Pennsylvania Water Resources Research Center
Annual Technical Report
FY 2013

Introduction

The Pennsylvania Water Resources Research Center (PA-WRRC), founded in 1964, is authorized by Congress as one of the nation's 54 water resources research institutes comprising the National Institutes of Water Resources (NIWR). The program is administered by the U.S. Department of the Interior through the U.S. Geological Survey, in a unique Federal-State-University partnership. The PA-WRRC is located on the main campus of the Pennsylvania State University, the primary land-grant University within Pennsylvania. The Center resides administratively within, and is strongly partnered with, the Penn State Institutes of Energy & the Environment (PSIEE). Within the large Pennsylvania State University system, PSIEE and PA-WRRC are organized under the Office of the Vice President for Research.

Aligned with the land grant mission, the PA-WRRC emphasizes the role of research in solving problems of water availability (quantity and quality) and in conserving water resources. The PA-WRRC is committed to encouraging scientific research on state and regional water issues of societal relevance; and educating students and the public about water resources. Primary objectives of the Pennsylvania Water Resources Research Center are: 1) To plan, facilitate, and conduct research to help resolve water resource problems of societal relevance in Pennsylvania; 2) To promote information transfer and the dissemination and application of research results; and 3) To train water scientists, managers, and engineers through participation in water resources research and outreach. Funding priority has been given to innovative research projects addressing high priority water problems. Further, we have encouraged proposals by new faculty, projects that support students, projects that stress water resources technology transfer, and projects spanning a range of public and private educational institutions in Pennsylvania.

The PA-WRRC receives USGS 104B federal base funding that is distributed via a small grants competition to researchers at academic institutions across Pennsylvania. This fiscal year, a request for proposals for this competition was broadly disseminated. Given the level of funding available, we were able make several awards, intended to be one-year seed grants allowing faculty to initiate research programs on problems important to Pennsylvania, and to disseminate information about Pennsylvania’s water resources via information transfer activities. None of the federal funding was used to pay overhead costs, and PA-WRRC matched every dollar of its federal base appropriation with at least two dollars from non-federal sources. In addition, The PA-WRRC continues to receive significant support contributions from PSIEE, which funds the Director's time spent in water center administration and provides additional staff support for administrative, accounting, communications, and research functions.

Research Program Introduction

USGS 104B Base Administration Project:

Research Activities by PAWRRC during the project reporting period (March 1, 2013 through February 28, 2014)

In FY 13, PA-WRRC received funding via Penn State Institutes of Energy and the Environment to sponsor a high-profile water colloquium where weekly research presentations were archived for perpetual viewing (online at: http://www.psiee.psu.edu/news/2013_news/jan_2013/springWaterSeminars.asp).

Research Presentations by PAWRRC Director Elizabeth W. Boyer during the project reporting period (March 1, 2013 through February 28, 2014)

(Invited) Boyer EW. Riverine carbon loadings to the Gulf of Mexico. Ocean Carbon Biogeochemistry Workshop, Tampa, Florida, March 2013.

Britson AJ, DH Wardrop, and EW Boyer. Determining a measure of biogeochemical structure relevant to denitrification in six central Pennsylvania wetlands. Ecological Society of America, Minneapolis, MN, August 2013.

Eklöf K., Sørensen R., Schelker J., Kraus A., Åkerblom S., Meili M., Weyhenmeyer G., von Brömsen C., Laudon H., Garcia A., Bertilsson S., Skyllberg U., Björn E., Kronberg R., Boyer E.W., Drohan P.J., Lin H.S. and Bishop K. Forestry effect studies on Hg mobilization and methylation. Gordon Research Conference on Catchment Science, July 10-15, 2011, Lewiston, ME, USA.

Eklöf K., Fölster J, Sonesten L, Boyer EW and Bishop K. The importance of organic carbon characteristics for the mobilization of mercury in catchment runoff. The 11th International Conference in Mercury as a Global Pollutant, July 28 - August 2, 2013, Edinburgh, Scotland.

Iavorivska, L, EW Boyer, J Grimm, and J Fuentes. Dissolved Organic Carbon Dynamics in Precipitation of Central Pennsylvania as Influenced by Climatic Variability. Graduate Exhibition, Penn State University, March 2013. Student award for 2nd place best presentation in physical science and mathematics.

Iavorivska L, EW Boyer, J Grimm, J Fuentes. Dissolved Organic Carbon Dynamics in Precipitation of Central Pennsylvania as Influenced by Climatic Variability. Gordon Research Conference on Catchment Science, June 16-21, 2013, Proctor Academy, NH.

Lawler, D., E Boyer, and P Drohan, Effects of atmospheric mercury deposition on wetland environments of central Pennsylvania. Graduate Exhibition, Penn State University, March 2013.

Reed, B and EW Boyer. Atmospheric Deposition Effects on Water Quality in Reference Watersheds of Pennsylvania. 16th annual Environmental Chemistry Student Symposium, Penn State University, March 2013.

Tzilkowski SS, EW Boyer, A Buda, R Bryant, E May. Watershed processes controlling urea transport in a coastal plain river network. 19th annual Graduate and Undergraduate Research Expo, College of Agricultural Sciences and Gamma Sigma Delta, Penn State University, March 2013. Student award for 3rd place best presentation.

Iavorivska L, EW Boyer, J Grimm, J Fuentes. Dissolved Organic Carbon Dynamics in Precipitation of Central Pennsylvania as Influenced by Climatic Variability. Susquehanna River Basin Commission Water Science Forum, Harrisburg, PA, October 2013.

Lawler, D., E Boyer, and P Drohan, Effects of atmospheric mercury deposition on wetland environments of central Pennsylvania. Susquehanna River Basin Commission Water Science Forum, Harrisburg, PA, October 2013. Student award for 2nd place best presentation.

Reed, B and EW Boyer. Atmospheric Deposition Effects on Water Quality in Reference Watersheds of Pennsylvania. Susquehanna River Basin Commission Water Science Forum, Harrisburg, PA, October 2013.

Tzilkowski SS, EW Boyer, A Buda, R Bryant, E May. Watershed processes controlling urea transport in a coastal plain river network. Susquehanna River Basin Commission Water Science Forum, Harrisburg, PA, October 2013. Student award for 3rd place best presentation.

(Invited) Alexander RB, EW Boyer, GE Schwarz, and RA Smith. Advances in Parameter and Uncertainty Quantification Using Bayesian Hierarchical Techniques with a Spatially Referenced Watershed Model. B24B-01, American Geophysical Union, San Francisco, CA, December 2013.

Boyer EW, C Grant, J Grimm, PJ Drohan, J Bennett, and D Lawler. Wet and dry atmospheric mercury deposition accumulates in watersheds of the northeastern United States. B41C-0408. American Geophysical Union, San Francisco, CA, December 2013.

Bishop KH, J Hytteborn, J Temnerud, RB Alexander, EW Boyer, M Futter, SW Lyon, and M Winterdahl. Significant 20 Year Increases in Organic Carbon Concentrations have not changed how Intra-Annual Variability is Driven by Hydrology and Seasonality across a Boreal Landscape. B53A-0427. American Geophysical

Lawler, D, E Boyer, & P Drohan. Effects of Atmospheric Mercury Deposition on Wetland Environments. 2014 Canadian Geophysical Union, Hydrology and Biogeosciences Sections Eastern Student Conference, Toronto, Ontario, January 2014.

Herrmann, M; RG Najjar, WM Kemp, RB Alexander, & EW Boyer. Net ecosystem production and organic carbon balance of US east coast estuaries: a synthesis approach. 2014 Ocean Sciences Meeting, Honolulu, Hawaii, February 2014.

Award--Long-term Responses of Stream Chemistry to Changes in Atmospheric Deposition in Mid-Appalachian Forests of Pennsylvania

Basic Information

Title:	Award--Long-term Responses of Stream Chemistry to Changes in Atmospheric Deposition in Mid-Appalachian Forests of Pennsylvania
Project Number:	2009PA120S
Start Date:	7/1/2009
End Date:	6/30/2014
Funding Source:	Supplemental
Congressional District:	5
Research Category:	Climate and Hydrologic Processes
Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Elizabeth W. Boyer

Publications

1. Boyer, E.W., J.W. Grimm, K.S. Horner, J.S. Lynch, and M.A. Borden (2010). Atmospheric Deposition in Pennsylvania: Spatial and Temporal Variations 2009. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, 255 p.
2. Boyer, E.W., J.W. Grimm, K.S. Horner, and M.A. Borden (2010). Atmospheric Mercury Deposition in Pennsylvania in 2009. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, 65 p.
3. Boyer, E.W., J.W. Grimm, K.S. Horner, J.S. Lynch, and M.A. Borden (2010). Atmospheric Deposition in Pennsylvania: Spatial and Temporal Variations 2009. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, 255 p.
4. Boyer, E.W., J.W. Grimm, K.S. Horner, and M.A. Borden (2010). Atmospheric Mercury Deposition in Pennsylvania in 2009. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, 65 p.
5. Boyer, E.W., J.W. Grimm, K.S. Horner, J.S. Lynch, and M.A. Borden (2010). Atmospheric Deposition in Pennsylvania: Spatial and Temporal Variations 2009. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, 255 p.
6. Boyer, E.W., J.W. Grimm, K.S. Horner, and M.A. Borden (2010). Atmospheric Mercury Deposition in Pennsylvania in 2009. Report prepared for the Pennsylvania Department of Environmental Protection by the Pennsylvania Water Resources Research Center, 65 p.

USGS 104S PROJECT UPDATE FY2013

PROJECT TITLE & PRINCIPAL INVESTIGATOR

Long-term Responses of Stream Chemistry to Changes in Atmospheric Deposition in Mid-Appalachian Forests of Pennsylvania

Elizabeth W. Boyer, Department of Ecosystem Science & Management, Pennsylvania State University

PRINCIPAL FINDINGS AND SIGNIFICANCE

Acidic atmospheric deposition has impacted forests and waterways of the northeastern United States; largely attributed to emissions of compounds to the atmosphere stemming from fossil fuel combustion. As forested ecosystems of the eastern USA continue to adjust to dynamic changes in atmospheric deposition, long term monitoring (LTM) is critical in order to understand effects on water quality. This project continues long-term observations within 5 acid-sensitive forested watersheds (known as the LTM watersheds) within the Mid-Appalachian region of Pennsylvania.

Acidic atmospheric deposition can have serious effects on aquatic ecosystems. For example, acidified waters can impair the ability of fish gills to extract oxygen from water and change the mobility of certain trace metals (e.g., aluminum, cadmium, manganese, iron, arsenic, mercury), which in turn can place fish and other species sensitive to these metals at risk. Major negative impacts of acid deposition on forested watersheds that have been documented in various watersheds in the northeastern USA include: 1) Declines in pH of stream water which can lead to decreased biodiversity especially in fishes and macro-invertebrates; 2) Increases in dissolved inorganic aluminum concentrations in stream water which can lead to mortality of aquatic life; and 3) Leaching of base cations from soils which decrease the ability of a watershed to buffer itself from incoming acids.

Due to the Clean Air Act Amendments of 1990 and other policies, rates of acidic atmospheric deposition have greatly decreased in the eastern United States in recent decades. Questions remain about whether acid-sensitive forested watersheds are able to recover from the legacy of acid deposition, and the length of time that it will take for recovery to occur.

The susceptibility of a water body to acidification depends on the ability of the water and catchment soils to neutralize the acid deposition it receives. The best measure of this ability is acid neutralizing capacity (ANC), which characterizes the amount of dissolved compounds that will counteract acidity. Every body of water has a measurable ANC, which depends largely on the surrounding catchment's physical characteristics, such as geology, soils, and size. The ANC of a body of water reflects the relative proportions of positive and negative ions entering the water from sources such as atmospheric inputs and the soil and bedrock surrounding and underlying the water body. The higher the ANC, the more acid a water body can neutralize and the less susceptible it is to acidification. Considering long term results over the past three decades in the five study catchments, gradual decreases in stream sulfate

and increases in ANC levels in streams have been noted, largely in response to the reductions in emissions associated with the Clean Air Act Amendments of 1990.

During FY13, we conducted synoptic sampling of stream segments throughout three forested, headwater catchments under summer base-flow conditions. While all three watersheds have been subject to heavy loadings of acid rain in recent decades, two of the watersheds are poorly buffered and thus acid-sensitive (LTM watersheds), while one of the watersheds is well buffered and thus acid-tolerant (non LTM watershed). Results show that some chemical recovery (i.e. increased pH, decreased aluminum concentrations) has occurred in the acid-sensitive LTM streams. However, these watersheds are still considered to be chronically acidified in terms of acid neutralizing capacity of the stream waters, which has not decreased. The two acid-sensitive LTM streams thus still show high risk of episodic acidification, and biological recovery has not yet occurred.

During FY13, we also continued to measure the basic stream chemistry and stream flow with monthly, base flow sampling in the 5 acid-sensitive LTM watersheds of Pennsylvania (considered to be the "LTM" or long term monitoring streams), to further establish a record of change. The project is ongoing and is not yet complete.

