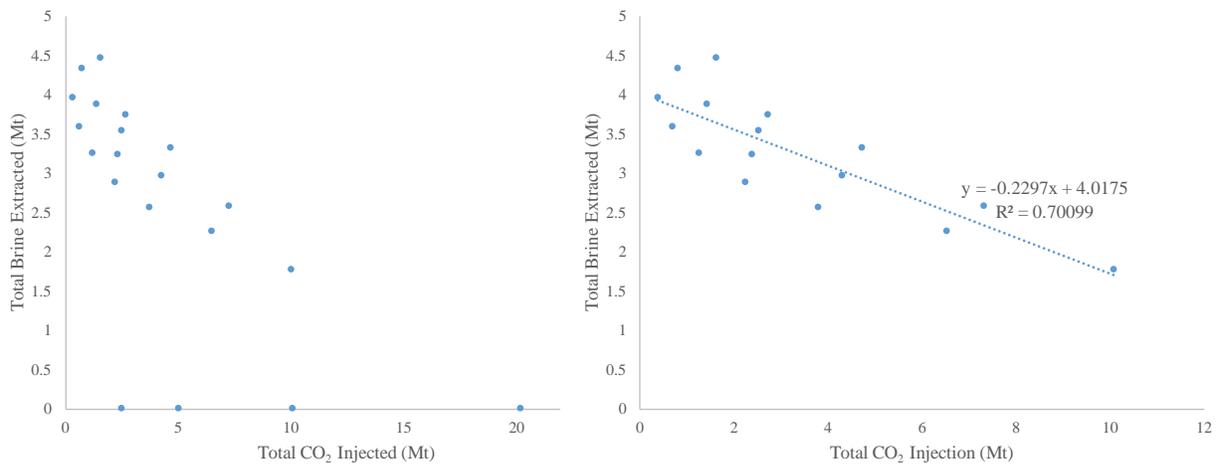
Well, located in the center of the mesh, and brine extraction at a well approximately 1,042m northeast of the injection well. The CO<sub>2</sub> injection and brine extraction rates were constant during a model run but changed between the different modeled scenarios. All other variables were kept constant in the code. CO<sub>2</sub> injection rates were limited to mass flow rates of 4 kg/s, 8 kg/s, 16 kg/s and 32 kg/s. The brine extraction rate was calculated as the mass equivalent to the CO<sub>2</sub> mass extraction rate and included scenarios with no brine extraction. A total of twenty scenarios were modeled with each CO<sub>2</sub> injection rate paired with each brine extraction rate.

FEHM modeled results included the reservoir pressure and temperature of CO<sub>2</sub> and brine at the base of the injection and extraction wells. The surface pressure of the CO<sub>2</sub> or extracted brine was back calculated using the depth of the well and modeled pressure and temperature in order to determine the surface pressure, temperature, and enthalpy needed to pump CO<sub>2</sub> into the reservoir and extract brine. Assumptions included the use of a typical diameter of 0.41m for the injection and extraction well, pipe friction factor of 0.02, and surface CO<sub>2</sub> temperature of 20°C. The enthalpy was multiplied by the mass flow rate in order to determine the pumping power needed to inject the CO<sub>2</sub>. This pumping power will be translated as a cost in order to integrate the impacts of the reservoir in the cost-minimization optimization.

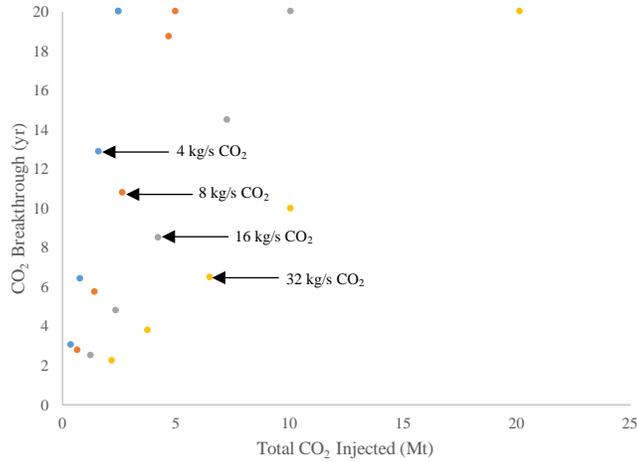
### **3.2 Principle findings**

Figure 1 shows the relationship between total CO<sub>2</sub> injected and brine extracted for the twenty modeled scenarios. The initial expectation was that brine extraction increased the storage capacity of CO<sub>2</sub> within the reservoir. Yet a decreasing linear correlation between the total CO<sub>2</sub> injected and brine extracted resulted in higher CO<sub>2</sub> storage for scenarios with less extraction. The four points on the x-axis are the modeled scenarios with zero brine extraction and were excluded in the plot fitted with the linear relationship. The reservoir behaved differently with exclusive CO<sub>2</sub> injection and the optimization must compare the benefits or costs of using CO<sub>2</sub>-EWR by comparing them through separate reservoir analysis. The modeled scenarios with zero brine extraction will be incorporated through a binary variable in the optimization.

The negative linear regression in Figure 1 was associated with the early breakthrough time of brine extraction rates represented in Figure 2. The expected lifetime assumed for this model was twenty years. The model was terminated after the twenty-year time frame or once CO<sub>2</sub> breakthrough occurred at the extraction well. The high brine extraction rate pulled CO<sub>2</sub> through the reservoir at a faster rate because CO<sub>2</sub> could travel with less restriction in empty pore space. This indicated that the brine extraction rate had greater impact on the lifetime of the CO<sub>2</sub>-EWR system compared to the CO<sub>2</sub> injection rate and storage.

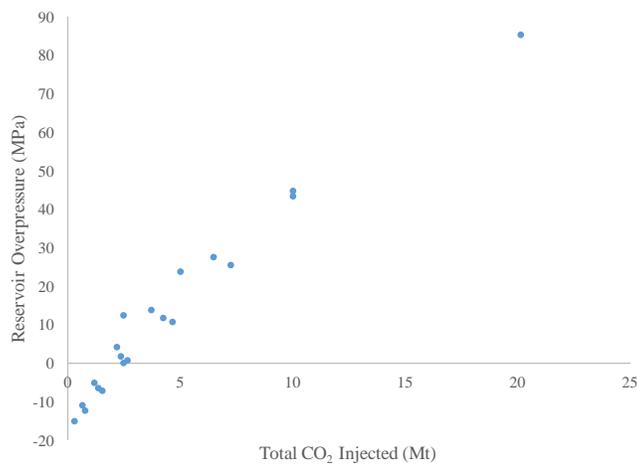


**Figure 1: Observed relationship with CO<sub>2</sub> injection and brine extraction.** The first plot included all data points. The second plot excluded CO<sub>2</sub> injection with zero brine extraction and superimposed a linear relationship which was used in mixed-integer linear optimization.



**Figure 2: Breakthrough time associated with modeled reservoir scenarios.** The CO<sub>2</sub>-EWR system had an expected lifetime of twenty years. The model terminated after twenty years or when CO<sub>2</sub> pore saturation at the extractor exceeded 0.001, indicating CO<sub>2</sub> breakthrough. Colors indicated the rate of CO<sub>2</sub> injection. The observable grouping represented the brine extraction rate. A higher brine extraction rate indicated a faster breakthrough time.

The change in overpressure pressure due to CO<sub>2</sub> storage also displayed a linear trend (Figure 3), with a higher change in pressure from more CO<sub>2</sub> injected. The negative overpressures were scenarios with high brine extraction rates, which indicated that a higher extraction rate of brine did allow more CO<sub>2</sub> to be injected. This indicated that an optimal brine extraction rate will be balanced between opening pore space and decreasing the time before CO<sub>2</sub> breakthrough at the extraction well.



**Figure 3: The relationship between reservoir overpressure and total CO<sub>2</sub> injected.** Overpressure was limited to 53 MPa. The scenario with 32 kg/s of CO<sub>2</sub> injected and zero brine extraction exceeded this

limit. The negative overpressure consisted of high brine extraction rates that decreased the pressure more significantly than pressure build-up from CO<sub>2</sub> injection due to fast breakthrough times.

## 4 Generalized reservoir equation

### 4.1 Methodology

The detailed reservoir simulations conducted in the first part of this research is site specific to the RSU formation in Wyoming. The goal of this project is to understand how CO<sub>2</sub>-EWR can be implemented in various deep, saline aquifers, specifically in Ohio. As a result, the second component, which is currently in progress, will be to develop a generalized reservoir pressure equation that is parameterized by the FEHM modeled results. This equation will incorporate the complex interactions of changes in injection or extraction rates of the reservoir and the resulting change in pressure. The equation can then be used in any reservoir to determine if CO<sub>2</sub>-EWR is viable.

The generalized equation, will be based on the Theis solution for non-leaky aquifers (Fetter 2001). The general Theis equation is applied to a basic, homogeneous, confined, groundwater aquifer with a transient radial flow.

$$S \frac{\partial h}{\partial t} = T \left[ \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} \right] + w$$

Where S is storativity [dimensionless]; h is hydraulic head; t is time [day]; T is transmissivity [m<sup>2</sup>/day] which assumes flow through an aquifer is horizontal; r is the distance between wells [m]; and w is the Theis well function for nonleaky aquifer [dimensionless]. The initial condition assumed is that the hydraulic head is constant in all directions at any time. Darcy's law at the well head is used to account for pumping of groundwater.

$$\lim_{r \rightarrow 0} \left( r \frac{\partial h}{\partial r} \right) = \frac{Q}{2\pi T}$$

Where Q is the pumping rate of the well [m<sup>3</sup>/day]. The solution for the difference in hydraulic head over time and distance is as follows:

$$h_0 - h(r, t) = \frac{Q}{4\pi T} \int_u^\infty e^{-u} \frac{du}{u}$$

The limit is the well function is  $w(u) \approx -0.5772 + \ln u + u - \frac{u^2}{2-2!} - \frac{u^3}{3-3!} - \frac{u^4}{4-4!} \dots$

Wenzel developed a lookup table for this function (Wenzel 1942) which is incorporated in the final equation.

$$h_0 - h(r, t) = \frac{Q}{4\pi T} w(u)$$

This general equation is used for modeling simple aquifer systems and requires significant assumptions (Fetter 2001). The following assumptions are maintained in the reservoir modeling of the first part of this research. (1) The aquifer is bounded on the top and bottom by a confining layer. (2) The potentiometric surface of the aquifer is horizontal prior to the start of pumping and not changing with time prior to the start of pumping. As a result, all changes in the position of the potentiometric surface are due to the effect of the pumping well with no source of recharge into the aquifer. (3) All flow is radial toward the well. (4) Groundwater flow is horizontal. (5) Darcy's law is valid. (6) The pumping well and the observation wells are fully penetrating and screened over the entire thickness of the aquifer with an infinitesimal diameter and 100% efficient. (7) The aquifer is compressible and water is released instantaneously from the aquifer as the head is lowered. (8) The well is pumped at a constant rate. Since the Theis equation is used for a simple aquifer system, several assumptions used in the Theis equation are not valid. The assumption that all geologic formations are horizontal and have infinite horizontal extent will need to be addressed due to the current closed boundaries of the FEHM mesh. Additionally, the aquifer material composition is heterogeneous not homogeneous and the groundwater does not have a constant density and viscosity. Finally, we modeled a multi-fluid system (CO<sub>2</sub> and brine). The original Theis equation does not account for multiple fluids.

The FEHM code was validated by the Theis Equation to compare modeled results and demonstrate that the pressure equations implemented in the code were executing properly. This validation test used a revised Theis Equations from Matthews and Russell (Matthews and Russell 1967).

$$p(r, t) = p_i - \frac{q\mu}{2\pi kh} \left[ -\frac{1}{2} Ei \left( -\frac{\phi\mu cr^2}{4kt} \right) \right]$$

$$-Ei(-x) = \int_x^{\infty} \frac{e^{-u}}{u} du$$

Where  $k$  is the reservoir permeability in the radial direction [ $m^2$ ];  $\phi$  is the reservoir porosity [dimensionless];  $c$  is the fluid compressibility [ $MPa^{-1}$ ];  $\mu$  is the fluid viscosity [ $Pa \cdot s$ ];  $h$  is the reservoir thickness [ $m$ ];  $\Delta h$  is the vertical node spacing [ $m$ ];  $r$  is the radial reservoir length [ $m$ ];  $\Delta r$  is the radial node spacing;  $q$  is the flow rate [ $kg/s$ ];  $p_i$  is the initial pressure [ $MPa$ ];  $T$  is the isothermal temperature [ $^{\circ}C$ ];  $\Delta t$  is the time step [ $s$ ];  $t$  is the total elapsed time [ $day$ ]. Using the Theis equation and the modified version used as a check within the FEHM simulator, we will develop an equation and parameterize it to the FEHM simulation results. The resulting equation will have the capabilities to estimate the viability of  $CO_2$ -EWR in various deep, saline aquifers and remove the current requirement to run a site specific subsurface flow model.

## 5 Optimization format

### 5.1 Methodology

The final component of this research involved the use of a cost-minimizing approach to determine how to co-optimize  $CO_2$ -EWR in the most economically stable manner. This optimization will be a mixed-integer linear program that will incorporate the reservoir characteristics and tradeoffs associated with the use of enhanced water recovery and the costs associated with a CCUS operation.

The tradeoffs include both the economic and physical perspectives of the amount of  $CO_2$  injected and stored in a single formation compared to the amount of brine removed. Reservoir model results indicate

total storage is more sensitive to the rate of brine extraction compared to the amount of CO<sub>2</sub> stored. Additionally, CO<sub>2</sub> injection is costly, and these costs increase as the pressure in the reservoir increases from injection. While the removal of brine from the reservoir is similarly expensive, it could reduce reservoir pressure and increase CO<sub>2</sub> storage capacity, if extracted at the optimal rate. Producing brine at a specific pressure could reduce the costs associated with treating water through technologies such as reverse osmosis. This will also depend on the level of TDS in the brine and the degree to which water will be treated. Finally, the value of water and CO<sub>2</sub> emissions provide an additional consideration. Water in a water abundant area might not be valued as high as a water stressed region, changing the value of water in the model based on the environment. In addition, CO<sub>2</sub> emissions through a cap-and-trade mechanism or tax program could put a value on the cost to emit CO<sub>2</sub> and provide more incentive for CCUS operations. These tradeoffs will be incorporated into a cost minimization optimization in order to determine the viability of CO<sub>2</sub>-EWR operations in aquifers in Ohio.

The following equation is the initial objective function of the optimization.

$$\min \sum_{t=1}^{t=20} (F + M_C(C_C - P_C) + M_B(C_B - P_B) + M_T(C_T - P_T))$$

This minimization equation is subject to the following constraints.

$C_C$  and  $C_{BP} = (\Delta h \times \text{electricity conversion factor})$  in which  $\Delta h$  is a function of  $M_{BP}$  and  $M_C$

These two constraints for the cost to inject CO<sub>2</sub> and cost to extract brine through a pump place a value on the tradeoffs associated with changes in the reservoir pressure. The change in enthalpy is calculated using the pressure and temperature from the wells modeled in FEHM. The results are back calculated using the depth of the well to determine the surface pressure, temperature, and enthalpy. The change in enthalpy

from the surface to the base of the well is the pumping power necessary to inject or extract from the reservoir. This power can be converted to a cost with price of electricity needed to run the pump.

$$M_{BT} \leq M_{BP}$$

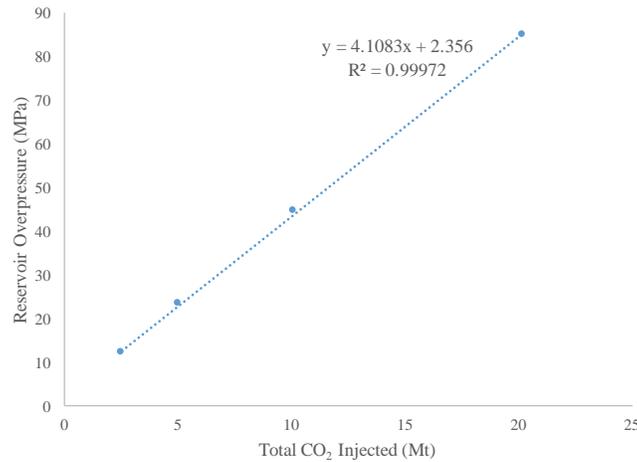
The brine treated must be less than or equal to the brine produced.

$$0 \leq M_{BP} \leq 41 \frac{\text{kg}}{\text{s}} \text{ of brine}$$

Highest flow rate established in the system with a 20-year life-time.

$$0 \leq M_C \leq 12.3 \text{ Mt CO}_2$$

The total CO<sub>2</sub> injected into the reservoir is limited by the overpressure and the fracture gradient. The injection node, initially 37 MPa, is limited to 90 MPa, resulting in an allowable overpressure of 53 MPa. Based on the linear trend of total CO<sub>2</sub> injected compared to reservoir overpressure, for CO<sub>2</sub> injection with zero brine extraction, the maximum CO<sub>2</sub> injected was limited to the allowable overpressure (Figure 4).



**Figure 4: Linear trend of CO<sub>2</sub> injected excluding brine production.** This linear trend was used to calculate the maximum amount of CO<sub>2</sub> that could be injected into the reservoir without exceeding the fracture pressure.

$$M_C = U_1(M_C) + U_2(-3.051M_B + 13.246)$$

$$U_1 = 1 \text{ when } M_{BP} = 0, 0 \text{ otherwise}$$

$$U_2 = 1 \text{ when } M_{BP} > 0, 0 \text{ otherwise}$$

This constraint incorporates a binary variable that will indicate when CO<sub>2</sub>-EWR is implemented and when CO<sub>2</sub> is injected with zero brine extraction. This will determine if it is more economical to exclude extraction or include enhanced water recovery.

Below are the variables incorporated into the optimization.

t = Time (years)

F = Fixed cost of operating CO<sub>2</sub> injection and brine production and treatment facility [\\$]

M<sub>C</sub> = Mass of CO<sub>2</sub> injected [tonnes]

C<sub>C</sub> = Variable operating cost of CO<sub>2</sub> injection [\$/tonnes CO<sub>2</sub>]

P<sub>C</sub> = Price of CO<sub>2</sub> (i.e. benefit) [\$/tonnes CO<sub>2</sub>]

M<sub>B</sub> = Mass of brine produced [tonnes]

C<sub>B</sub> = Variable operating cost of producing brine [\$/tonnes brine produced]

P<sub>B</sub> = Price of brine extracted [\$/tonnes brine produced]

M<sub>T</sub> = Mass of brine treated [tonnes]

C<sub>T</sub> = Variable cost of brine treated [\$/tonnes brine treated]

P<sub>T</sub> = Price of water [\$/tonne brine treated]

ṁ = Mass flow rate

Δh = Change in enthalpy

## 5.2 CO<sub>2</sub>-EWR operational costs and the water treatment model

A key component of this research is the analysis of the operational costs for CO<sub>2</sub>-EWR and the brine treatment or disposal costs. These costs will drive the cost minimization optimization presented in the previous section. The fixed cost of the operational CCUS system will be based on previously published

literature, which focused on relating the geologic heterogeneity to the costs and capacities of brine production (Heath et al. 2012; Kobos et al. 2011). The Integrated Environmental Control Model (<http://www.cmu.edu/epp/iecm/>) will also be used to estimate variable costs, energy requirements, and water usage for CO<sub>2</sub> capture. This model is based on data provided by U.S. EPA eGRID and U.S. EIA forms.

Brine treatment is highly dependent on water chemistry and the intended water end quality. The Water Treatment Model (WTM) developed by LANL is a system-level, mesoscale analysis module within the CO<sub>2</sub>-PENS model that analyzes the feasibility of brine extracted during CO<sub>2</sub>-EWR operations (Sullivan et al. 2012, 2013; Sullivan, Chu, and Pawar 2015). The only publicly available version of the WTM includes the cost of treatment, the value of energy recovery for specific treatment technology, and the cost of brine concentrate disposal. The treatment methods in the WTM only include single applications of reverse osmosis, nanofiltration, and thermal desalination. We planned to use the WTM but upon discovering its limitations once we were at LANL and could peer into the code, we realized that we needed to do a more fundamental analysis of treatment methods and costs. That work is ongoing, as is the development of a method to generalize from single observations of water quality in a particular formation within the hydrostratigraphic sequence underlying Ohio. Ultimately, the potential costs of treating this water will be inputs to the cost minimization optimization to determine the value of CO<sub>2</sub>-EWR operations provided the benefits of pressure control and increased CO<sub>2</sub> storage in the reservoir.