STUDENTS & POSTDOCS SUPPORTED

Kristen Brubaker, PhD student in Forest Resources, Department of Ecosystem Science and Management, Pennsylvania State University

Brendan Reed, MS Student in Forest Resources; Department of Ecosystem Science and Management; Pennsylvania State University.

PUBLICATIONS

Brubaker KM, WL Myers, PJ Drohan, DA Miller, and EW Boyer. (2013). The Use of LiDAR Terrain Data in Characterizing Surface Roughness and Microtopography. *Applied and Environmental Soil Science*, vol. 2013, Article ID 891534, 13p, 2013. Doi:10.1155/2013/891534.

Sebestyen SD, J Shanley, EW Boyer, C Kendall, and D Doctor. (2014). Coupled hydrological and biogeochemical processes controlling variability of nitrogen species in streamflow during autumn in an upland forest. *Water Resources Research, DOI: 10.1002/2013WR013670.*

PRESENTATIONS

Boyer EW. Acid Rain in Pennsylvania. Northwestern Pennsylvania Acid Deposition Workshop, Pennsylvania Department of Environmental Protection, Warren, PA, March 2013.

Reed, B and EW Boyer. Atmospheric Deposition Effects on Water Quality in Reference Watersheds of Pennsylvania. 16th annual Environmental Chemistry Student Symposium, Penn State University, March 2013.

Reed, B and EW Boyer. Atmospheric Deposition Effects on Water Quality in Reference Watersheds of Pennsylvania. Susquehanna River Basin Commission Water Science Forum, Harrisburg, PA, October 2013.

Boyer EW, C Grant, J Grimm, PJ Drohan, J Bennett, and D Lawler. Wet and dry atmospheric mercury deposition accumulates in watersheds of the northeastern United States. B41C-0408. American Geophysical Union, San Francisco, CA, December 2013.

PHOTO(S) OF PROJECT

This forested, headwater stream in the mid-Appalachian region of Pennsylvania is poorly buffered and acid sensitive. In response to decreases in acidic atmospheric deposition, this stream has shown partial chemical, yet not biological recovery to date.

Statistical Evaluation of Triclosan Measurements in Wastewater using ELISA protocol.

Basic Information

Title:	Statistical Evaluation of Triclosan Measurements in Wastewater using ELISA protocol.
Project Number:	2012PA186B
Start Date:	3/1/2012
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	11
Research Category:	Water Quality
Focus Category:	Methods, Models, Treatment
Descriptors:	None
Principal Investigators:	Holly Frederick

Publications

There are no publications.

PA-WRRC ANNUAL REPORT
USGS 104B PROJECT UPDATE FY2013

PROJECT TITLE: Statistical Evaluation of Triclosan Measurements in Wastewater using ELISA protocol.

PRINCIPAL INVESTIGATOR(S): Holly Frederick, Assistant Professor, Wilkes University, Wilkes-Barre, PA. E-mail: Holly.Frederick@wilkes.edu.

SHORT DESCRIPTION OF PROJECT & FINDINGS: This research found that consistent laboratory protocol was more significant that incubation time in obtaining precise data using ELISA kits to measure triclosan. Highly concentrated solutions from a solid phase extraction process are needed to measure triclosan concentrations in wastewater using Gas Chromatography-Mass Spectrometry techniques.

PROBLEM & RESEARCH OBJECTIVES.

The original research objectives are defined below.

1. Evaluate the correlation between part per billion triclosan measurements from an ELISA kit with no pre-concentration, with a pre-concentration step and with a GC-MS technique that uses pre-concentration.
2. Establish the precision and accuracy of part per billion triclosan measurement in water and wastewater using available ELISA kits.
3. Establish the reproducibility of triclosan measurements using ELISA kits from different manufacturers
4. Develop a protocol for the ELISA procedure for water and wastewater.

As the work on the project began and continued, the objectives were periodically reviewed to be sure the work was achieving appropriate goals.

In reviewing the first objective, the pre-concentration step was eliminated for the ELISA tests because the values measured are at a maximum of 2.0 ppb. Triclosan concentration in the inflow to wastewater treatment plants often exceeds 2.0 ppb, so concentration of the samples would exceed the detection limit. Dilution of the inflow is generally a more appropriate technique.

Significant data was taken with ELISA kits and statistical evaluation of the data was performed to determine the variability as well as the accuracy of the ELISA tests.

Upon further research, triclosan ELISA kits were only available from one manufacturer, Abraxis in Warminster, Pennsylvania. Other manufacturers create ELISA kits for other trace organic chemicals, so these research techniques apply to broader application of the work and consistency of the ELISA tests for measuring trace organics.

The final protocol is available in draft form and we continue to develop this process as we continue this work on trace organics in natural waters.

Several additional objectives were explored as a part of this work. The first was to establish the effect of final incubation time on the triclosan measurements found using ELISA kits from Abraxis. There are two different spectrophotometers available for our analysis of the final concentration, and these two techniques as well as the length of the final incubation time was evaluated to determine the limit for effective data measurement.

Based on the suggestion of our chemistry department, an additional instrument, the High Performance Liquid Chromatograph, was explored as an analytical approach to measure the concentration of triclosan in wastewaters.

METHODOLOGY

Wilkes University is an independent institution of higher education with programs in the liberal arts, sciences and professional programs. The University has maintained an ABET accredited engineering programs in the areas of mechanical, electrical and environmental engineering since 1995. Within the school of science and engineering, the school has active research programs in several departments including Engineering and Physics, Chemistry, Biology and Environmental Engineering and Earth Sciences. Cooperation between the departments allows the varied expertise of the faculty to be applied to research questions across disciplines.

The Environmental Engineering and Earth Sciences (EEES) Department maintains a series of state of the art water quality and drinking water quality testing laboratories. The laboratory personnel have been involved in projects that focus on applied research, research and development, and homeowner water testing. University students are employed in the lab, building upon their experiences with the water quality testing experiences they have in their classes. The EEES department maintains two atomic absorption spectrophotometers as well as a variety of equipment required in standard water quality analysis. Research projects to evaluate ELISA protocols would be well suited for the water quality laboratories within the EEES department.

The Chemistry department will be partnering with the EEES department for this research by supplying the expertise and equipment needed to measure triclosan using a GC-MS procedure. The Chemistry department maintains an Agilent Mass Spectrometer (GC-MS) that is used for chemical separation and chemical identification. This instrument is widely used throughout the chemistry curriculum. It will enable triclosan to be measured using the methods typically employed in research literature.

The equipment and resources available at Wilkes University will allow our students and faculty to employ the following methods to address the objectives defined above.

1. Collect water samples from at least three local wastewater treatment plants and measure triclosan concentrations using two different ELISA techniques and GC-MS procedures.
    - In our work we collected samples from four wastewater treatment facilities including the Tunkhannock Borough Municipal Authority, the Lower Lackawanna Valley Sewer Authority, the Central Wayne Regional Authority and the Hazelton Sewer Authority. In addition, as part of the Environmental

Engineering and Science curriculum, we collected samples from the Wyoming Valley Sanitary Authority and evaluated triclosan concentrations following a similar procedure.

2. Measure triclosan concentration on standard solutions using two different ELISA techniques and GC-MS procedures.
    - Two different ELISA techniques were not available and the protocol to measure standard concentrations were used for the Abraxis ELISA kits as well as developed for the GCMS and HPLC procedures.
3. Measure triclosan concentrations on standard solutions using two different ELISA techniques with variability in the methods.
    - A number of samples were measured and the timing and concentration of the samples were varied. Many of the values focus on wastewater samples to determine consistency of the test for timing for different raw water matrices. Additional work would evaluate more known samples to evaluate the recovery from the known samples by the GCMS procedure.
4. Develop a protocol for the ELISA procedure with data to quantify the precision and accuracy of the measured results.
    - The protocol for using the ELISA test was defined, but data is still being evaluated and the protocol is being refined.

PRINCIPAL FINDINGS AND SIGNIFICANCE

GCMS data and HPLC data must have concentrations significantly higher than the ELISA test and the processing of the samples is much more time consuming. The solid phase extraction units we used and the extraction process followed a published procedure. We were able to extract the organics from wastewater, and were able to isolate triclosan peaks using the GCMS. Identification of the concentration using our instrumentation is more challenging. The results here indicated that GCMS is a promising technique to measure triclosan, but the concentration of the compound must be very high and so the amount of solvent added to the extracted material must be very low. In terms of application of the extraction technique to additional work examining triclosan or other trace organics in wastewater, the piece focusing on concentration is valuable. Based on our work, it seems that the extraction procedure could be improved to systematically separate the organics in the column to provide a purer sample for the GCMS analysis, so that the triclosan, or selected organic chemical can be identified clearly with fewer interfering species.

The procedures for the HPLC were not determined to be effective at isolating the triclosan in the wastewater. Given the challenging matrix of wastewater and the variability of retention time in the HPLC, we will not work to further develop this technique for wastewater unless we are able to combine it with a mass based detection method. The challenge of higher concentrations of extracted organics and the variety of organics challenge the correct identification of a triclosan peak in the current data set. With GCMS, the mass data allows the correct identification of the mass peak associated with triclosan.

A number of wastewater samples were evaluated to determine the precision of triclosan measurements. The data demonstrated replicate samples have a standard deviation between 0.05 and 0.79 ppb. The undergraduate students running the tests, although trained, may not have had the same level of analytical experience. The ELISA test has been shown to demonstrate high precision, but the experience of the laboratory personnel is an essential part of the work. Significant effort and laboratory equipment is required to obtain quality analytical data. Future work will focus on establishing the variability of the results for operators with one year of laboratory experience.

The final test evaluated the effect of different incubation times on the final sample measurement. A plot of absorbance measured at different times demonstrated a high level of correlation using both the Pearson and Spearman correlation coefficients. For 32 data points, the correlation was a minimum of 0.993 for the Spearman correlation coefficient and 0.998 for the Pearson correlation coefficient when considering time intervals between 0 and 60 minutes of incubation time. The incubation time, as long as it is within an hour, and measured efficiently, will not affect the interpretation of results. Laboratory technique is a much more significant component in assessing the quality and consistency of results from the ELISA kits.

There is still data analysis work to be completed on this project. It is unlikely that enough data has been collected to make a direct correlation between the ELISA data and the GC-MS data at this point. The development of the extraction techniques for the solid phase extraction units needs to be enhanced to improve isolation and evaluate recoverey. The project has been significant in offering us the following valuable pieces of information as we continue work on this topic.

- Sequential extraction from the solid phase extraction units with different solvents may help to more effectively isolate organic compounds of interest.
- Concentrations of trace organic above 5 mg/L in the extracted samples is necessary for more effective GC-MS analysis.
- Our next set of experimental work will focus on full recovery of a known concentration of triclosan from a synthetic wastewater to determine the concentration recovered using GC-MS.

STUDENTS & POSTDOCS SUPPORTED

Katherine Cirone, B.S. Environmental Engineering – Independent study collecting data on HPLC and performing data analysis on triclosan data.

Steven Adames, B.S. Environmental Engineering – Work Study Student involved in sample collection, triclosan extraction and analyzing samples on the GC-MS.

Matt Gunther, B.S. Environmental Engineering – Summer Employee. Collected water samples from four water treatement plants, preserved samples for ELISA analysis and extracted triclosan for GC-MS analysis.

Chris Kemple, Environmental Engineering Student – Summer Employee. Collected water samples from four water treatement plants, preserved samples for ELISA analysis and extracted triclosan for GC-MS analysis.

Alison Duda, B.S. Chemistry. Instrumentation Consultant. Assisted engineering students in the operation of the GC-MS and the HPLC instruments. Helped to develop a method to effectively measure triclosan in extracted samples.

Megan Gershey, undergraduate student, Environmental Engineering. Assisted in the laboratory with HPLC procedure and with maintaining equipment.

PUBLICATIONS

In preparation.