## **6 Significance**

This research builds and expands on the need to address challenges surrounding the nexus between energy and water. The final product of this research will identify viable locations for CO<sub>2</sub>-EWR, the potential costs associated with a location, and optimal injection/production management strategies. Results will be site-specific and further implementation of CO<sub>2</sub>-EWR will require in-depth analysis and characterization of specific locations, but this research provides the first step in implementing CO<sub>2</sub>-EWR

## 12 References

- Environmental Protection Agency. 2015. “Clean Power Plan for Existing Power Plants.”  
<http://www.epa.gov/cleanpowerplan/clean-power-plan-existing-power-plants> (July 12, 2015).
- Fetter, C. W. 2001. *Applied Hydrogeology*. 4th ed. Upper Saddle River, New Jersey: Prentice-Hall, Inc.
- Hartmann, D. L.; Tank, A. M. G. K; Rusticucci, M. 2013. *Working Group I Contribution to the IPCC Fifth Assessment Report, Climate Change 2013: The Physical Science Basis*.
- Heath, J. E. et al. 2012. “Geologic Heterogeneity and Economic Uncertainty of Subsurface Carbon Dioxide Storage.” *SPE Econom. Manag.* 4(1): 32–41.
- Kobos, Peter H et al. 2011. “Combining Power Plant Water Needs and Carbon Dioxide Storage Using Saline Formations: Implications for Carbon Dioxide and Water Management Policies.” *International Journal of Greenhouse Gas Control* 5(4): 899–910.
- Matthews, C.S., and D. G. Russell. 1967. *Pressure Buildup and Flow Tests in Wells*. New York and Dallas.
- Melillo, Jerry M., Terese C. Richmond, and Gary W. (Eds) Yohe. 2014. *Climate Change Impacts in the United States: The Third National Climate Assessment*. U.S.
- Rogers, John et al. 2013. July Union of Concerned Scientists *Water-Smart Power: Strengthening the U.S. Electricity System in a Warming World*. Cambridge, MA.
- Stauffer, Philip H, Hari S Viswanathan, Rajesh J Pawar, and George D Guthrie. 2009. “A System Model for Geologic Sequestration of Carbon Dioxide.” *Environmental Science & Technology* 43(3): 565–70.
- Sullivan, Enid J. et al. 2013. “A Method and Cost Model for Treatment of Water Extracted during Geologic CO<sub>2</sub> Storage.” *International Journal of Greenhouse Gas Control* 12: 372–81.
- Sullivan, Enid J., Shaoping Chu, Philip H. Stauffer, and Rajesh J. Pawar. 2012. “A CO<sub>2</sub>-PENS Model of Methods and Costs for Treatment of Water Extracted during Geologic Carbon Sequestration.” *Desalination and Water Treatment*: 1–7.
- Sullivan, Enid J, Shaoping Chu, and Rajesh J Pawar. 2015. “Probabilistic Cost Estimation Methods for

- Treatment of Water Extracted during CO<sub>2</sub> Storage and EOR.” *International Journal of Greenhouse Gas Control* 41: 316–27.
- Surdam, Ronald C. 2013. Springer Science & Business Media *Geologic CO<sub>2</sub> Storage Characterization: The Key to Deploying Clean Fossil Energy Technology*. Springer Science & Business Media.
- . 2013. “Site Characterization of the Highest-Priority Geologic Formations for CO<sub>2</sub> Storage in Wyoming.” : 605.
- Surdam, Ronald C., and Zunsheng Jiao. 2007. “The Rock Springs Uplift - An Outstanding Geological CO<sub>2</sub> Sequestration Site in Southwest Wyoming.” *Challenges in Geologic Resource Management* (2): 31.
- U.S. EPA. 2016. *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. Washington, DC.
- Wenzel, L.K. 1942. U.S. Geological Survey *Methods for Determining Permeability of Water-Bearing Materials with Special Reference to Discharging-Well Methods*. Washington, DC.
- WRI. “World Reserouces Institute: Aqueduct Water Risk Atlas.” <http://www.wri.org/applications/maps/aqueduct-atlas> (November 12, 2015).
- Zhang, Chao et al. 2014. “Water-Carbon Trade-off in China’s Coal Power Industry.” *Environmental Science and Technology* 48(19): 11082–89.
- Zyvoloski, George. 2009. “FEHM: A Control Volume Finite Element Code for Simulating Subsurface Multi-Phase Multi-Fluid Heat and Mass Transfer.” *Laur-07-3359*: 1–47.

## Information Transfer Program Introduction

The Ohio WRC conducted a number of activities designed to transfer water related information to a wide range audience throughout Ohio, including state, federal, county, and municipal agencies, as well as to the academic community of researchers and students. In addition, many of our efforts target non-professional audiences including children, and private citizens. The Ohio WRC conducted information transfer by (1) promoting center activities, researchers, and research projects via newsletters, the Ohio WRC website, email correspondence, brochures, booths at conferences, personal meetings with water professionals and agencies representatives; (2) organizing, sponsoring, and participating in workshops, seminars, guest lectures and conferences; (3) serving and volunteering in various water organizations and their advisory boards such as the Water Management Association of Ohio, Ohio Water Resources Council and Friends of Lower Olentangy Watershed NGO; and (4) leading two information transfer projects. Specific activities included:

(1) Promoting Ohio WRC research, results of projects, and investigators a)Preparation of Ohio WRC website content (wrc.osu.edu), website updates of events and news, and general maintenance of website. We had over 1,200 website hits, the majority of which came from new visitors and 20% from returning visitor. b)Preparing one page summaries of completed research projects, including the importance of the research topic for the State, relevant outcomes and results, and investigator background. These summaries were distributed to our Advisory Board members and other stakeholders. c)Publishing research project summaries in the Ohio Water Table, a quarterly newsletter published by the Water Management Association of Ohio (WMAO). During the reporting period, the highlighted researchers and projects were: Dr. Bielicki's project #2015OH465B, Dr. Sivandran's project 2015OH453B, Dr. Singer's project #2015OH441B and Dr. Jefferson's project #2014OH318B. This newsletter is distributed to about 600 people and organizations in Ohio in the water resources field from private sector (33%), universities (8%), nonprofit/citizens (17%) and federal, state and local government agencies (42%) d)Preparing and publishing an Ohio WRC brochure highlighting the annual activities and projects of the Ohio WRC. These are distributed at various events and presented at the Ohio WMAO conference. e)Responding to questions from public regarding water resources issues in the State of Ohio. f)Maintaining and updating statewide database of investigators in Ohio universities with research interests related to water. Currently, the database contains around 250 researchers from 15 different Ohio Universities. g)Meeting with Ohio Congress and Senate members' office staff to discuss Ohio WRC activities, research results, and their impact for the State.

(2)Organizing and sponsoring information transfer events a)Co-organized quarterly Ohio WRC-WMAO luncheon seminars, which includes assisting with luncheon administration and securing speakers. This past year the four luncheons were attended by approximately 112 water professionals from government, academia, NGOs and industry. The speakers and topics in this reporting period were: Allison MacKay (OSU): "Can Sunlight Attenuate Pharmaceutical Compounds Downstream of Wastewater Treatment Plants?"; Ben McCament (Ohio Department of Natural Resources): "Update: ODNR Acid Mine Drainage Program"; Miles Hebert (EMHT consultant): "Building partnerships to accomplish flood mitigation"; Justin Chaffin (OSU): "Harmful algal bloom research at Stone Lab: Monitoring blooms and determining drivers of toxin production." b)Sponsored 45th Annual Water Management Association of Ohio (WMAO) conference titled: "Voices for Water" and organized "Green Infrastructure" session of the conferences (3 invited speakers plus leading the session). In 2016 around 300 professionals attended the conference, including academic researchers, students (40), representatives of State and Federal Agencies, industry and NGO's. The conference is attracting increasing amount of academic researchers, including Ohio WRC researchers, based on our promotion of the conference. We also helped with selecting the student candidate for WMAO award, talked to students during the "Careers in Water Resources" session, and set up a booth at the conference to discuss Center activities. c)Two lectures and hands-on activity in a 3rd grade class for 28 students discussing drinking water treatment, causes of lead in drinking water and how to protect against excessive lead. Analysis of students' household water for lead and explanation of results. d)Sponsoring Earth Day seminar titled "The tale

## Information Transfer Program Introduction

of triclosan in Minnesota: from the lab, to the field, to the legislature.” Invited speaker William Arnold, attendance 50. e)Organizing and leading a 25 minute, hands-on workshop for 5th grade students on principles of buoyancy in the 2016 Central Ohio Children’s Water Festival

(3)Serving in multiple water organizations a)Serving on Water Management Association of Ohio (WMAO) board as a Director of Research and Data Management. In this role, we focus on promoting water resources research in the State, and attend bimonthly meetings. b)Member of WMAO student awards committee – evaluating student proposals and deciding the best candidate for the award. c)National Institute of Water Resources Regional Representatives of the Great Lakes Region. d)Participating in quarterly meetings of the Ohio Water Resources Council meetings, forum for collaboration and coordination among state agencies. e)Serving on board to plan mission and goals of new established Lake Erie Area research Network (LEARN) – collaboration with Ohio Sea Grant f)Serving on Friend of Lower Olentangy Watershed (FLOW) NGO Science committee, helping organize events, write outreach and education proposals. g)Helping to judge Future City Competition for middle school students h)Member of strategic group to define mission, vision and goals of Water Resources Working Group under the Mid-Ohio Regional Planning Commission. i)Member of Water Technology Board of Ohio American Water Works Association

4)Information Transfer Projects a)Dr. Bohrerova’s collaborative project with OSU Extension and other partners (conducted by Ohio WRC but funded by other funds) titled “Management Of Algal Growth In Ohio's Medium-Sized Lakes” focuses to initiate research, education and outreach to address sustainable algal management of Ohio’s medium-sized lakes. Medium-sized lakes are frequently managed by multiple private owners or homeowner associations and are currently highly underserved in Ohio.

b)Dr. Bohrerova’s project (conducted by Ohio WRC but funded by other funds) titled “Adopt Your Waterway” focuses on citizen volunteer lead monitoring of streams in urbanized areas around Columbus, OH for water chemistry and macroinvertebrates. The goal is to educate public about stream health and support water stewards in the area.

# Adopt Your Waterway

## Basic Information

<b>Title:</b>	Adopt Your Waterway
<b>Project Number:</b>	2015OH4820
<b>Start Date:</b>	6/1/2016
<b>End Date:</b>	8/31/2017
<b>Funding Source:</b>	Other
<b>Congressional District:</b>	3rd
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Education, Water Quality, Surface Water
<b>Descriptors:</b>	Membrane separations; water treatment; biomimetic
<b>Principal Investigators:</b>	Zuzana Bohrerova

## Publications

There are no publications.

**Adopt Your Waterway  
March 1, 2016 through February 28, 2017 Progress Report**

- a. Collaborators:** This project brought together three FLOW Science Committee members that had not collaborated on a project before: Friends of the Lower Olentangy Watershed (FLOW), Sierra Club’s Ohio Chapter and the Ohio Water Resources Center. Our collaboration has been successful and yielded significant amounts of coordination, knowledge and resources leveraged. Joe Bevan and later in the summer Danielle Johnson, FLOW student contractors, did most of the program coordination this reporting period. They are both FLOW volunteers and had experience in water sampling. The collaboration between FLOW, the Sierra Club and the Ohio Water Resources Center continues to be a success. Sierra Club has donated the Water Alert Reporting Network (WARN) Training Materials and Water Sentinel Chemistry Sampling kits as match. They are pleased to have so many new steam monitoring volunteers but were happy with FLOW finding suitable sampling locations. Ohio Water Resources Center is helping coordinate volunteers’ involvement and interest in water resources by organizing sampling and data dissemination while getting staff support and volunteer recruitment and organization from FLOW.
- b. Project Activities:** The list of our main activities since last reporting period are presented in the table below, more detailed description follows.

Activity	Description	Frequency	#Participants
<b>Coordination meeting</b>	Meeting between FLOW, Ohio WRC and Sierra Club Central Ohio Chapter to discuss program coordination	1	6
<b>FLOW Water Steward Facebook Group</b>	Private Facebook group for only water stewards, used for sharing photos, materials, sampling inquiries etc.	4 posts /month	42
<b>Scouting Tributaries</b>	Finding new sampling locations on new tributaries for our program	3	3
<b>FLOW Public Meeting</b>	What is watershed and Adopt Your Waterway program introduction	1	30
<b>WARN Training</b>	Water Alert Reporting Network – broad public education on watershed issues, organized in conjunction with Ohio Chapter of Sierra Club	3	50
<b>Water Sentinel Training</b>	Hands-on volunteer training to use Sierra Club equipment for measurement of physical and chemical water quality parameters	3	39
<b>Macro-invertebrates Training</b>	Hands-on volunteer training to sample and recognize macroinvertebrates	1	17
<b>Train the Trainer Session</b>	Training the new trainers in FLOW and Sierra Club methods, preparing training materials for trainers	1	6
<b>Spring Stream Monitoring</b>	We sampled the four tributaries and eight locations from last year – some volunteers asked for trainers helps. We also sampled additional 9 tributaries, some of them having two locations. These were coordinated with trainers and provided additional training for the volunteers.	23	52

<b>Summer Stream Monitoring</b>	We sampled 21 locations at 11 tributaries (some have two locations) between 7/7/2016 to 9/5/2016	23	46
<b>Fall Stream Monitoring</b>	We sampled 21 locations at 11 tributaries (some have two locations) between 9/15/2016 – 11/10/2016. Volunteers send data files to FLOW and record it on Sierra Club's Water Sentinel page	23	46
<b>WARN Events</b>	Possible pollution events were sent to FLOW and Laura Fay contacted appropriate people to investigate	3	3
<b>Survey of Volunteers</b>	Online survey was sent to volunteers (n=44) to give us feedback about the program	1	18
<b>Newsletter</b>	Article in the Fall FLOW newsletter delivered to 500 members. E-Newsletter is also available on-line	1	500
<b>Water Steward Annual Meeting</b>	Meeting with our volunteers to present the sampling results and discuss program and plans for next year	1	20

**Coordination Meeting** – the proposal collaborators FLOW, Ohio WRC and Ohio Chapter Sierra Club met in March to discuss and coordinate this year's program

**FLOW Water Stewards' Facebook group** posts were for sampling reminders, sampling photos and occasional communication. By the end of the year some people posted macroinvertebrate photos to help with identification and others posted requests for sampling coordination (i.e. looking for sampling help). During our water steward annual meeting, we discussed broader use of the group or other "group platform" to create a photo album of our area macroinvertebrates and communicate more frequently about sampling help, macroinvertebrate identification and other training opportunities.

**Scouting Tributaries** – new sampling tributaries and their location were identified early in the season (February, March), so we have location to sample for all our new volunteers. In total 19 new sampling locations were identified. We created online sign in sheet for volunteers so they can pick desirable sites. Once the volunteers were divided into sampling groups (after the sentinel training), we assigned a trainer to each of the groups that coordinated the sampling, went with first time volunteers to sample, made sure data are recorded and transferred to FLOW and Sierra Club websites.

**FLOW Public Meeting** – FLOW organized public meeting in March about the Adopt Your Watershed program. Many people who signed via FLOW website to volunteer for FLOW attended this meeting and were recruited for the program. FLOW also presented information about all of our local programs to Stone Laboratory staff and students in November 2015, resulting in new 2016 volunteers from the Buckeye Friends of Stone Lab.

**WARN Training** – Ohio Chapter Sierra Club conducted 3 separate Water Alert Reporting Network training for our program, where about 50 citizens attended. The first WARN training in 2016 was organized in January, second in March and third in the beginning of May. We advertised the first two WARN trainings broadly via emails and program presentations.

**Water Sentinel Training** – two of these were conducted by Ohio Chapter Sierra Club for our program. We trained 39 volunteers on methods of chemical and physical water monitoring using meter and testing strips. Volunteers were put into preliminary sampling groups and the sentinel sampling kits were distributed.

**Macroinvertebrates Training** – We conducted one hands-on macroinvertebrates training by Adena Brook in early May. 17 volunteers attended this training. The volunteers were additionally trained at their sites by trainer during their first sampling session in the spring.

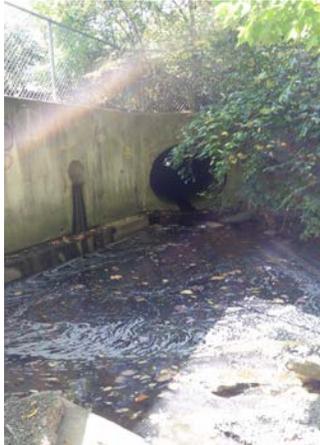
**Train the Trainer Session** – We met with our trainers (see table below) and discussed the program and their responsibilities. We created trainer guidance document for trainers (Appendix A).

Trainer	Tributaries
<b>Zuzana Bohrerova</b> – last year’s group	Glen Echo A+B, Adena Brook A+B, Turkey Run A and Kempton Run A+B
<b>Doug Berube</b>	Rush Run A+B
<b>Kris McKinnon</b>	Slyh Run A+B and Turkey Run B
<b>Joe Bevan</b>	Bill Moose Run A+B and Walhalla
<b>Erin Monaco</b>	Ackerman Run A+B
<b>Kim Banks</b>	Coe Ditch and Fisher Run
<b>Marci Bird</b>	Wildcat Run A+B and Big Run A+B
<b>Danielle Johnson</b>	All

**Spring, Summer and Fall Stream Monitoring** - Our volunteers sampled 21 locations at 11 tributaries (Appendix B). Most of the locations have been sampled three times (2016’s new locations) during this grant, some of them already have five sampling points (2015 locations). Photos from the sampling are attached by the end of the document. Although there is a limited amount of data to perform analysis on or talk about trends, the data generally seem in good agreement with scientific literature (Appendix C). Some of the chemical parameters were correlated (such as conductivity and salinity, pH and alkalinity and free and total chlorine), the macroinvertebrate index was influenced strongly by water conductivity and we saw seasonal difference in macroinvertebrate diversity and differences between the different sites. Most of the sites had a fair to poor macroinvertebrate index throughout the year. The highest macroinvertebrate index/diversity was found in Adena brook, the poorest at Ackerman Run site B, Rush Run site A and Slyh Run site A (see Appendix A for some of the data summaries).

Some volunteers were able to sample independently, while other asked for additional help from a trainer. Some of the trainers became more involved in the program, helping multiple groups of volunteers and filling in when help was needed (Zuzana Bohrerova, Erin Monaco, Joe Bevan), while others were less active with the program. In the survey and during our meeting volunteers indicated scheduling problems when planning sampling and better interconnectivity and “filling in” is desired. Furthermore, some

volunteers feel unsure about proper identification of macroinvertebrate and different solutions were discussed (such as photo album, fast identification via Facebook post etc.).



Slyh Run - soap like pollution

**WARN Events** - Our volunteers reported three separate Water Alert Reporting Network pollution events, two of them were resolved. These events were on Kempton Run, Slyh Run and Adena Brook, two of the concerns were about soap scum pollution (see photo on the left) and one “milk” type pollution, respectively.

**Survey of Volunteers** - In November, we conducted an online survey of our volunteers – see the survey questions in Appendix D. The survey participation rate was 41% - 18 out of 44 of our volunteers responded to the survey. Although the participation was not large, at least one person participated per location. Survey questions are in Appendix B. As for the program, the

majority of volunteers that filled out the survey were satisfied with the program (see table below). There was some comments about the training session and we plan to add a more thorough macroinvertebrate identification training in spring. We also will post on the Facebook page more educational materials, such as training sampling videos, photos of macroinvertebrates etc.