PHOTOS OF PROJECT

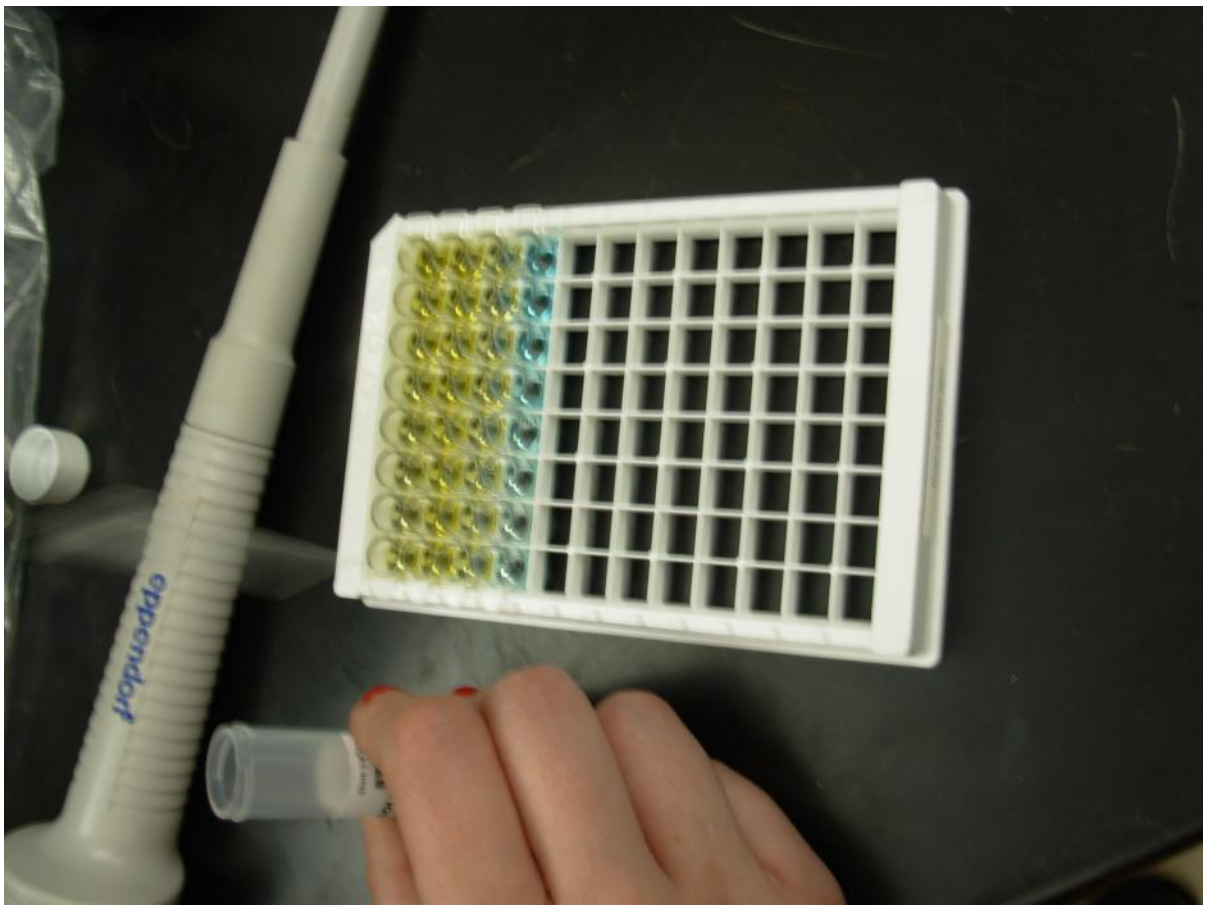


Figure 1. Wilkes University Student running Abraxis ELISA test to measure triclosan concentrations in wastewater samples.

Figure 2. Wilkes University Students monitoring results of triclosan measurements using the Agilent Gas Chromatograph Mass Spectrometer.

Removal of Benzoic Acids by Anion Exchange Resins as Analogues for Natural Organic Matter and Emerging Contaminants

Basic Information

Title:	Removal of Benzoic Acids by Anion Exchange Resins as Analogues for Natural Organic Matter and Emerging Contaminants
Project Number:	2012PA189B
Start Date:	3/1/2012
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Treatment, Water Quality, Water Supply
Descriptors:	None
Principal Investigators:	Huichun Judy Zhang

Publications

There are no publications.

PA-WRRC final report

PROJECT TITLE & PRINCIPAL INVESTIGATOR

Removal of Benzoic Acids by Anion Exchange Resins as Analogues for Natural Organic Matter and Emerging Contaminants

Huichun (Judy) Zhang, Ph. D.
Assistant Professor
Department of Civil and Environmental Engineering
Temple University
Phone: (215)204-4807
Email: hjzhang@temple.edu

ONE-SENTENCE SOUND BYTE STYLE DESCRIPTION OF THE PROJECT OR FINDINGS: This research provided a mechanistic understanding of the removal of carboxylate anions and neutral aromatic contaminants by three selected anion exchange resins.

PROBLEM & RESEARCH OBJECTIVES

This study was meant to help address the growing concern caused by the presence of pharmaceuticals and other organic contaminants in drinking water in the state of Pennsylvania and across the nation. Current water treatment technologies are insufficient in removing the wide range of classes of these contaminants. Thus further treatment technologies must be de0veloped to help address this issue. This research was performed to further develop a novel water treatment technique using polymeric resins to target organic compounds.

Organic Contaminants

Over the past few decades, a continued exponential growth in human population has led to an increase in industrial processes and consumption of pharmaceutical and household chemical products. Because of this, the USGS performed a study in 1999 that examined 139 different streams across the United States. They discovered that 82 different organic contaminants (OCs) were found in low concentrations within 80 percent of the water tested[1]. The compounds found in this study included steroids, antibiotics, other different drug products, insecticides, and fire retardants. Since this study, further research has been performed to determine how widespread pharmaceuticals and other OCs are in the environment. Further research from the USGS has determined similar findings to the 1999 study; that is, organic contaminants are found in many water sources including wastewater, drinking water, and ground water across the nation[2-5]. In response to this growing problem, the EPA and state governments have put into place regulations on many organic compounds and have developed a program to examine further compounds dubbing them as "emerging contaminants (ECs)". The term EC can refer to any compound without a regulatory standard that has recently been discovered in water systems and has a perceived or real adverse effect on human health, water quality, aquatic life, or environmental health. Every year the EPA classifies new chemicals as ECs in order to study it's impact, develop analytical techniques, and research methods of remediation. There are over tens of thousands of potentially hazardous ECs that persist in the environment, and their exact impact is not yet quantified. There are many different categories of ECs but some of the major groups are: persistent organic pollutants (POPs), pharmaceuticals and personal care products (PPCPs), agricultural compounds, and endocrine-disrupting chemicals (EDCs)[6].

There are many concerns driving the regulation and removal of OCs from the environment. For instance, OCs can be very water soluble and degrade at extremely slow rates. This is a particular problem for POPs and PPCPs, which may persist in the environment for years[7]. This also means that their concentrations are slowly increasing as more chemicals are added daily, faster than the rate of degradation. EDCs or hormone disruptors mimic or impede natural hormones in humans or animals, causing birth defects, infertility, and kidney and liver damage. Some aquatic animals such as amphibians and fish have demonstrated an overall feminization in their population from synthetic estrogen released in the environment[8].

Another growing concern is from the amount of antibiotics persistent in the environment. This has allowed pathogens to develop a general resistance to commonly used antibiotics such as penicillin, ampicillin, cephalosporin, and vancomycin[9]. The amount of resistant bacteria found in water systems has increased throughout the United States[10]. An increase in sicknesses caused by resistant bacteria has the potential to increase the general use of antibiotics, which will in turn increase the concentration of antibiotics in the environment, potentially creating a worsening cycle.

Water Treatment Techniques to Remove OCs

A number of studies have focused on examining typical water and wastewater treatment processes and their ability to remove organic contaminants[8,11-14]. These processes include: settling and sedimentation techniques such as coagulation, flocculation, and lime softening; oxidative and similar processes such as

chlorination, ozonation, and ultraviolet photolysis; membrane filtration and adsorption treatment. Coagulation, flocculation, sedimentation, and lime/soda ash softening are commonly used in most water/wastewater treatment plants to remove suspended solids and other compounds that may precipitate out of solution. However, these water treatment processes demonstrated little ability to remove many OCs, usually less 20%[8] and in some cases having no significant removal efficiency at all[11].

Chlorination of drinking water is required by law for all water treatment plants in the U.S., while other methods of disinfection, such as ozonation and UV radiation have also been employed. Ultraviolet radiation demonstrated the least effectiveness of these three techniques, sometimes removing only 40% of PPCPs, suggesting that UV treatment alone is not sufficient[8]. Many water treatment processes successfully removed PPCPs using ozonation and chlorination at up to 90% removal efficiency[11,13]. However, there is a growing concern over the byproducts that are produced from chlorination and oxidation. Some of these byproducts can be more harmful than the parent compounds and these processes do not remove many other types of OCs suggesting that an alternative removal treatment prior to oxidation is needed.

Nanofiltration, biofiltration, and reverse osmosis have been very successful in removing most classes of OCs with efficiencies greater than 90%[8,14]. However, these processes are typically slow and expensive and therefore, not employed in water treatment systems. A more economical and comparatively efficient process is to use adsorption. Granular activated carbon (GAC) and powdered activated carbon (PAC) are currently the most common adsorbents in drinking water facilities. While these adsorbents are highly effective in removing many organic pollutants, they do have some significant drawbacks. Once saturated with pollutants, activated carbons (ACs) are typically regenerated using high thermal techniques. These techniques cause a 5-10% attrition rate of the activated carbons[15]. The replacement costs from attrition and energy costs from regeneration make activated carbons economically unfavorable. They also cannot be custom synthesized towards specific pollutants as they tend to indiscriminately remove organic contaminants. Therefore, they may become saturated with nontarget compounds, which would require additional regeneration. Finally, ACs have poor removal efficiencies when the contaminants of concern are highly water soluble and/or are ionic species. This is a significant problem as many pharmaceutical compounds are ionic within in typical water treatment pHs.

The overall objective of this project was to use the principles behind the previously proposed model by Pan and Zhang[21], which is based on the modified DA equation and polyparameter linear free energy relationships (pp-LFERs) to predict isotherms of anion exchange resins. The pp-LFER expression was altered to include the –jJ term for anion electrostatic interactions and an ideal gas reference state was assumed to determine the Gibbs free energy of the phase change. While doing this, this project explored the various interactions and mechanisms of removal in order to develop a deeper understanding of the anion exchange and adsorption processes. This includes looking into the effects of the resins' structure, functional groups, and physiochemical properties as well as the effects of sorbate properties, sorbate functional groups, and solution conditions (such as pH and ionic strength).

METHODOLOGY

pH Effect on the Contribution of Adsorption and Ion-Exchange

Because pH is often variable in environmental systems between the range of 5 to 9, experiments were performed to verify the relative contributions of ion exchange and adsorption to the removal process. In order to do this, removal experiments were performed with two types of compounds, benzene sulfonate and nitrobenzene. Benzenesulfonate is an extremely weak base and exists in its deprotonated or ionic form in most systems (pK_a = -2.8). Nitrobenzene on the other hand, is strictly a neutral compound and has no charge. Nitrobenzene was therefore chosen as a neutral species to demonstrate effects on adsorption and benzenesulfonate was chosen as an ionic species for ion exchange effects only. The removal of these two compounds was tested for four resins, IRA-910 and IRA-96 (strong and weak exchangers) as well as MN200 and MN100 (adsorbents). The ion exchange resins (IRAs) can have their removal efficiencies of an ion and neutral compound explored, showing how much of a compound is removed from ion exchange as compared to adsorption. Not much adsorption removal is expected from the IRAs as compared to their ion exchange removal.

The resins (MNs) were tested to see the exact contributions of ion exchange and adsorption for adsorption resins. MN200 has no functional groups and therefore are not expected to remove the ionic compound. MN100 does contain some functional groups, though only a small amount (exchange capacity = 0.1 – 0.3 eq/L); therefore, MN100 is expected to have some success in removing benzenesulfonate.

Examination of Resin Functional Groups

Titrations were performed on some representative resins to determine the charge status of the resins' functional groups. Weak base resins are expected to have their functional group protonated or deprotonated depending on the solution pH, while strong base resins and adsorption resins are not expected to demonstrate any significant change due to pH. Through the titration experiment, pK_a values of the resins were determined to see if the resin is affected by pH within the 5-9 range of typical environmental systems. The same four resins were used for these experiments: MN100 (primarily adsorbent), MN200 (adsorption only), IRA-910 (strong base exchanger), and IRA-96 (weak base exchanger). Strong base exchangers are not expected to demonstrate a pK_a value, therefore, the results of IRA-910 can be applied to any strong base exchanger, such as the polyacrylate exchanger, A860.

Verification of Adsorption Kinetics

It was also necessary to verify the kinetics of the ion exchange process. Previous experience with adsorption isotherms demonstrated that equilibrium was reached within a 48 hour period. A kinetic experiment was performed on each of the major three resins using benzoic acid as the representative compound for all of the adsorbates. This test verified that no additional removal processes were occurring beyond the 48 hour period that had to be accounted for.

Determination of pp-LFER Normalizing Factors and Freundlich Modeling of Isotherms

To use the polyparameter linear free energy relationships (pp-LFER) expression, first the normalizing factors must be determined through experimental data; the theory of which is explained in Pan and Zhang 2012.[16] Because this model has seven variables to determine (v, s, e, a, b, j, c) the resins had adsorption isotherm experiments tested on a large number of representative compounds to ensure the models accuracy over many different compound classes.

The adsorption capacities (Q_e) were determined across a wide range of concentrations using batch adsorption experiments to create adsorption isotherms. Q_e values will be calculated based upon the following equation:

$$Q_e = \frac{(C_i - C_e)V}{m}$$

Where C_i and C_e are the initial and equilibrium concentrations respectively in µM, V is the volume of the solution in mL, and m is the mass of resin in mg. Q_e is in units of µmoles of sorbate per gram of sorbent. Based on the experimental data, adsorption capacities can be fit to a Freundlich model. We have used carboxylic acids with pKa's well below the standard water treatment pH (5-9), phenols, anilines, and sulfonic acids as representative compounds.