### Stream Quality Monitoring Volunteer Survey Results 2016

#	Field	Disagree	Somewhat disagree	Neither agree nor disagree	Somewhat agree	Agree	Total
1	Volunteer training sessions at FLOW were convenient	0.00% 0	0.00% 0	0.00% 0	26.67% 4	73.33% 11	15
2	The training sessions were very useful	0.00% 0	6.25% 1	0.00% 0	50.00% 8	43.75% 7	16
3	It was easy to get along with the volunteers in my group	0.00% 0	0.00% 0	6.67% 1	6.67% 1	86.67% 13	15
4	The staff at FLOW was friendly	0.00% 0	0.00% 0	0.00% 0	6.25% 1	93.75% 15	16
5	I felt appreciated by my volunteer supervisors	0.00% 0	0.00% 0	0.00% 0	0.00% 0	100.00% 15	15
6	The facebook water steward site was useful	0.00% 0	0.00% 0	6.67% 1	33.33% 5	60.00% 9	15

**Water Steward Annual Meeting** – We held our annual meeting on the first Monday of December in order to appreciate the work of our volunteers, network, present this year data sampling results and discuss the program with our volunteers. Additionally, during the fall we also discovered that some of the Sierra Club Water Sentinel testing strips were expiring, so we asked volunteers to return their kits in order to update them and exchange expired parts. We awarded a Water Steward Certificate to volunteers that sampled with us for at least two years (Appendix E), to show our appreciation and motivate this year’s volunteers to continue. We also prepared short presentation (Appendix F) during which present volunteers asked many questions and gave us important suggestion. We talked

about the best social platform for communication and will further explore this topic. We discussed our plans of presenting the monitoring results in a more publically digestible form, such as a watershed score card, and got a lot of input and some volunteers were interested in helping with this part of the program. We also heard about some of the problems volunteers encountered, such as difficulty finding common time with their sampling partner, or difficulty in identification. It was suggested that there are people “on call” that can jump in and sample if needed. This was already somewhat done this sampling season, but could be formalized and improved by more having more people in this position. The meeting was a big success, the volunteers that attended showed high interest in the program.

- c. **Attendance** – Per our proposal, the trainers were following up with volunteers and reminding them to sample in the summer and fall, record data on Sierra Club’s website and send data sheets to FLOW. We lost contact with one of the trainers (Kim Banks), and one sampling event after that we did not manage to keep the contact with the volunteers at her sites (Coe Ditch and Fisher Run) and the sites ceased being monitored. This experience made it clear for us that trainers are an integral part of the program and maintaining the program without trainers or “site champions” would be hard.

Furthermore, many site volunteers from last year (about half) needed help on their sampling site due to their uncertainty with the sampling protocols, or due to unexpected circumstances or their site volunteers ceasing monitoring. In those instances, trainer would help with sampling and that helped with consistent monitoring of those sites. More connectivity between the trainers and the citizen monitors will be important for the project longevity and volunteer retention.

Currently our volunteers are a diverse group of people including retirees, young professionals, OSU students, and Upper Arlington high school students along with their science teacher. Seven Science Classes at Upper Arlington High School are each monitoring a location on Turkey Run and helping us with other educational projects like videos, calendars and write ups for our Watershed Wiki! We also have two OSU student organizations involved in our program – TerAqua and Buckeye Friends of the Stone Lab (BFOSL). The Ohio Sea Grant (Erin Monaco) is coordinating BFOSL students, but also helped as a trainer with macroinvertebrate identification, training and sampling on other sites.

- d. **Highlights** – The majority of our sampling sites had active volunteers and were monitored three times this year. Some of the trainers went above and beyond their responsibilities (like Erin Monaco and Joe Bevan) and helped the program tremendously. One of the biggest highlights of this reporting period was the Water Stewards meeting, where volunteers were discussing the program and coming up with practical solutions and ideas to make the program continuing success.
- e. **Educational objectives:** We managed to train large number of citizens in Sierra Club’s WARN (Water Alert Reporting Network) and water quality monitoring

methods. Over 45 of these in classroom and hands on trained volunteers did at least one additional in field monitoring with a trainer and with other volunteers. About 30 volunteers have been consistently sampling the whole season and gained additional experience in understanding their stream and the monitoring technique. Additional training materials were posted on the Facebook page, ranging from book recommendations, and data ranges for chemical parameter in healthy streams. After each sampling season the results were posted in an easy map format as well. We are further working on making the data more accessible for our volunteers but also for their neighbors and broader public. Some volunteers became more interested in their stream quality and noticed some of the stormwater effects – like erosion – and relationships between maintained lawns and high nutrients concentrations. Surprisingly, many of the volunteers did not feel confident in macroinvertebrate identification after the training and hands on sampling with trainer and needed further help and involvement of trainers or more experienced volunteers. In the survey, volunteers suggested that pairing less experienced with more experienced volunteers would be helpful. Additionally, many of the longer term volunteers were not interested in becoming trainers or getting more involved possibly due to their uncertainty with the methods and time limitations. In the survey, our volunteers indicated that they talked about the program with their neighbors and friends, which is a desirable outcome of our program. Surveyed volunteers indicated interest in further education to understand their watersheds or measured variables, which we will try to enable them to do by posting educational events of other partners in the watershed.

**f. Listing Materials Produced**

Volunteer Survey

Flow Water Steward Facebook Page

FLOW Water Steward Certificate

Public Meeting Water Steward Program Presentation

FLOW Fall 2016 Newsletter

## Appendix A. Trainer Responsibilities Instructions

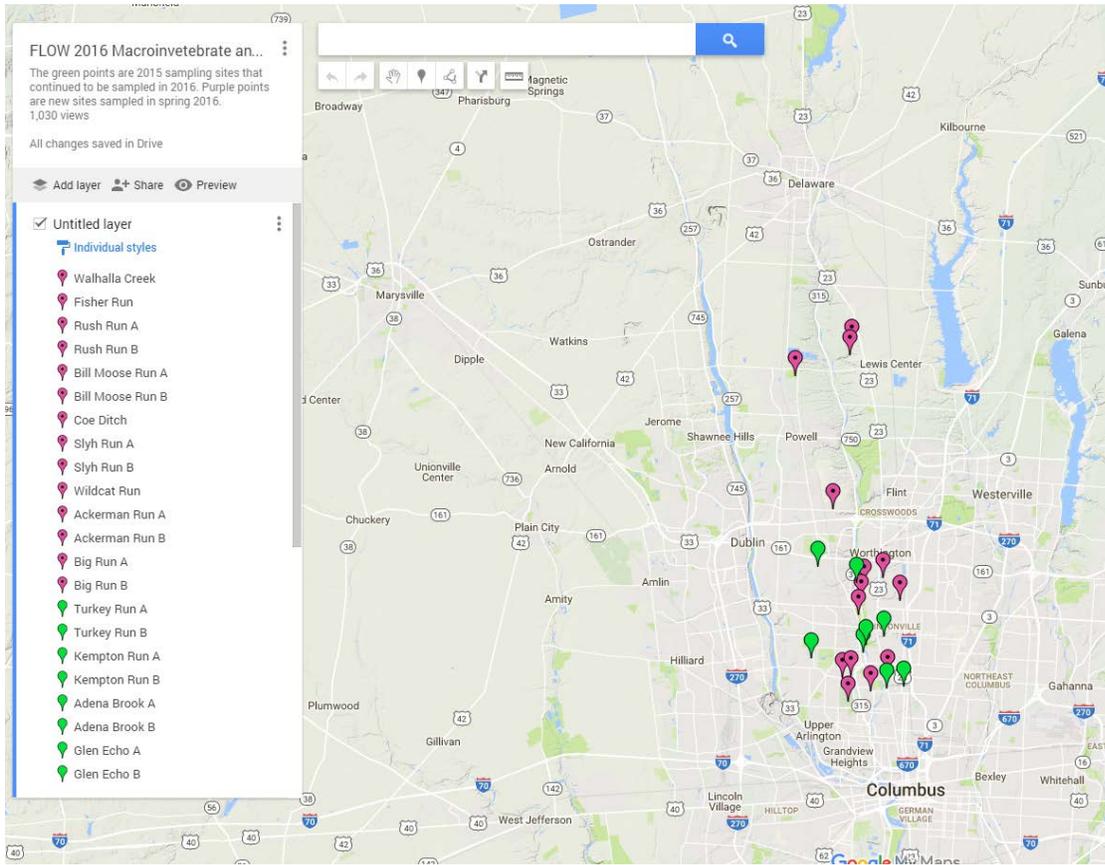
### FLOW Water Steward Area Leader Role and Responsibility

- 1) **Site selection** – You will be assigned a site (or several sites) with volunteers by FLOW. Please make sure whether you need to contact someone on the site prior going to sample (such as Ohio School for Deaf on Bill Moose Run B) – it is always good to make sure people know that FLOW volunteers are sampling. You can check with FLOW about the conditions of your particular sites.
- 2) **First Sampling** – You will need to go with your team(s) to their site and do a complete sampling with them, as this is the final phase of their training. This will include...
  - a. Distributing sampling kits – 1 sentinel and 1 macro kit per site, volunteers can decide who wants to hold what. Kits owners MUST sign lease forms.
  - b. Measuring out a 100 foot reach within which they will sample. The teams will take a picture, set a gps coordinate or find a tree or other fixed object to remember the start and finish points of the reach so that the data over the years is consistently taken within these points.
  - c. Add immediately GPS coordinates into sampling sheets and use them consistently.
  - d. Helping (working with) the Water Sentinel Trained team members to do the water chemistry sampling.
  - e. Training those team members that need macro invert training and working with others that need to have help with their ID'ing.
  - f. Showing the folks how to tally the data and fill in the forms.
- 3) **Additional Sampling:**
  - a. Follow up with teams to make sure that they are getting out to do the sampling 3 times a year (once per spring, summer, fall season)
  - b. Make sure that teams are submitting their data to FLOW at: [info@olentangywatershed.org](mailto:info@olentangywatershed.org) via a camera shot or scan. AND that they are submitting their data to the Water Sentinel system of the Sierra Club <https://docs.google.com/forms/d/1wEfJWrUPKCDYxxdq3YMui2fIXOFFbje11uyv5j0IEMO/viewform?formkey=dGtZG1aQU12VHdnY1VEMFVgMmo1Nmc6MQ#gid=0>
  - c. Answer questions from your team regarding timing of sampling
    - i. 48hours after rain is not always required depending on the rain event. Typical months to sample: May, July and September
    - ii. We would rather get three samples per year than not so if the dates are not 2 months apart, it is generally OK.
  - d. Help team problem solve
    - i. How to ID a macro that is hard to ID
    - ii. How to replace equipment that is broken (intermediary with FLOW)
  - e. Act as a substitute or correlate a substitute from another of your teams when necessary

**Remember, be available for the volunteers and take tons of photos!!!**

## Appendix B – Sampling Location Map:

[https://www.google.com/maps/d/u/0/edit?mid=1OCXPHgUi5R4aHf\\_9iITGAz5MBS0&ll=40.15001641395445%2C-83.00653957355956&z=11](https://www.google.com/maps/d/u/0/edit?mid=1OCXPHgUi5R4aHf_9iITGAz5MBS0&ll=40.15001641395445%2C-83.00653957355956&z=11)

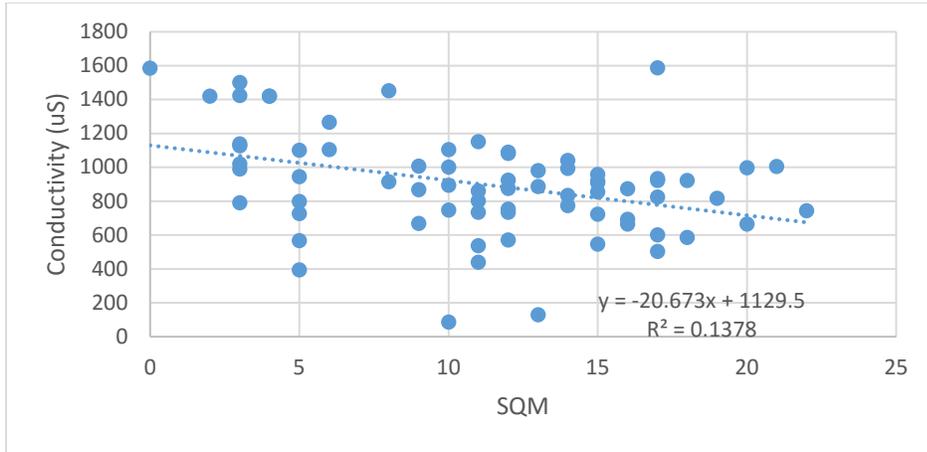


## Appendix C – Data summary and analysis

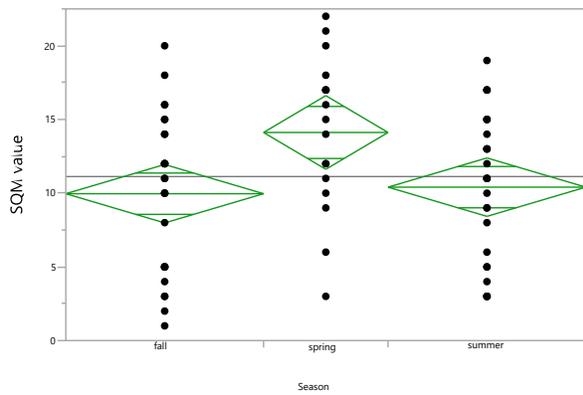
Average Values of Selected Parameters (SQM= macroinvertebrates)

Location	SQM	Phosphate	Nitrate	TDS	Conduct
Adena Brook A	17	1.0	0.7	528	755
Adena Brook B	17	5.0	0.8	437	725
Wildcat Run C	15	6.7	0.5	470	927
Kempton Run A	14	0.0	2.8	333	672
Kempton Run B	13	6.0	0.5	549	784
Ackerman Run A	13	5.0	8.3	551	633
Bill Moose Run A	12	13.3	0.1	696	991
Walhalla	12	28.3	0.5	709	956
Rush Run B	12	5.0	0.0	841	1048
Wildcat Run B	12	0.0	1.5	678	967
Glen Echo B	12	5.0	1.1	619	766
Turkey Run B	11	12.5	0.4	836	942
Slyh Run B	11	5.0	2.0	971	1343
Big Run A	10	0.0	2.0	541	763
Big Run B	9	0.0	2.0	526	766
Bill Moose Run B	9	3.3	0.2	575	796
Glen Echo A	8	8.8	0.3	713	1021
Turkey Run A	7	8.8	0.8	564	755
Rush Run A	5	0.0	0.3	813	1079
Slyh Run A	5	18.5	2.8	815	1422
Ackerman Run B	3	8.3	0.2	697	1446

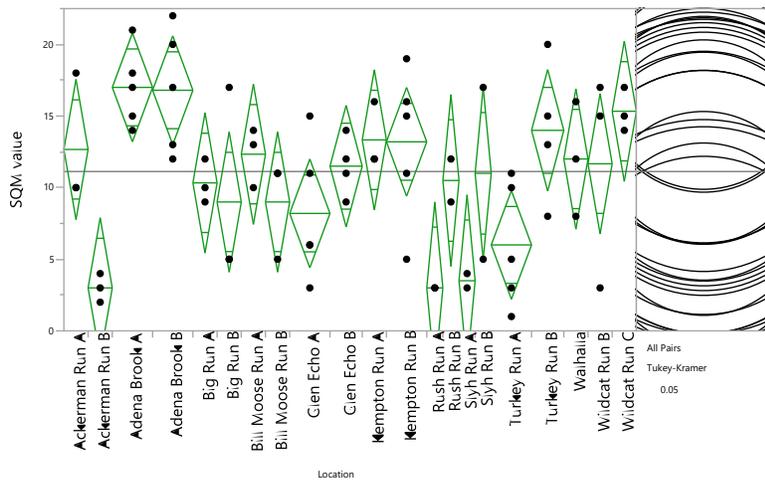
## Conductivity vs SQM



## Seasonal Differences – all sites pooled together



## SQM Index by location



## Appendix D – Survey Questions for Stream Quality Monitoring Volunteers

FLOW Water Stewards Survey – Name \_\_\_\_\_

Q1 What prompted you to participate in the program?

Q2 What support, tools or practices have been most helpful in your time as a volunteer with the program?

Q3 Please provide a specific example of a hurdle you faced in volunteering with this program? What do you think would have helped you?

Q4 Have you encouraged others to get involved with the program? If so how?

Q5 What suggestions would you offer volunteers new to the program?

Q6 If you could change one thing about the program, what would it be?

Q7 How much of an impact do you feel your volunteer work had?

- A great deal (1)
- A lot (2)
- A moderate amount (3)
- A little (4)
- None at all (5) \_\_\_\_\_

Q8 Please fill in this table how you agree or disagree with the statement

	Disagree (1)	Somewhat disagree (2)	Neither agree nor disagree (3)	Somewhat agree (4)	Agree (5)	N/A (6)
Volunteer training sessions at FLOW were convenient (1)	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
The training sessions were very useful (2)	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
It was easy to get along with the volunteers in my group (3)	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
The staff at FLOW was friendly (4)	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
I felt appreciated by my volunteer supervisors (5)	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
The Facebook water steward site was useful (6)	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>

Q9 Overall, were you satisfied with your volunteer experience with FLOW?

- Extremely satisfied (1)
- Quite satisfied (2)
- Somewhat satisfied (3)
- Neither satisfied nor dissatisfied (4)
- Somewhat dissatisfied (5)
- Quite dissatisfied (6)
- Extremely dissatisfied (7)

Q10 How likely are you to continue volunteering at FLOW in the future?

- Extremely likely (1)
- Quite likely (2)
- Moderately likely (3)
- Slightly likely (4)
- Not at all likely (5)

Q11 How likely are you to recommend FLOW to others as a place to volunteer?

- Extremely likely (1)
- Quite likely (2)
- Moderately likely (3)
- Slightly likely (4)
- Not at all likely (5)

Q12 How hard was it to coordinate sampling dates/times with other volunteers at your site?

- Extremely easy (1)
- Slightly easy (2)
- Neither easy nor difficult (3)
- Slightly difficult (4)
- Extremely difficult (5)

Q13 Do you need additional volunteers/help at your site?

- Yes (1) \_\_\_\_\_
- Maybe (2)
- No (3)

Q14 Do you recommend your site for future sampling?

- Yes (1)
- Maybe (2)
- No (3) \_\_\_\_\_

Q15 Are you willing to sample for FLOW next year?

- Yes (1)
- Maybe (2)
- No (3) \_\_\_\_\_

Q16 Are you satisfied with your sampling site?

- Yes (1)
- Maybe (2)
- No (3) \_\_\_\_\_

Q17 Do you need additional supplies for sampling?

- Yes (1) \_\_\_\_\_
- Maybe (2)
- No (3)

Q18 Other Comments

**Appendix E. FLOW water steward certificate**



*Certificate of Appreciation*

This certificate is awarded to **FLOW WATER STEWARD**

**KYLIENNE CLARK**

in recognition of valuable contributions towards water quality monitoring of Olentangy River tributaries, Columbus OH

*Luzana Bohrerova, FLOW Science Committee*

*12/5/2016*

*Photo of Big Run, Olentangy River Tributary*

# Appendix F. Public Meeting Water Steward Program Presentation

**FLOW Water Stewards program**

Friends of the Lower Olentangy  
Sierra Club - Ohio Chapter  
Ohio Water Resources Center  
Citizen Scientists

### Program Overview

<p><b>2015 – summer, fall</b></p> <ul style="list-style-type: none"> <li>• 4 tributaries, 2 sites each</li> <li>• About 14 volunteers and 2 student groups</li> <li>• Dedicated FLOW staff (Roxanne)</li> </ul>	<p><b>2016 – spring, summer, fall</b></p> <ul style="list-style-type: none"> <li>• 11 tributaries, 21 sites</li> <li>• About 38 volunteers and 3 student groups BFOSL, TerrAqua and UA highschool</li> <li>• Dedicated FLOW staff – Marci, Joe, Danielle</li> <li>• Trainers – Zuzana, Lisa, Marci, Kristen, Joe</li> </ul>
---	---

### Data

- [Water Sentinel Maps](http://www.sierraclub.org/ohio/water-sentinel-maps)  
<http://www.sierraclub.org/ohio/water-sentinel-maps>
- [FLOW SQM](#)
- [FLOW Wiki](http://wiki.oleantangywatershed.org/home)  
<http://wiki.oleantangywatershed.org/home>

### Locations

South of 270 - inner      North of 270

Legend  
SQM  
● Good  
● Fair  
● Poor

### Location, location - Macro

- Adena Brook both locations consistently best in terms of macroinvertebrates
- Turkey Run A, Slyh Run A and Rush Run A (upstream) and Ackerman Run B worse

### Season Macro

1 year data! Not conclusive year specific etc.