Because there is also a wide variety of anion exchange resins available, a representative set of resins must also be considered for the adsorption isotherms. This project primarily focused on three resins from three major types of anionic exchange groups to demonstrate the usefulness of the model. This project also explored additional resin types and subtypes in lesser detail to develop a basic understanding of the effect of resin properties on the removal process. The three representative resins that were used for the majority of the isotherm experiments are:

1. Amberlite IRA-910 (strong base Type II polystyrenic)
2. Amberlite IRA-96 (weak base polystyrenic)
3. Purolite A860 (strong base polyacrylate)

Brief Examination of Various Resin Properties

A final determination was to measure and verify the properties of the resins used in these experiments. These properties include the ion exchange capacity, porosity, water content, surface area, pore size, functional groups, and elemental composition. Knowing these properties can help understand behavior of each type of resin and can further increase the ability to better select resins for the removal of OCs.

To summarize the above, the experimental data that were performed:

1. Isotherms using three major classes of resins (strong and weak base, polystyrene and polyacrylate) against many representative compounds including carboxylates, phenols, anilines, and neutral compounds.
2. Determining the exact contribution of ion exchange and adsorption over a range of pH using both benzenesulfonate and nitrobenzene. This was done on a representative group of resins: strong and weak base exchangers, and two primarily adsorption resins.
3. Determining the pK_a values of the resin functional groups and verifying that strong base exchangers and adsorption resins do not change their removal capacities of a range of pH values using titration experiments.
4. Verification of the kinetics for the ion exchange process. This determined whether there is any additional removal of contaminants beyond the 48 hour shaking period allotted during an adsorption batch study.
5. Examining the removal capacities of the various subclasses of resins (besides the major 3) on benzoic acid to further understand the effect of resin characteristics on removal efficiency.
6. Verify and determine certain resin properties, including exchange capacity, porosity, water content, functional groups, and elemental composition.

With the above experimentation completed, data analysis were performed to create Freundlich equations for the ion exchange isotherms. pp-LFERs parameters were determined using an ideal gas phase as the reference state and multiple linear regressions. After this is complete, the predictive model will be developed. A model will be created for each of the three major resins: IRA-910, IRA-96, and A860. Each resin will have a model based on a training set of compounds. After this is complete, a small number of compounds outside of the training set can be used to verify the accuracy of the model and its predictive ability.

PRINCIPAL FINDINGS AND SIGNIFICANCE

Titration Experiments

Titration experiments were performed on the resins to understand the differences, if any, in adsorption over typical environmental pH values (between 5 and 9). IRA-910 is a strong base anion exchanger; therefore, no change was expected to the functional groups. MN100 has a relatively small exchange capacity and therefore has only a small number of exchange functional groups on its surface which is not significant enough to demonstrate a sizable buffering capacity. Our experiment shows a pK_a value for IRA-96 averaging at a pH of 6. This agrees with the work done by Miyazaki and Nakai[17], which determined a pK_a to be about 6.4 for IRA-96.

Effect of pH on Contaminant Removal

Although the resins of concern are primarily ion exchangers, there will be some amount of adsorption associated with the process that occurs from Van der Waals attractions between the adsorbate and adsorbent. Our results suggest that the ion exchange resins have significantly poorer adsorption capacity for neutral compounds, but significantly higher adsorption capacity for ionic compounds (Q_e values at approximately 350 µmol/g for the ionic compound as compared to Q_e values between 10 and 40 µmol/g for the neutral compound). The relative amounts of adsorption versus ion exchange were thought to be pH dependent. Although IRA-910 does not show any significant change in adsorption capacity over the pH ranges, IRA-96 (pKa=6.0) does. Below the pK_a, the protonated amine functional group has less adsorption capacity for nitrobenzene while the capacity begins to increase above the pK_a. This is caused by the competition of water molecules to the charged resin. IRA-910 shows no significant trend in adsorption capacity over the pH ranges because it is a strong base exchanger. However, in the higher pH range, IRA-96 demonstrates a loss of efficiency.

The Macronet resins clearly demonstrated a poor ability in removing benzenesulfonate. MN200 is not affected either positively or negatively by the changes in pH. MN-100 does however, have a small ion exchange capacity due to the few tertiary amine functional groups on its surface. The notable decrease in its ion exchange capacity is likely due to the pK_a of these functional groups; as the amine groups are deprotonated, MN-100 loses its ability to perform ion exchange and begins to mimic MN-200, which has negligible ion exchange capacity.

In order to demonstrate the importance of the speciation of the solute for the removal process, experiments using benzoic acid as a representative solute were performed against the MN and IRA resins. Above the pK_a of benzoic acid (4.21), removal efficiency was severely reduced while the MN resins demonstrated sufficient removal efficiency when the neutral species was present. Although MN-100 and MN-150 both have some functional groups associated with their surfaces and have a small ion-exchange capacity, their primary mode of contaminant removal must be adsorption. The opposite trend was observed for ion-exchange resins, IRA-910 and IRA-96, where the removal capacity was increased as the charged compound became the predominant species present in solution.

Adsorption Isotherms

As mentioned above the adsorption isotherms must be performed to fit the Freundlich equation ($Q_e = kC_e^{\,n}$) and develop a relationship between the equilibrium concentration C_e and the adsorption capacity Q_e. All the selected compounds in Table 1 each had a batch experiment performed to create an isotherm using each of the three resins chosen to represent the major classes of ion exchange resins. Creating these isotherms is the first step to creating the overall model and determining the pp-LFER coefficients. Once all of the compounds have been adsorbed onto the three resins, multiple linear regressions can be performed based on the Q_e and C_e values. Each isotherm was fitted to the Freundlich equation and an R^2 value was obtained. The Freundlich data is displayed in Table 1. As the table show, the isotherms fit very well to the Freundlich equation, with R^2 values generally greater than 0.99. Additional experiments are underway to complete all the remaining isotherms.

A general trend can thus far be observed based on the isotherm data of IRA-910 and IRA-96. The order of the removal of various compound classes is as follows: aromatic carboxylates > benzenesulfonate > anilines > phenols > nitrobenzene. Though it is of interest to note that benzenesulfonate appears to more preferred on A860. This is likely because of the resin structure and will be further analyzed during the statistical determination of the pp-LFER data.

Table 1. Freundlich equation data for IRA-910, IRA-96, and A860.

Compound	IRA-910			IRA-96			A860		
	R^2	K	n	R^2	K	n	R^2	K	n
benzoate	0.9959	4.4288	0.6153	0.9559	1.8673	0.8049	0.9805	0.7226	0.7907
p-chlorobenzoate	0.9969	2.339	0.9238	0.9941	6.7867	0.8355	0.9981	0.1601	1.0084
3-methyl-2-nitrobenzoate	0.9987	2.8919	0.8448	0.996	5.2166	0.8221	0.9978	0.1066	1.0598
3-methyl-4-nitrobenzoate	0.9987	3.4786	0.8784	0.9933	11.084	0.7792	0.9998	0.098	1.0033
p-anisic acid	0.9864	1.0256	0.9156	0.9927	1.5995	0.9016	0.9996	0.0854	1.0364
1-naphthoic acid	0.9968	3.098	0.9015	0.9968	3.098	0.9015	0.9995	0.2145	1.0095
Benzenesulfonate	0.9791	1.7165	0.8353	0.9921	1.447	0.8636	0.9975	0.2366	0.9845
4-chloroaniline	0.9856	0.117	0.8967	0.9915	0.5547	0.828	-	-	-
4-nitroaniline	0.9979	0.3967	0.8875	0.9929	1.3558	0.8007	-	-	-
phenol	0.9965	0.0412	0.9518	0.9968	0.1996	0.9009	-	-	-
p-cresol	0.9998	0.1048	0.8938	0.9987	0.4562	0.8659	-	-	-
nitrobenzene	0.9906	0.0439	0.8801	-	-	-	-	-	-

pp-LFER Determination and Predictive Model Development

After all experimental data has been collected; data analysis will be performed on each of these experiments. Briefly, after fitting all of the isotherms to Freundlich equations, a relationship between the aqueous-adsorbent coefficient and the Gibbs free energy can be created. This is done through determining the Gibbs free energy from aqueous to the ideal gas phase and then from the ideal gas phase to the adsorbent phase. The pp-LFER values necessary can be determined using multiple linear regressions. A final analysis of the effects of the various sorbent and sorbate properties will also have to be performed to provide a better insight into the individual mechanisms and their causes. Analyzing the properties associated with each compound and resin structure in light of the pp-LFER values can help determine which mechanisms are the dominating mechanisms behind the ion exchange process. Finally, a predictive model will be developed based on the obtained pp-LFERs so that adsorption capacity of a given anion by a resin will be estimated at a particular concentration.

Significance

The occurrence of ECs in our water systems and in the environment is among the greatest environmental challenges facing the commonwealth of Pennsylvania. Meeting this challenge with conventional technologies alone is difficult and costly. Armed with a wealth of information concerning water treatment technologies using activated carbon, the development of a new technology to remove ECs using polymeric resins seems promising. Given these premises, this project provided a mechanistic understanding of the adsorption mechanisms of EC analogues by various polymeric resins, and established quantitative relationships that can be used to guide the selection of the type and quantity of resins needed for a given treatment scenario. This fundamental understanding of the adsorption mechanisms will contribute to a major advance in the development of polymeric sorbents as a new water treatment technology targeting ECs removal. Removal of ECs from drinking water will protect human health directly while cleaned wastewater will protect receiving waters from contamination and enable more wastewater to be recycled to alleviate increasing shortages of fresh water supplies.[18]

STUDENTS & POSTDOCS SUPPORTED

Dr. Bingjun Pan, postdoc associate
Mr. Anthony J. Shields, master student majoring in Environmental Engineering
Mr. Maurice Nelson, undergraduate research student majoring in Civil Engineering with environmental engineering concentration.

PUBLICATIONS

Pan, Bingjun; Huichun Zhang, 2013, Interaction Mechanisms and Predictive Model for the Adsorption of Aromatic Compounds onto Nonionic Resins, *Environmental Science and Technology*, In review.

Shields, Anthony; Huichun Zhang 2013, Understanding and modeling the sorption of anion exchange resins using poly-parameter linear free-energy relationships and phase conversion, *Environmental Science and Technology*, manuscript in preparation.

Anthony Shields, 2013, Understanding and modeling the sorption of anion exchange resins using poly-parameter linear free-energy relationships and phase conversion, "MS Dissertation" to be submitted in August 2013 to the Department of Civil and Environmental Engineering, Temple University, Philadelphia, PA. 73 pages.

Shields, Anthony; Huichun Zhang 2013, Understanding and modeling the sorption of anion exchange resins using poly-parameter linear free-energy relationships and phase conversion, PA-WRRC, Temple University, Philadelphia, PA. 11 pages.

PRESENTATIONS

Pan, B.; Zhang, H.; "A Modified Polanyi-based Model for Mechanistic Understanding of Adsorption of Phenolic Compounds onto Polymeric Adsorbents", 244th ACS National Meeting, Division of Environmental Chemistry, Philadelphia, PA, USA, Aug. 19 – 23, 2012.

Shields, Anthony; Huichun Zhang, "Understanding and modeling the sorption of anion exchange resins using poly-parameter linear free-energy relationships and phase conversion", 245th ACS ACS National Meeting, Division of Environmental Chemistry, Indianapolis, IN, Sept. 8-12, 2013.

Zhang, H. "Emerging Contaminants: Oxidation by Binary Metal Oxide Mixtures and Removal by Polymeric Sorbents", Invited Talk at the Department of Chemistry, The City College of New York, New York, March 4, 2013.