## Chemistry – Sierra Club sentinel

Optimum Values	Tributaries
pH 6.5 – 9.0	None lower than 6.5, strips measure until 8.4
Conductivity 150-500 uS	All higher than 500 uS, Ackerman Run B year average 1446 (worse), Adena Brook A year average 755 (best)
Salinity <1000 ppm (desirable <500 ppm)	None higher than 1000, 33% samples higher than 500
TDS 50-250 mg/L healthy (<500)	Almost all higher than 250, majority higher than 500
Hardness 15-375 ppm	Most samples within this range
Alkalinity 20-260 mg/L	Most 180 or 240 or higher
Nitrate <0.6 mg/L (1.0 mg/L Ohio EPA, 1.5 mg/L eutrophic streams)	30% samples more than 0.5, in average 33% locations eutrophic, Kempton Run A and Slyh Run A 2.8 mg/L, Ackerman Run A highest 8.3 mg/L
Phosphate <0.1 mg/L	54% of samples higher than 0.1

## Chemical Parameters vs SQM

	Temperature	TDS mg/L	Conductivity uS	Salinity ppm	Total Hardness ppm	Total Chloride ppm	Free Chlorine	Alkalinity	pH	Nitrate ppm	Phosphate ppm	SQM Index	
Temperature	1.0000												
TDS mg/L	0.3003	1.0000											
Conductivity uS	0.0864	0.5764	1.0000										
Salinity ppm	0.3097	0.6963	0.6488	1.0000									
Total Hardness ppm	-0.0566	0.3703	0.3776	0.4211	1.0000								
Total Chloride ppm	-0.1329	-0.1734	0.0909	-0.0797	-0.2112	1.0000							
Free Chlorine	-0.1747	0.0108	0.2235	-0.0119	-0.0635	0.5346	1.0000						
Alkalinity	0.1220	0.2305	0.2916	0.2605	-0.1271	-0.2566	-0.0618	1.0000					
pH	0.2402	0.3205	0.3489	0.1905	0.2054	-0.2964	-0.0225	0.9666	1.0000				
Nitrate ppm	0.0070	0.0087	-0.0130	-0.0553	0.0563	0.0536	0.0607	-0.0775	-0.0449	1.0000			
Nitrite	-0.0739	0.1385	0.0969	0.0882	0.0280	0.0755	-0.0481	0.1175	0.1238	-0.0260	1.0000		
Phosphate ppm	0.1650	0.2373	0.3311	0.3827	-0.0194	-0.0070	0.0642	-0.1763	0.0573	-0.1688	0.1278	1.0000	
SQM value	-0.0763	-0.2328	-0.2798	-0.3897	-0.0815	-0.0870	-0.0270	-0.0159	-0.1946	-0.0419	-0.0423	-0.0488	1.0000

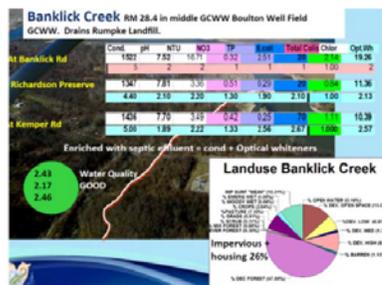
## Chemical Parameters vs SQM

- Conductivity (as well as TDS and salinity) had significant effect on the SQM value (macroinvertebrates diversity)
- Flow (low versus high) had marginal effect on SQM value



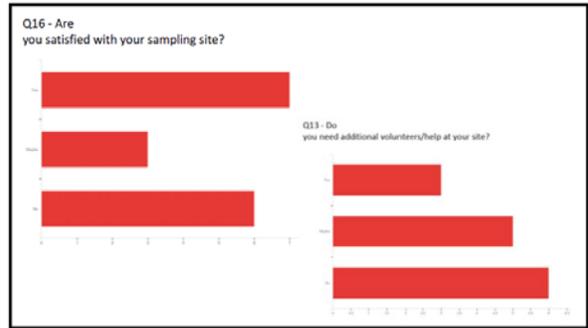
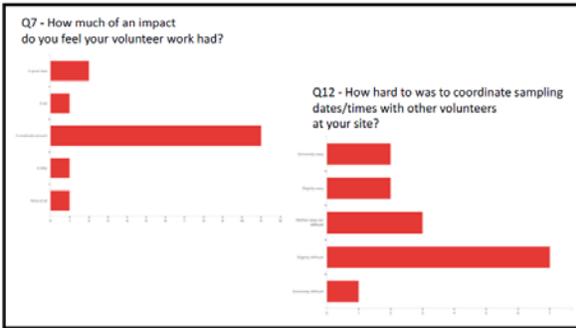
## How are these data valuable?

- Getting people to the streams – more eyes on the streams – “WARN” events
- Getting first peak on tributaries water quality and hope to see improving trend (Blue Print Columbus, FLOW honeysuckle removal, Ackerman run future restoration etc.)
- Data will guide FLOW activities by identification of critical areas/hot spots
- In process of writing grant to create easily digestible “score card” about water quality that can be distributed more widely



## Survey preliminary results/remarks

- Survey sent to 44 people, about 17 responses so far
- Most respondent satisfied with volunteering experience and will continue to monitor next year, will recommend FLOW to other volunteers.



### 2017 Plan

- Not adding additional sites
- Training more volunteers to fill in sites that need help
- Changing sites for those who need it
- Renewing supplies for sites
- Preparing more materials for volunteers and sites – educational materials
- Letting you know about additional training opportunities



### Other

- Let us know if you won't be able to sample next year
- Please make sure you are part of the FLOW Water Steward facebook page – a lot of information is published there
- Please fill in the survey if you did not do so yet...





## Photos



Marcoinvertebrate Hands-On Training, May 2016



Water Sentinel sampling on Ackerman Run, spring 2016



Rush Run macroinvertebrates sampling, fall 2016



Volunteer Stream Quality Monitoring Feedback Session, December 2016

# Prevention of harmful algal blooms through nutrient zero wastewater treatment using a vertical membrane bioreactor with food waste

## Basic Information

<b>Title:</b>	Prevention of harmful algal blooms through nutrient zero wastewater treatment using a vertical membrane bioreactor with food waste
<b>Project Number:</b>	2016OH5420
<b>Start Date:</b>	6/1/2016
<b>End Date:</b>	8/31/2017
<b>Funding Source:</b>	Other
<b>Congressional District:</b>	OH-001
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Education, Nutrients, Treatment
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Zuzana Bohrerova

## Publications

There are no publications.

## Title: **Management Of Algal Growth In Ohio's Medium-Sized Lakes**

PI: Zuzana Bohrerova, OSU Ohio WRC

co-PI/collaborators: Joe Bonnell, Eugene Braig, and Ashley Kulhanek, OSU extension; Susan James, Ohio Lake Management Society

Funded by OSU CARES program

### **Summary**

We created a new partnership between OSU Extension personnel and the Ohio Water Resources Center to leverage our resources and initiate research, education and outreach to address sustainable algal management of Ohio's medium-sized lakes. Medium-sized lakes are frequently managed by multiple private owners or homeowner associations and are currently highly underserved in Ohio. Managers of medium-sized lakes often act on limited information and in isolation from other lake managers. However, if informed and supported properly, these locations might be the optimal "testing beds" for new and sustainable lake management technologies. This funding initiated a Lake Management Stewardship program in Medina County with potential to grow and develop in other counties. Medina County Soil and Water Conservation District estimated that the county has around 7800 impoundments of ponds and lake, making it number one in Ohio. From our survey and interaction with medium-size lake managers, majority relayed on advice on consultant treating their lake. Although the project year was one of the lowest on algae occurrence, most of the lakes under investigation were chemically treated for algae though owners did not indicate algal problems or knowledge about water quality of their lake. The surveyed lakes water quality was high, with microcystin concentrations below detection limit and very low or below detection limit concentrations of chlorophyll A and total phosphorous. The rest of the project will focus on more water quality sampling and development of educational materials and training of pond owners.

### **Work accomplished - progress**

The overarching program goal is to improve knowledge and interaction of managers of medium-sized lakes and encourage more sustainable and novel lake management practices.

#### Objectives:

- 1) Evaluate current methods of lake management in Medina County and the current educational resources used by water managers

We identified twenty-nine pond owners in Medina County that might fit our study requirements (medium size pond owned by multiple owners) via pond clinics organized by Medina County Soil and Water Conservation District and via news release in local newspaper. We sent surveys to these owners (see attachment A for survey) and received 15 filled surveys back (52% participation rate). Survey results confirmed our hypothesis and showed that nine pond owners relayed only on the private consultant advice. Additionally, only two lakes were not chemically treated for algae, although pond owners are not aware of any prior water quality testing on their ponds (except of 1) and majority of them do not report any previous algal problems.

- 2) Monitor basic water quality of selected medium-sized lakes during the summer season

Quality monitoring during the summer of 2016. Each lake was visited at least four times during the season. Citizen Lake Awareness and Monitoring (CLAM) methods were used monitoring parameters such as Secchi disk depth (indicator of eutrophication), water color, water temperature, depth and waves. Furthermore, water was analyzed on site every half feet for temperature (oC), dissolved oxygen (mg/L), pH, turbidity (NTU), and conductivity (uS/cm2), and for phycocyanin and chlorophyll a. Once a season sample was collected from each of the lake for more in depth laboratory analysis. The summary of these results is shown in table 1 below.

Lake	Total Phosphorous (mg/L)	Total Chlorophyll (mg/L)	Microcystin (ppb)
Mallard	0.07	0.07 (BDL)	0.08 (BDL)
Wolf	0.03	0.05 (BDL)	0.09 (BDL)
Sunset	0.10	0.18	0.10 (BDL)
Granger	0.00 (BDL)	0.01 (BDL)	0.07 (BDL)
<b>Detection limit</b>	0.02	0.08	0.15

BDL = Below detection limit = zero

In general, most of the parameters of interest were low or below detection limit. Summer of 2016 was generally low in terms of algae blooms in Ohio lakes and the project was extended to summer 2017 so that one more season can be analyzed.

3) Create educational materials for managers of medium-sized lakes based on identified needs

Currently we are in the process of creating concise educational materials for managers. Our survey confirmed that lake managers are lacking support for their lake management and rely on recommendation of companies that sells them product.

In addition, we are preparing pond management training for people that responded to our survey and this workshop was scheduled for May 6<sup>th</sup> (see draft of the invite in attachment B). We will present some typical management techniques to lake managers and introduce pond owners to Secchi disk analysis via CLAM workshop. The owners will be encouraged to use this measurement as an early indicator of water quality problems. Secchi disk kits will be provided to lake managers as a part of this project.

4) Assess outcomes of the partnership and materials – this will be concluded by the end of the project

**Project impact**

Currently in the beginning of this project we gained valuable information about current medium-size lake management practices in Medina county. We also got some data on private sites that were not analyzed for many years (at least five) and saw lake stratification during our visits. Sometimes we observed methods used that were not very practical and one of the sites reported massive fish kills the year before our project. The collaborators on this project leveraged expertise and resources. The Ohio Water Resources Center was able to analyze water samples in the laboratory, OSU extension Eugene Braig provided his expertise in pond management and OSU extension expert Joe Bonnell conducted the survey. Ashley Kulhanek, the OSU Medina county extension personnel was able to put us in contact with pond owners and will learn about water quality and pond management techniques during our training.

**Attachments**

**Attachment A** – Participation Survey

**Attachment B** – Pond managers workshop

Please answer the following questions as best you can. You may skip any questions you feel uncomfortable answering.

## Developing Educational Programs and Materials for Managers of Medium-sized Lakes in Ohio

### 1. Who was involved in responding to this survey?

Myself	<input type="checkbox"/>
Members of the designated lake management committee	<input type="checkbox"/>
Members of the homeowners association	<input type="checkbox"/>
Private consultant	<input type="checkbox"/>
Other (please explain)	<input type="checkbox"/>

### 2. What is the approximate surface area of the lake you manage?

_____ Acres
_____ Check here if you don't know

3. Approximately how many owners have some say in how the lake is managed? Number of owners:

Please provide any additional information that will help us understand who is involved in making lake management decisions for your lake.

4. Which of the following recreational activities occur on the lake?

*(Check all that apply.)*

Swimming	<input type="checkbox"/>
Fishing	<input type="checkbox"/>
Boating	<input type="checkbox"/>
None	<input type="checkbox"/>
Other (please explain)	<input type="checkbox"/>

## 5. What was the original purpose of the lake?

*(Check all that apply.)*

Recreation	<input type="checkbox"/>
Flood risk reduction	<input type="checkbox"/>
Storm water retention/detention	<input type="checkbox"/>
Other (please explain)	<input type="checkbox"/>

## 6. Who is involved in making management decisions for this lake?

*(Check all that apply.)*

Myself	<input type="checkbox"/>
Designated lake management committee	<input type="checkbox"/>
Homeowners association	<input type="checkbox"/>
Other private owners	<input type="checkbox"/>
Private consultant / company	<input type="checkbox"/>
Other (please explain)	<input type="checkbox"/>

7. Please describe the training and experience in lake management of the individual(s) with the primary responsibility for making lake management decisions.

8. What resources do you individually or as a group typically rely on for information about lake management techniques?

*(Check all that apply.)*

Books/Manuals	<input type="checkbox"/>
Private consultant	<input type="checkbox"/>
Other lake managers	<input type="checkbox"/>
OSU Extension	<input type="checkbox"/>
Ohio Lake Management Society	<input type="checkbox"/>
Herbicide or other product sales representative	<input type="checkbox"/>
Herbicide or other product label recommendations	<input type="checkbox"/>
Websites (please provide examples)	<input type="checkbox"/>
Other (please explain)	<input type="checkbox"/>

## 9. What are your primary lake management concerns?

*(Check all that apply.)*

Algal growth for:	
Aesthetics	<input type="checkbox"/>
Swimming	<input type="checkbox"/>
Boating	<input type="checkbox"/>
Fishing	<input type="checkbox"/>
Emergent vegetation (e.g., cattails)	<input type="checkbox"/>
Water levels for recreation	<input type="checkbox"/>
Shoreline erosion	<input type="checkbox"/>
Fisheries	<input type="checkbox"/>
Water levels for storm water retention / detention	<input type="checkbox"/>
Other (please explain)	<input type="checkbox"/>

## 10. Have you applied herbicides or other chemicals to the lake in the past five years?

*(Check all that apply.)*

Yes <input type="checkbox"/>
No <input type="checkbox"/>
Don't know <input type="checkbox"/>
If yes, what did you apply and for what reason?

**11. Is anyone sampling and testing for water quality in the lake?**

Yes <input type="checkbox"/>
No <input type="checkbox"/>
Don't know <input type="checkbox"/>
If yes, what parameters are tested for (e.g., clarity, nitrogen, phosphorus)?
Who conducts the tests?

**12. Have water quality problems been identified in the lake in the past five years?**

Yes <input type="checkbox"/>
No <input type="checkbox"/>
If yes, what issues were identified?
What strategies were used to address these issues?

**13. Would you be willing to be contacted by a member of our team to gather more information about your lake?**

Yes *	<input type="checkbox"/>
No	<input type="checkbox"/>

\* If yes, please be sure to fill out the name and contact information in the bottom section of the cover letter and mail it back with your survey.

**14. Are you interested in having your lake water sampled and tested for water quality?**

Yes *	<input type="checkbox"/>
No	<input type="checkbox"/>

**15. Would you or members of your group be interested in attending a program on lake management strategies and techniques?**

Yes *	<input type="checkbox"/>
No	<input type="checkbox"/>

\* Note: Responding 'Yes' does not guarantee that you will be contacted or provided these services. Limited funding is available for water testing and educational programs and we may not be able to serve all interested parties.

# Small Lake Management Workshop

MAY 6, 2017

9:00 AM – 12:00 PM

FREE to study participants!

Hello Pond Study Participants!

FREE MATERIALS TO  
TAKE HOME!

It seems so long since you completed the OSU Extension pond surveys for your large, multi-property pond! To thank you for your participation, and prepare you for pond season, we are offering a **training designed especially for YOU!**

## **We will cover:**

**Pond Management:** Eugene Braig, Program Director for Aquatic Ecosystems with the School of Environment and Natural Resources, will be joining us to talk about managing large ponds and lakes for long-term health! Learn about aeration, algae, pond weeds, muck and more. How do ponds age and what can we do to keep them young? Fish management, water quality and more.

**Citizen Lake Awareness & Monitoring Training:** Join Susan James, of Ohio Lake Management Society, to learn about taking meaningful measurements in your lakes and ponds. Every property will receive a Secchi disk and training to use at your own ponds and lakes.



While Free, Please RSVP! We need to know how many people are attending from each property.



**DATE:** May 6, 2017

**TIME:** 9:00 AM– 12:00 PM

**COST:** FREE

Light snacks included

**LOCATION:** Letha House West

5800 Richman Rd. , Spencer, OH 44275

**RSVP by May 2, 2017 330-725-4911 X106**

*Questions? Please contact Eugene Braig, Project Leader*

*Please RSVP Ashley Kulhanek, Medina County Extension as your local contact*

**Ashley Kulhanek, MS**

OSU Extension, Medina County

120 W. Washington St., Suite 1-L Medina, OH 44256

330-725-4911 X 106

[kulhanek.5@osu.edu](mailto:kulhanek.5@osu.edu)

## Contact:

**Eugene C. Braig IV** Program Director, Aquatic Ecosystems  
Ohio State University Extension

379a Kottman | 2021 Coffey Rd. Columbus, OH 43210

614-292-3823 Office

[braig.1@osu.edu](mailto:braig.1@osu.edu)

# 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>	2	0	0	3	5
<b>Masters</b>	1	0	0	1	2
<b>Ph.D.</b>	2	0	0	2	4
<b>Post-Doc.</b>	0	0	0	0	0
<b>Total</b>	5	0	0	6	11

## **Notable Awards and Achievements**

2016OH508B Best Student Poster Award at the CO2 II: Summit Technology and Opportunities Conference, which was hosted by Engineering Conferences International.

2016OH507B NSF Environmental Biology Doctoral Dissertation Improvement Grant (1601224) - The nexus of observation and modeling of methane emissions from inland water bodies (PI, thesis supervisor). With Timothy Morin (Trainee). 2016-2017, (\$19,056)

## Publications from Prior Years

1. 2014OH312B ("Scenario Analysis for the Impact of Hydraulic Fracturing on Stream Low Flows and Water Supplies: A Case Study of Muskingum Watershed in Eastern Ohio") - Articles in Refereed Scientific Journals - A Shrestha, S Sharma, CE McLean, BA Kelly, SC Martin (2017). Scenario analysis for assessing the impact of hydraulic fracturing on stream low flows using the SWAT model. Hydrological Sciences Journal, 62(5): 849-861, DOI:10.1080/02626667.2016.1235276
2. 2015OH481O ("Spatial Demand Estimation: Moving Towards Real-Time Distribution System Network Modeling") - Articles in Refereed Scientific Journals - SM Masud Rana, DL Boccelli (2016). Contaminant Spread Forecasting and Confirmatory Sampling Location Identification in a Water-Distribution System. Journal of Water Resources Planning and Management, 142(12): 1014, DOI: 10.1061/(ASCE)WR.1943-5452.0000704
3. 2014OH316B ("Surface water quality and ecosystem health with shale energy development") - Dissertations - Bond L: Impacts of Hydraulic Fracturing Infrastructure on Storm Runoff Characteristics
4. 2014OH327B ("Linked geomorphic and ecological responses to river restoration: Influence of dam removal on river channel structure and fish assemblages") - Dissertations - Dorobek, Alayna. Short-term consequences of lowhead dam removal for fish community dynamics in an urban river system