OTHER INFORMATION TRANSFER ACTIVITIES

"What happens to your medicine pills once they are disposed?", Lab tour and demonstrations during the National Engineers Week, College of Engineering, Temple University, 1-3pm, February 19, 2013

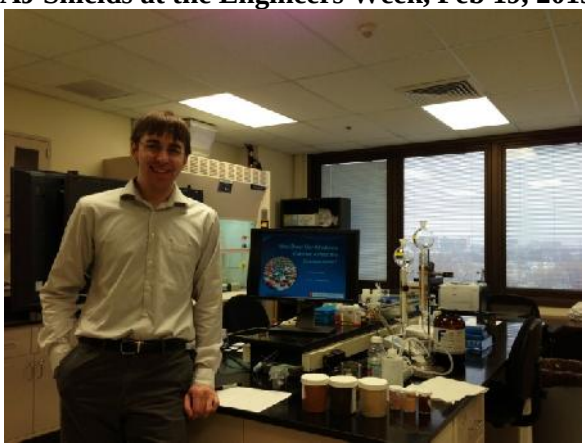
NOTABLE AWARDS & ACHEIVEMENTS

Senior design team (Anthony Shields, Jenna Fink, Hasan Malik, and Nicola Horscroft) won one of the two university-wide prizes on "the 2011-2012 Library Prize for Undergraduate Research in Sustainability and the Environment", Temple University. Title: The treatment of drinking water using polymeric sorbents. Faculty Advisor: Dr. Huichun (Judy) Zhang

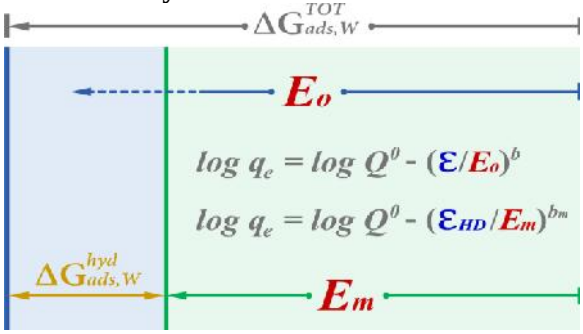
ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY
(source, amount, starting and ending dates, title)
None

PHOTOS OF PROJECT
Please include 2 photos with captions. These photos may be used in our annual report, web page, and/or brochure, and may be used by the National Institutes of Water Resources.

AJ Shields at the Engineers Week, Feb 19, 2013



Modified Polyani D-A Model



References:

1. Kolpin DW, Furlong ET, Meyer MT, et al. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. *Environ Sci Technol*. 2002;36(6):1202-1211. http://dx.doi.org/10.1021/es011055j. doi: 10.1021/es011055j.

2. Barnes KK, Kolpin DW, Furlong ET, Zaugg SD, Meyer MT, Barber LB. A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the united states--I) groundwater. *Sci Total Environ*. 2008;402(2):192-200.

3. Focazio MJ, Kolpin DW, Barnes KK, et al. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the united States—II) untreated drinking water sources. *Sci Total Environ*. 2008;402(2):201-216.

4. Frick EA, Henderson AK, Moll DM, Furlong ET, Meyer MT. Presence of pharmaceuticals in wastewater effluent and drinking water, metropolitan atlanta, georgia, july-september 1999. . 2001.

5. Lee KE, Barber LB, Furlong ET, et al. Presence and distribution of organic wastewater compounds in wastewater, surface, ground, and drinking waters, minnesota, 2000-02. *US Geological Survey Scientific Investigations Report 2004*. 2004;5138:47.

6. Hoff DJ, Beaman J, Ankley GT, et al. Aquatic life criteria for contaminants of emerging concern part I: General challenges and recommendations. *Environmental Protection Agency, Emerging Contaminants Workgroup*. 2008.

7. Damstra T. Potential effects of certain persistent organic pollutants and endocrine disrupting chemicals on the health of children. *Clin Toxicol*. 2002;40(4):457-465.

8. Yoon Y, Westerhoff P, Snyder S, Song R, Levine B. A review on removal of endocrine-disrupting compounds and pharmaceuticals by drinking water treatment processes. . 2002:10-14.

9. Levy SB, Marshall B. Antibacterial resistance worldwide: Causes, challenges and responses. *Nat Med*. 2004;10:S122-S129.

10. Fogarty LR. *Antibiotic-resistant fecal bacteria, antibiotics, and mercury in surface waters of oakland county, michigan, 2005-2006.* US Department of the Interior, US Geological Survey; 2007.

11. C. Adams MA, Y. Wang, K. Loftin, and M. Meyer. Removal of antibiotics from surface and distilled water in conventional water treatment processes. *Journal of Environmental Engineering*. 2002:253-260.

12. Scruggs C, Hunter G, Snyder E, Long B, Snyder S. EDCS in wastewater: What's the next step. *Proceedings of the Water Environment Federation*. 2004;2004(12):642-664. http://www.ingentaconnect.com/content/wef/wefproc/2004/00002004/00000012/art00046. doi: doi:10.2175/193864704784138403".

13. Westerhoff P, Yoon Y, Snyder S, Wert E. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ Sci Technol*. 2005;39(17):6649-6663.

14. Yoon Y, Westerhoff P, Snyder SA, Wert EC, Yoon J. Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes. *Desalination*. 2007;202(1–3):16-23. doi: 10.1016/j.desal.2005.12.033.

15. Xu Z, Zhang Q, Fang HHP. Applications of porous resin sorbents in industrial wastewater treatment and resource recovery. *Crit Rev Environ Sci Technol*. 2003;33(4):363-389.

16. Pan, B. and Zhang, H. 2012. “A Modified Polanyi-based Model for Mechanistic Understanding of Adsorption of Phenolic Compounds onto Polymeric Adsorbents”, *Environ. Sci. Technol.* 46(12), 6806−6814.

17. Miyazaki Y, Nakai M. Protonation and ion exchange equilibria of weak base anion-exchange resins. *Talanta*. 2011;85(4):1798-1804.

18. Benotti, M. J.; S. A. Snyder. Pharmaceuticals and endocrine disrupting compounds: Implications for ground water replenishment with recycled water. *Ground Water* **2009**, *47*, 499-502.

Developing A Treatment Option for Marcellus Shale Wastewater Through Cultivation of the Algae Dunaliella salina

Basic Information

Title:	Developing A Treatment Option for Marcellus Shale Wastewater Through Cultivation of the Algae Dunaliella salina
Project Number:	2013PA208B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	14
Research Category:	Engineering
Focus Category:	Wastewater, Water Use, None
Descriptors:	None
Principal Investigators:	Kyle Bibby

Publications

There are no publications.

PA-WRRC ANNUAL REPORT
USGS 104B PROJECT UPDATE FY2013 (March 1, 2013 to February 28, 2014)

PROJECT TITLE: Developing A Treatment Option for Marcellus Shale Wastewater Through Cultivation of the Algae *Dunaliella salina*

PRINCIPAL INVESTIGATOR: Kyle Bibby, Assistant Professor, University of Pittsburgh, Department of Civil and Environmental Engineering, bibbykj@pitt.edu, 412-624-9207

SHORT DESCRIPTION OF PROJECT & FINDINGS
High volume hydraulic fracturing, commonly known as 'fracking', produces millions of gallons of wastewater. This wastewater is termed flowback water. Flowback water contains extremely high salt levels, up to five times those found in ocean water. Appropriate management and disposal of this wastewater is of high environmental and regulatory concern. This research investigated the potential of growing the algae *Dunaliella salina* in flowback water as a reuse or treatment option. Growth or application of algae as a treatment option could reduce the energy required by other treatments and be applied on-site, reducing economic and environmental burden. Results demonstrated that growth of *D. salina* is limited in flowback water but *D. salina* has promise as a biosorbent for constituents of concern in flowback water.

PRINCIPAL FINDINGS AND SIGNIFICANCE
Hydraulic fracturing for hydrocarbon extraction produces millions of gallons of hypersaline wastewater, termed flowback water. The growth of the saline tolerant algae *D. salina* was evaluated in flowback water as a possible treatment or reuse option. Growth was determined using optical density (OD), dry mass measurement, and cell counting (Hemacytometer). Results of the experiments revealed that optical density measurement is the most effective method for the determination of *D. salina* growth. Experiments were conducted under a variety of conditions (not presented) in an attempt to maximize growth. Growth results presented here include synthetic flowback water (50,000 mg/L NaCl media) and real flowback water (See Figure 1). All experiments were performed in triplicate. Multiple rounds of experiments were employed in order to determine an appropriate laboratory set-up to evaluate growth (see Figure 5) and minimal nutrient requirements. Experiments demonstrated that pH is an important factor in *D. salina* growth in real flowback water and that pH control is necessary to optimize growth. In the following experiments, pH was monitored and a slight decrease was observed in every 3 days. In order to maintain optimal growth conditions, pH was adjusted to 7.5-8 with NaOH. Results of these experiments are shown in Figure 2.

Experiments were conducted to determine if algal growth resulted in removal of salts from flowback water as a treatment mechanism. Results of these measurements demonstrated that there is no significant decrease in the bulk conductivity of the samples after the algae growth but particular constituents of concern (e.g. iron, calcium) were partially removed following algal growth. These results demonstrate the potential of algae as a biosorbent in flowback water treatment. Specifically, atomic absorption spectrophotometry (AAS) was used to analyze the chemical content of the flowback water before and after the experiment to determine removal of the dissolved salts and metals in the samples after they were exposed to algae growth. The growth curve for this experiment was shown in Figure 2. Analyses revealed that there is

significant removal of multiple constituents of concern, including Fe, Ca, St, and Mn. Experimental replication (Figure 4) demonstrated consistent trends.

Due to relatively poor growth characteristics, ongoing and future work is investigating the use of *D. salina* biomass as a biosorbent for constituents of concern in flowback water, focusing on constituents of concern in flowback water management (e.g. iron, radium).

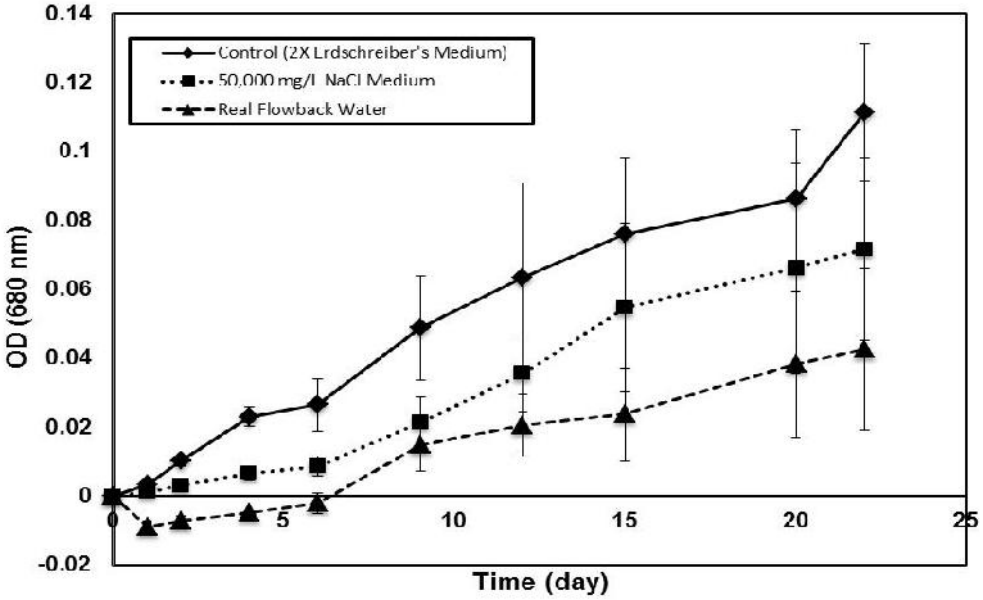


Figure 1. Comparative *D. salina* growth curves represented as optical density (680 nm) versus time.

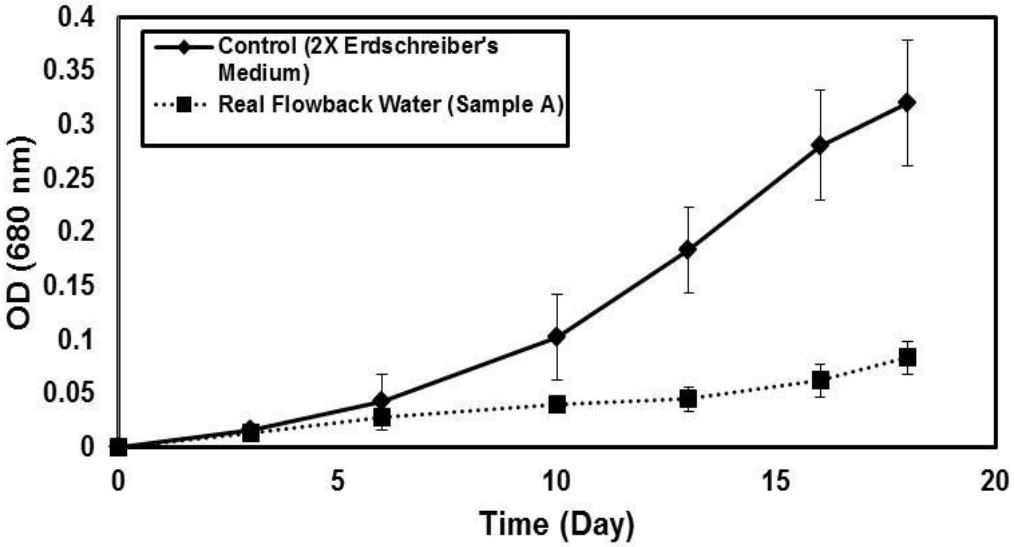


Figure 2. *D. Salina* growth curves for control and real flowback water sample, pH adjustment was provided

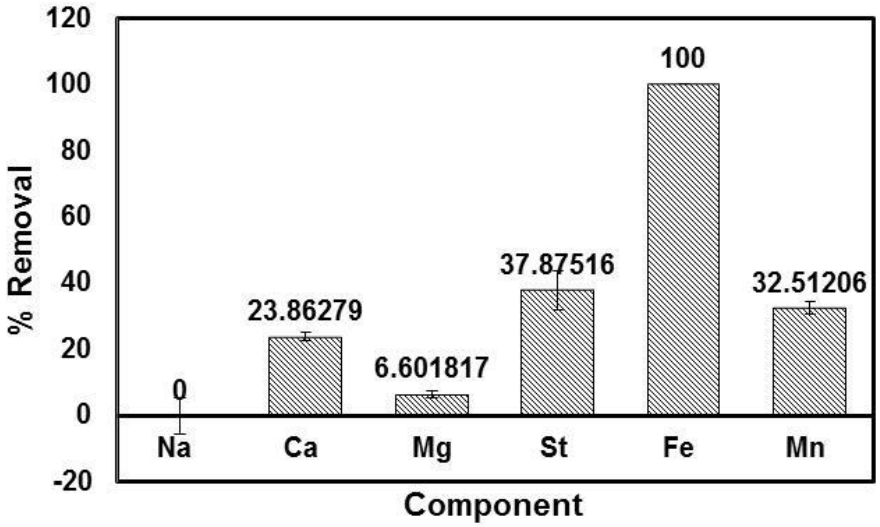


Figure 3. Removal of constituents of concern from flowback water following *D. salina* growth

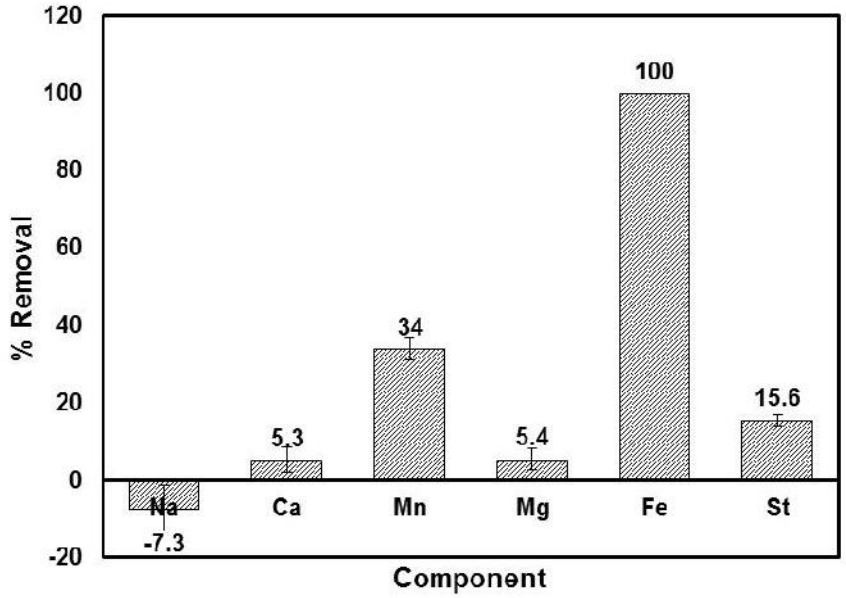


Figure 4. True (biological) replication of experiment from Figure 3.

STUDENTS & POSTDOCS SUPPORTED

Name: Benay Akyon
Major: Environmental Engineering
Degree: Ph.D. Student

Unsupported students involved with the project:
Name: Elyse Stachler
Major: Environmental Engineering
Degree: Ph.D. Student

Name: Tieyuan Zhang
Major: Environmental Engineering
Degree: Ph.D. Student

Name: Arthur Moncrieffe
Major: Environmental Engineering
Degree: MS Student

Name: Nicole Golen
Major: N/A
Degree: High School Student

PUBLICATIONS

Kyle J. Bibby, Susan L. Brantley, Danny D. Reible, Karl G. Linden, Paula J. Mouser, Kelvin B. Gregory, Brian R. Ellis, Radisav D. Vidic. Suggested Reporting Parameters for Investigations of Wastewater from Unconventional Shale Gas Extraction *Environmental Science and Technology.* 47 (23) 13220-13221. 2013.

Benay Akyon, Tieyuan Zhang, Elyse Stachler, Arthur Moncrieffe, Kyle Bibby. Algal biosorption of radium is limited by barium concentration. *In preparation*.

PRESENTATIONS

No presentations have yet resulted from this work, due to slow and poor *D. salina* growth performance. Initial results will be presented at the Shale Energy Engineering Conference (Pittsburgh, July 2014). Biosorption results are expected to result in additional conference presentations.

ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY

(source, amount, starting and ending dates, title)
The USGS grant was the PI's first in the area of flowback water treatment, and has enabled related research in the area of flowback water management as detailed below.

1. DOE-NETL RUA. $105k. 2/2014-11/2014. Microbial Ecology of Flowback Water from Hydraulic Fracturing.
2. Development of Microbial Mats as a Treatment Option for Wastewater from Unconventional Gas Operations. National Science Foundation. $100k. 9/2013-8/2015.

PHOTOS OF PROJECT

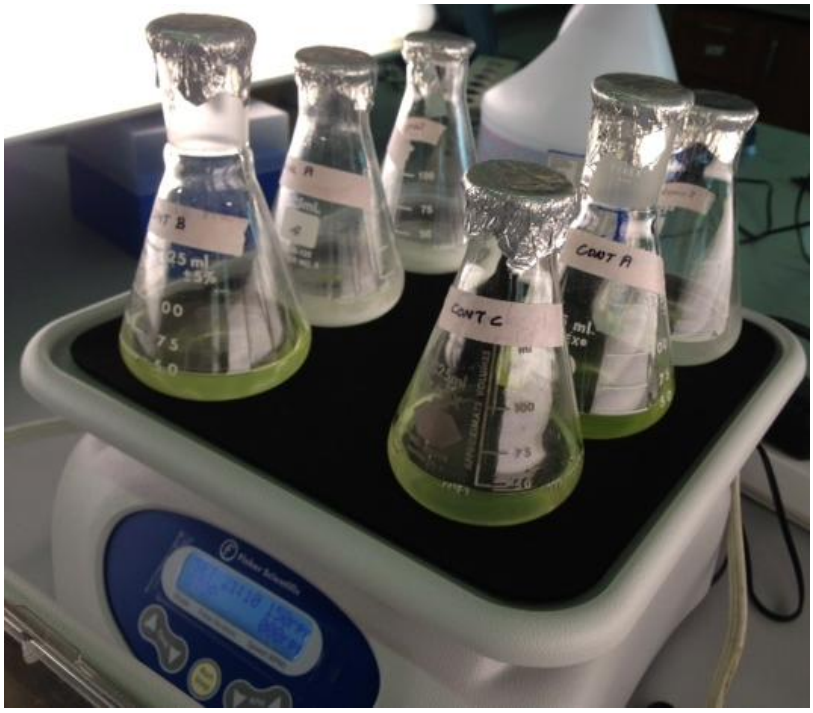


Figure 5. Experimental set-up for the *D. salina* growth experiments

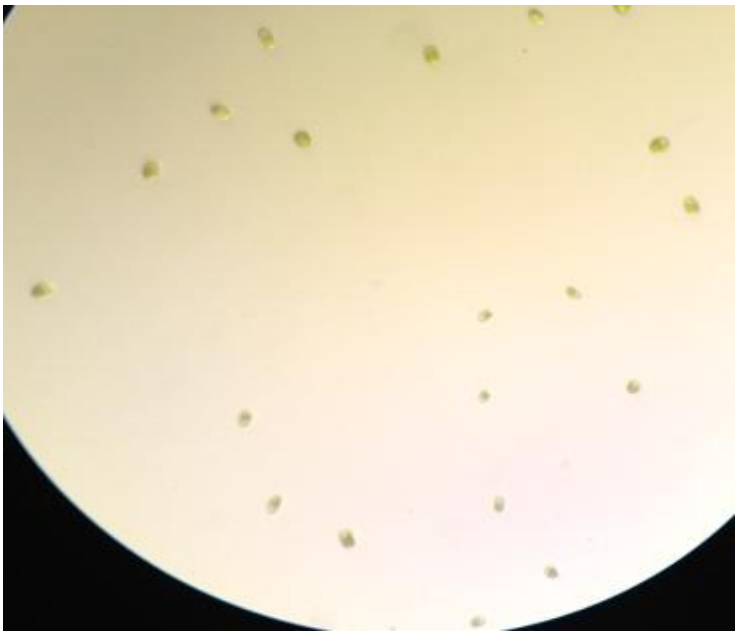


Figure 6. *D. salina* cells grown in 50 000 mg/L NaCl media

Figure 7. *D. salina* cells were grown in 50 000 mg/L TDS flowback water

Range Expansion and Genetic Population Structure of Five Pennsylvania State Threatened Fish Species using Environmental DNA (eDNA) and Molecular Genetic Techniques.

Basic Information

Title:	Range Expansion and Genetic Population Structure of Five Pennsylvania State Threatened Fish Species using Environmental DNA (eDNA) and Molecular Genetic Techniques.
Project Number:	2013PA209B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	14
Research Category:	Biological Sciences
Focus Category:	Conservation, Methods, Management and Planning
Descriptors:	None
Principal Investigators:	Brady Porter

Publications

There are no publications.

PA-WRRC ANNUAL REPORT
USGS 104B PROJECT UPDATE FY2013 (March 1, 2013 to February 28, 2014)

PROJECT TITLE & PRINCIPAL INVESTIGATOR

Range Expansion and Genetic Population Structure of Five Pennsylvania State Threatened Fish Species Using Environmental DNA (eDNA) and Molecular Genetic Techniques.

Brady A. Porter, Associate Professor of Biological Sciences, Duquesne University, porterb@duq.edu, 600 Forbes Ave., Pittsburgh, PA 15282, phone: (412) 396-5786.

SHORT DESCRIPTION OF FINDINGS

Field collections in 2013 have documented new Pennsylvania site records for *Etheostoma tippecanoe, Etheostoma camurum,* and *Percina shumardi* (on the Kiskiminetas, Beaver, and Monongahela Rivers), we've collected eDNA water samples below six lock and dams and four adjacent tributaries, and species-specific eDNA primers are currently being screened for specificity.

PRINCIPAL FINDINGS AND SIGNIFICANCE

Sites Sampled

Tributaries
Tributaries were selected for sampling based on the following criteria:

- They were located within 1 km of lock and dam (L/D) installations (downstream)
- Previous records from the Three Rivers Second Nature (3R2N project) assessment of tributaries of the Allegheny, Monongahela, and Ohio Rivers in western PA showed previous darter site records or streams that could potentially contain darter populations
- A minimum watershed size of ≥ 5 mi^2 – this was developed from my experience which is an estimate of the size of the watershed that is large enough to support imperiled darter species
    - Basin characteristic reports were generated for potentials streams using USGS Stream Stats (a web-based, GIS tool, http://water.usgs.gov/osw/streamstats/)

Streams were electrofished into seines from the first riffle upstream of the confluence for 100m. Fin clips were taken from species of interest and preserved in 100% ethanol in 1.5ml micro-centrifuge tubes. Water quality parameters were recorded with a YSI multi-meter (pH, dissolved oxygen, conductivity) and turbidity was taken with a Hach 2100P Turbidimeter. All species were identified, enumerated, and released. A fortuitous discovery of a bluebreast darter population was made at the Kiskiminetas River in Armstrong Co., PA. We returned to the Kiskiminetas on 7 August, 2013, and documented new site records for populations of both bluebreast and Tippecanoe darters at two locations near Vandergrift and Leechburg, PA. A total of six tributaries were sampled during the summer of 2013, Table 1.

Table 1. Summary of 2013 sampling sites and abundance of target species

		Tributaries Sampled				
		Abundance				
Site	**Tributary To:**	***E. camurum***	***E. tippecanoe***	***E. maculatum***	***P. evides***	***P. shumardi***
Little Sewickly Cr.	Ohio R.	13	—	—	—	—
Flaugherty Run	Ohio R.	—	—	—	—	—

Deer Cr.	Allegheny R.	23	1	—	—	—
Taylor Run	Allegheny R.	—	—	—	—	—
Kiskiminetas R., 1	Allegheny R.	10	25	—	—	—
Kiskiminetas R., 2	Allegheny R.	7	6	—	—	—

Electrified Benthic Trawling

		Abundance				
Site	**Lock & Dam**	***E. camurum***	***E. tippecanoe***	***E. maculatum***	***P. evides***	***P. shumardi***
Ohio River	Emsworth	—	—	—	—	—
Ohio River	Emsworth BC[1]	3	16	—	9*	1
Ohio River	Montgomery	—	2	—	—	19
Allegheny River	L/D #2	4	2	—	2*	1
Monongahela River	L/D #2	2	2	—	—	1
Beaver River	Dam #1	3	—	—	—	—

[1] Back Channel * hybrid

Electrified Benthic Trawling

Sufficient funding was available to sample below six L/D installations. Below each installation (by ~ 200 to 400 m) a transect was sampled using seven, 2 min trawls. The trawls were located – 1 at center channel, 3 to the left descending bank and 3 to the right descending bank. Water quality parameters were recorded with a YSI multi-meter (pH, dissolved oxygen, conductivity) and turbidity was taken at the surface and at the river bottom with a Hach 2100P Turbidimeter (bottom samples were drawn from the eDNA water sample). All small fish were preserved in 100% ethanol. Fish were identified and enumerated at the lab. Large fish were measured to total length, identified and released. A total of six L/D installations were sampled between 23 August and 6 November, 2013, Table 1. We are currently awaiting the most recent PA fish records (from the PA Natural Heritage Program at the Western PA Conservancy) to confirm that we have identified new site records for the presence of *E. camurum*, *E. tippecanoe,* and *P. shumardi* in the Monongahela, Kiskiminetas and Beaver River. In addition, we discovered 11 specimens of potentially new *Percina* hybrid(s) that appear to involve *P. evides* as a parent from the lower Allegheny and Ohio River. We will determine/confirm the species involved with the hybridization and the direction of the crosses using both mtDNA and nuclear gene sequences.

eDNA Sample Collection

Four trial water samples were collected from Deer Creek, Harmarville, PA. to assess which pore size filters to use. Two liters of water were collected for each sample. Using the sterile biological hood in the forensics laboratory, water was filtered using either 0.22 or 0.45 µm glass microfiber filters. The 0.22 µm filters clogged after approximately 500 ml. The 0.45 µm filters clogged after approximately 1L. Therefore, in anticipation of filtering more turbid river water samples and the fact that each sampling event would result in a minimum of 16 L of water, we decided that a larger pore size was logistically necessary. Pore sizes in the literature range from 0.22 to 1.5 µm, but we were concerned that pore sizes > 0.45 µm would be missing much of the potential eDNA. After consulting with Dr. Ian Reynolds, a mitochondrial expert and Senior Director of CNS Discovery at Teva Pharmaceuticals, we settled on 0.7 µm glass microfiber filters. Dr. Reynolds indicated that mitochondria with intact inner and outer membranes are > 1 µm, but that the genomic mtDNA plasmid is much smaller than 1 µm. Previous eDNA studies on Asian carp (Jerde et al., 2011) and charr (Wilcox et al., 2013), were most likely filtering intact mitochondria by using 1.5 µm filters. Our four trial filters from Deer Creek were processed with the PowerWater extraction protocol. Total DNA was quantified with a NanoDrop ND 1000 spectrophotometer and ranged from 43 to 55 ng/µL in a 100 µL elution.

eDNA water samples (3, two liter replicates) were collected in the tributaries just downstream of the first riffle where sampling started. In river sampling, a horizontal Van Dorn bottle was dropped to the bottom of the river at 7 locations spaced out across the transect. All samples were stored on ice and filtered within 24 h. Filters are stored at -80 °C until extraction. There are two major extraction kits used for eDNA work – MoBio PowerWater Extraction Kit and the Qiagen DNeasy Blood and Tissue Extraction Kit. We have purchased both to do comparisons on extraction efficiency.

Primer Design

Because we would like to attempt multi-plex PCR with our five target darter species, our first step was to download and align GenBank sequences of the mtDNA ND2 gene for all of our species of interest – including the species that will be used as positive controls to illustrate that PCR is working. The tributary and river sampling has indicated that three common species should be selected for both the aquarium experiments and the PCR-eDNA positive controls. In river samples, the channel darter, *Percina copelandi*, was the most abundant darter found at all river locations except the Beaver River. For tributary samples the rainbow darter, *Etheostoma caeruleum*, and the greenside darter, *E. blennioides*, will be used as controls. Therefore, any complete ND2 sequences from GenBank were downloaded and aligned using DNASTAR – MegAlign software (version 8.1.3) for all eight species. Using primers previously established by Howell (2007), DNA was extracted from finclips using phenol:chloroform, amplified with PCR primers GLN(F)/ASN(R), and sequenced using three sequencing primers for entire gene coverage: (MET(F), LAH(F), and END2(F). Primers have been manually designed for fragments of approximately 150 to 175 bp. Currently, *E. camurum* and *E. tippecanoe* primers have been tested and confirmed for specificity. *E. maculatum, P. shumardi, P. evides*, and *P. copelandi* primers are being screened. ND2 from local specimens of *E. caeruleum* and *E. blennioides* has been sequenced in order to determine intra-species variation for proper primer design.

STUDENTS & POSTDOCS SUPPORTED

Funding from this project provides equipment and supplies for Anthony Honick, Biology, Ph.D. candidate. It has also provided field sampling experience in electrified benthic trawling for Nathan Reinhart (M.S. Environmental Sciences), and in backpack electrofishing for Brian Trevelline (M.S. Environmental Science) and Shyama Attewattegama (M.S. Environmental Sciences). All are students at Duquesne University.

PUBLICATIONS (follow style formats on the next page)

In progress.

PRESENTATIONS

Honick, A.S. and Porter, B.A. *The design and implementation of environmental DNA (eDNA) techniques for threatened and endangered darters of the upper Ohio River watershed.* The American Fisheries Society, Pennsylvania Chapter – Spring Technical Meeting, April 25, 2014.

OTHER INFORMATION TRANSFER ACTIVITIES

Using our experience, we developed an eDNA protocol to detect brook trout from water samples by modifying the procedure of Wilcox et al. (2013) and adapting it for PCR and gel-based visualization. This protocol was sent to University Schools in Cleveland, Ohio to further strengthen a partnership between the Environmental Science Program at Duquesne University and this college prep high school. University Schools maintains a brook trout hatchery on their campus and incorporates trout propagation it into their science program. We are

attempting to transfer eDNA technology to their science program so they can better monitor the success of their brook trout stocking efforts.

NOTABLE AWARDS & ACHEIVEMENTS (of PIs or students or other staff on the project)

As a result of the active funding and the resulting research progress that has been achieved by the Ph.D. candidate Anthony Honick, he has been awarded a Duquesne University Bayer Fellowship by the Department of Biological Sciences. This will free Mr. Honick from his Teaching Assistantship responsibilities for the Fall 2014 academic year (1 July through 31 December 2014) and allow him to fully focus on this research project by providing him with a research assistantship stipend ($11,000 value).

PHOTOS OF PROJECT
See below.

Figure 1. eDNA sample collection using a Van Dorn bottle – by Anthony Honick (with Van Dorn) & Mike Koryak. Location: Braddock Lock & Dam Monongahela River, Pittsburgh, PA.

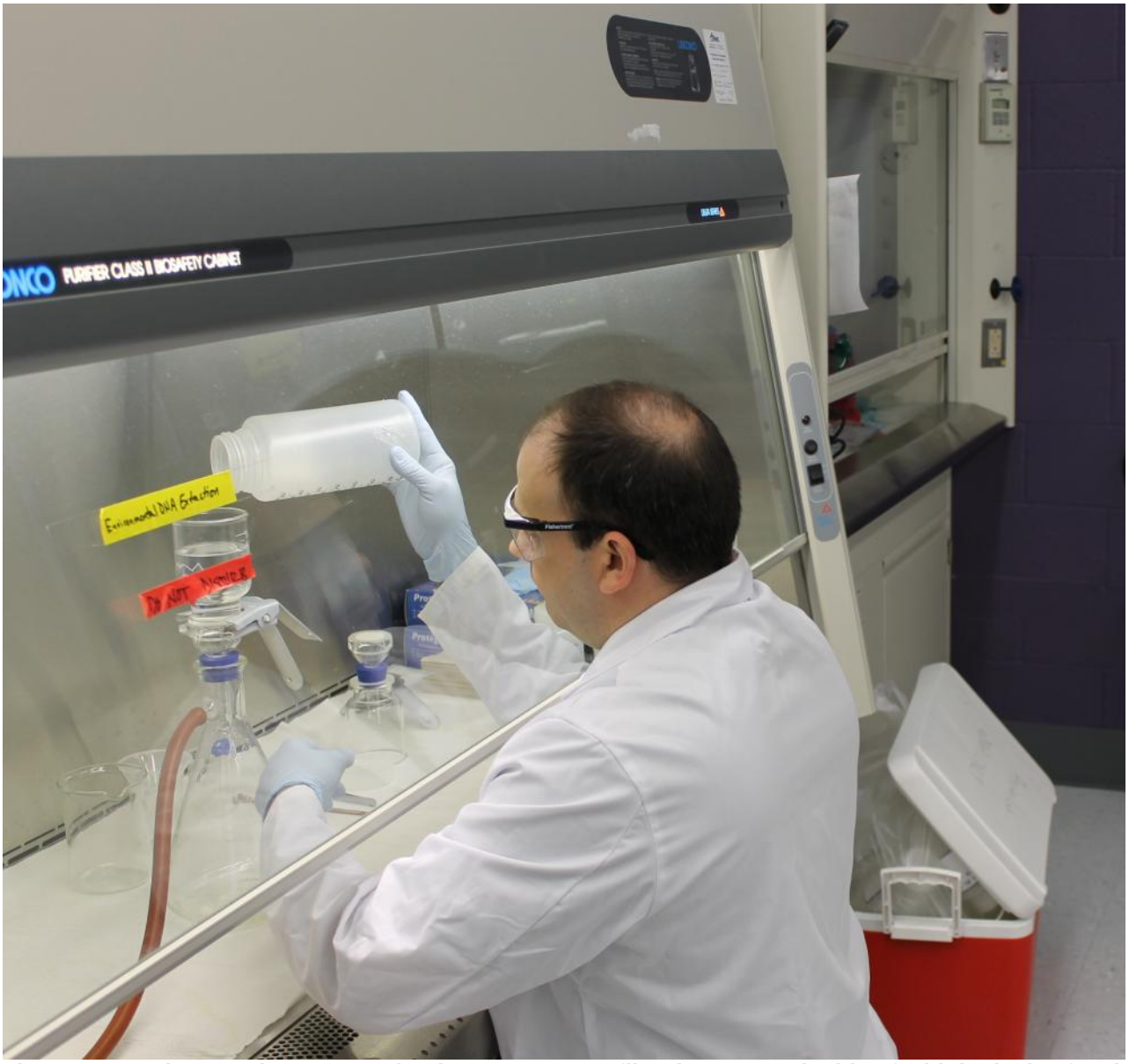


Figure 2. In order to reduce contamination eDNA water filtration occurs inside of a biological safety hood that is within a dedicated pre-PCR forensics room at Duquesne University - filtering performed by Anthony Honick.

Developing Quantitative Models for the Removal of Quaternary Ammonium Ions as Representative Cationic Emerging Contaminants by Cation Exchange Resins

Basic Information

Title:	Developing Quantitative Models for the Removal of Quaternary Ammonium Ions as Representative Cationic Emerging Contaminants by Cation Exchange Resins
Project Number:	2013PA210B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Treatment, Water Quality, Water Supply
Descriptors:	None
Principal Investigators:	Huichun Judy Zhang

Publications

There are no publications.

PA-WRRC ANNUAL REPORT
USGS 104B PROJECT UPDATE FY2013 (March 1, 2013 to February 28, 2014)

PROJECT TITLE & PRINCIPAL INVESTIGATOR

Developing Quantitative Models for the Removal of Quaternary Ammonium Ions as Representative Cationic Emerging Contaminants by Cation Exchange Resins

Huichun (Judy) Zhang, Ph. D., Assistant Professor, Temple University, Department of Civil & Environmental Engineering

SHORT DESCRIPTION OF FINDINGS

This research showed that polymeric cation exchange resins can selective remove cationic organic contaminants from contaminated water and the developed predictive model can accurately estimate sorption capacity of a diverse range of cationic solutes at different pH.

PRINCIPAL FINDINGS AND SIGNIFICANCE

pH effect on sorption capacities of resins. The pH effect on the sorption of neutral aromatic and quaternary ammonium compounds was studied to examine the contribution of electrostatic versus non-electrostatic interaction to sorption capacity. The sorption capacity of quaternary ammoinums on two strong cation exchange resins, MN500 and Amberlite200, is pH-independent. The quaternary cations are permanently charged, indicating that electrostatic interactions are pH independent. Sorption of nitrobenzene (NB) on the cation exchange resins is also pH independent but is significantly lower than that of the cations, this is because neutral NB does not have any electrostatic interactions with the ion exchange resins. The pH effect was then investigated for aniline (pK_a = 4.67) as a compound that undergoes proton transfer reaction under changing pH conditions. Aniline is protonated at pH < pK_a and neutral at pH > pK_a. Sorption of aniline is strongly pH-dependent which significantly decreased when the ratio of protonated aniline to neutral aniline decreased, showing that the protonated aniline had higher sorption capacity than neutral aniline. We attributed this to the fact that protonated aniline undergoes ion exchange reactions (electrostatic) in addition to hydrophobic (nonelectrostatic) interactions. Also, sorption of aniline slightly decreased when pH was lower than 3, due to competition with H^+ for the sorption sites.

Aqueous Sorption Isotherms. In general, MN500 exhibits higher sorption capacity than Amberlite 200, because MN500 has a high proportion of micropores (more than 48% of pore volume) which enhanced sorption energy due to superposition of force fields of the opposite walls[1]. Although Amberlite 200 has a lower moisture content than MN500, it has a significantly lower surface area (42 versus 370 m^2/g), thus, there are less sites available for solute sorption. Sorption affinity of organic compounds on MN500 and Amberlite 200 follows the order of: aromatic cations > aliphatic cations > neutral aromatic solutes. The higher affinity of the cationic compounds indicates that the primary sorption process is ion exchange. The interactions between the nonpolar moieties of the ions and of the resins and solvent-associated interactions are two important factors that influence on the resin selectivity. The higher sorption affinities of the aromatic cations can be attributed to the strong non-electrostatic interactions resulting from π - π interactions between the aromatic rings of the resin matrix and the aromatic cations. While the neutral aromatic compounds have the ability of forming π - π interactions, the lack of electrostatic interactions resulted in their much lower removal by the cation exchange resins.

The sorption behavior of two neutral compounds (phenol and NB) on ionic and nonionic resins was studied in order to investigate the effect of resin structure. The neutral resins showed much higher sorption capacities (at least 5 times higher) than the ionic resins with sorption capacity following the order of: MN200 > XAD-4 > XAD-7 > MN500 > IRA-96 > IRA-910. This behavior can be mainly contributed to the higher surface areas of the neutral resins and the highly hydrophilic nature of the ionic resins (due to the presence of functional groups). Sorption of the neutral compounds on MN200 exhibits the highest sorption capacity among the neutral resins due to its high surface area and microporous structure with high sorption potential[2]. Comparing with XAD-7, XAD-4 has a larger pore volume (1.25 versus 1.12 cm^3/g) and a higher proportion of miropores (12.4% > 2.3%). Moreover, XAD-7 has the highest moisture content (67%) due to its polar acrylic structure, while the moisture content of XAD-4 and MN200 is 56% and 58%. Lower sorption affinity of IRA-96 and IRA-910, two anion exchange resins, can be related to their higher moisture contents than the cation exchange resin MN500. IRA-910 and IRA-96 have higher ion exchange capacities (5.33 and 6.19 meq/g-dry respectively) than MN500 and Amberlite200 (1.07 and 2.43 meq/g-dry respectively), which can result in more hydrophilic structures.

Multiple linear correlations between the natural logarithm of selectivity and Abraham's solute descriptors was conducted at different sorbed concentrations to examine the contribution of different interactions to the overall selectivity of the cations. We found that selectivity was mainly promoted by dipolar/polarizability effects; induced dipole (E), electrostatic (J^+), and H-accepting interactions (A) had some positive effects on the selectivity. H-bond basicity (B) had a large positive effect which applies to the neutral compounds only since B is almost zero for all cations. After the gas phase conversion, the contribution of solvent-associated interactions to the Gibbs free energy change has been eliminated, and consequently the contribution of solute-sorbent interactions can be obtained. Unlike the aqueous phase, electrostatic interaction has the most dominant effect on the sorption of the cationic compounds from the gas phase.

Development of Predictive Model. A predictive model was developed based on the above obtained regression coefficients at various sorbed concentrations and was then used to estimate aqueous equilibrium concentration at any given Q_e. **Figures 1** illustrates the correlation of the estimated equilibrium concentrations using the predictive model with the experimental

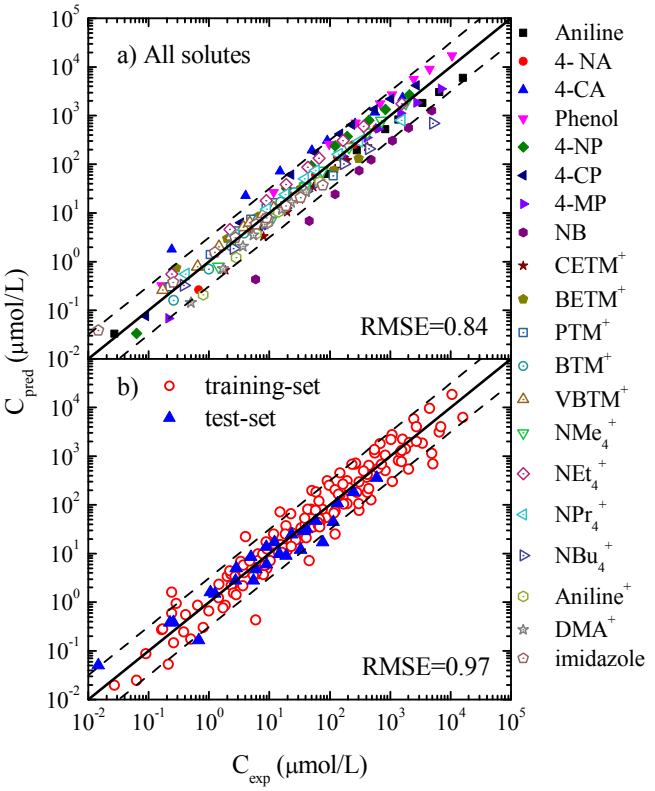


Figure 1. Aqueous equilibrium concentrations calculated based on the predictive model versus the experimental values for a) a training-sets including 12 cations and 8 neutral aromatic solutes with 169 data points and b) a training-set of 17 solutes with 153 data points and 3 test set solutes (4-NA, PTM+, and imidazole) with 27 data points for MN500. The predictive models were constructed based on the correlations between $\Delta G_{S\text{-}W,i}$ and solute descriptors. The solid lines show a perfect prediction, where the predicted value for C_e exactly equals the experimental value; the dashed lines are 0.5 log units above or below the solid lines.

values. The good correlation results indicate that the predictive model is able to accurately predict the sorption behavior of a diverse range of cationic and neutral solutes. Overall these findings will provide guidance to resin selection processes in a given treatment scenario, and will also help polymer industry synthesizing resins with desired physical-chemical properties.

STUDENTS & POSTDOCS SUPPORTED

Nastaran Jadbabaei, Environmental engineering, Ph.D. Candidate
Quiana M Waters, Civil &Environmental engineering, undergraduate student
Both at Temple University.

PUBLICATIONS

Jadbabaei, Nastaran; Zhang, Huichun*, 2014, Sorption Mechanism and Predictive Model for Removal of Cationic Organic Contaminants by Cation Exchange Resins, *Environmental Science and Technology* (In preparation).

PRESENTATIONS

Jadbabaei, Nastaran; Zhang, Huichun*, 2013, Revisit Sorption Mechanisms of Organic Compounds on Cation Exchange Resins, 246th ACS National Meeting, Division of Environmental Chemistry, Indianapolis, IN.

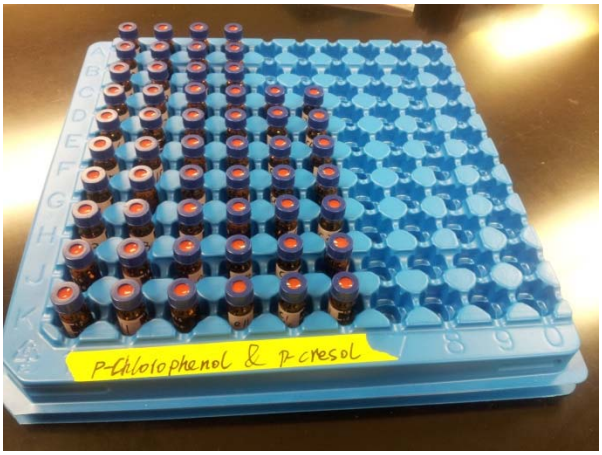
Jadbabaei, N.; Zhang, H.*; "Revisit sorption mechanisms of organic compounds on cation exchange resins", American Water Resources Association, Philadelphia Metropolitan Area Section (AWRA-PMAS) on "Constructed Wetlands for On-site Wastewater Treatment", Philadelphia, PA, Feb 20, 2014.

NOTABLE AWARDS & ACHEIVEMENTS

American Chemical Society, The Division of Environmental Chemistry, "**Certificate of Merit**" awarded to N. Jadbabaei and H. Zhang for the outstanding oral presentation "Revisit sorption mechanisms of organic compounds on cation exchange resins" at the 246th National Meeting

PHOTOS OF PROJECT

Amber bottle reactors containing a target contaminant and the studied resin.



Samples of the reaction solution before and after treatment using cation exchange resins.

Analytical instrument (HPLC) for analysis of the samples.

References:

1. Dubinin, M. M., 1960,The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces. *Chemical Reviews. ,60*, (2), 235-241.
2. Pan, B.; Zhang, H., 2013, Interaction mechanisms and predictive model for the sorption of aromatic compounds onto nonionic resins. *Journal of Physical Chemistry C, 117*, (34), 17707-17715.

Evaluation of Round Goby and Tubenose Goby Habitat Disturbance and Impacts to Native Fishes – Phase II

Basic Information

Title:	Evaluation of Round Goby and Tubenose Goby Habitat Disturbance and Impacts to Native Fishes – Phase II
Project Number:	2013PA211B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	3
Research Category:	Biological Sciences
Focus Category:	Invasive Species, Conservation, Ecology
Descriptors:	None
Principal Investigators:	Jay Stauffer

Publications

There are no publications.

PA-WRRC ANNUAL REPORT
USGS 104B PROJECT UPDATE FY2013

PROJECT TITLE & PRINCIPAL INVESTIGATOR
Evaluation of Round Goby Habitat Disturbance and Impacts to Native Fish Populations

Jay Stauffer, Professor, Department of Ecosystem Science & Management, Pennsylvania State University

SHORT DESCRIPTION OF FINDINGS The results from this study indicate: 1) the presence of Round Gobies, *Neogobius melanostomus*, shifted the habitat (eg., depths and flows) occupied by native benthic species in the tributaries of Lake Erie; 2) within the lake, neither the Round Goby nor the Tubenose Goby, *Proterorhinus semilunaris* are in direct diet competition with the Iowa Darter, *Etheostoma exile*; and 3) conversely, the Round Goby appears to be in direct competition with the Rainbow Darter, *Etheostoma caeruleum* relative to prey items.

PROBLEM & RESEARCH OBJECTIVES

Invasive species have significantly changed ecosystems of the Great Lakes and can have broad effects on food, water, and recreation of the region. Mechanistic studies of invasive fishes are critical toward predicting impacts of their invasions and population growth that, in turn, lead to the displacement of native benthic fishes. Previous sampling in watersheds that are tributary to Lake Erie resulted in significant discoveries of invasive fish species; documenting the first record of Tubenose Gobies in Pennsylvania; and documenting the presence of spawning Round Gobies in Elk Creek. Further, preliminary data indicate that the Tubenose Goby feeds primarily on zebra mussels and other gastropods. It may be that the tributaries do not support food sources needed to support Tubenose Gobies; however, may be able to switch diets to eat prey species found in these tributaries. Following from our pilot study, this project will address the following research questions: 1) Have Tubenose Gobies invaded the tributaries of Lake Erie?; 2) Do Tubenose Gobies have the potential to invade tributaries of Lake Erie?; 3) What are the diet preferences of Gobies in tributaries of Lake Erie?; and 4) What is the spawning season of Round Gobies in Elk Creek?

The homogenization of the Earth's biota by the introduction and spread of non-native species is one the most damaging anthropogenic impacts on biodiversity today (Mills et al. 1994, Kolar and Lodge 2002). Degradation of aquatic ecosystems by the introduction of nonnative fish species is exemplified in the Great Lakes of North America. Native fish communities in this region have been irreparably harmed by the introductions, both accidental and intentional, of exotic species (Jude et al. 1995). Infamous piscine invaders such as sea lampreys (*Petromyzon marinus*), alewives (*Alosa pseudoharengus*), and rainbow smelt (*Osmerus mordax*) have had cascading detrimental effects on the native biota of the Great Lakes region (Fuller et al. 1999, Jude et al. 1995). The most recent round of aquatic invaders that have impacted the integrity of the Great Lakes are mainly Pontio-Caspian natives including two bivalve species; the zebra mussel (*Dressnia polymorpha*), the quagga mussel (*Dressnia bugenis*), and three piscine species; the ruffe (*Gymnocephalus cernuus*), the tubenose goby (*Proterorhinus marmoratus*), and the round

goby (*Neogobius melanostomus*). Of the three most recent fish introductions, round gobies are the most prolific and widespread.

The round goby is a small benthic fish native to the Sea of Azov, the Caspian Sea, the Black Sea and the Sea of Marmara (Charlebois et al. 1997) (Fig 1.). Round gobies were first discovered by anglers in the Laurentian Great Lakes in 1990 in the St. Clair River at Saran, Ontario where they are assumed to have been introduced by ballast waters of freighters (Jude et al. 1992, Charlebois et al. 1997). Introduction via transatlantic ballast water is hypothesized to be the vector for many of the recent Pontio-Caspian invaders (Mills et al. 1993). Round gobies were thought to be confined to the St. Clair River until 1993 at which time they were found in the Calumet River near Lake Michigan and in Grand River Harbor Ohio (Charlebois et al. 1997). In 1995, round gobies were found in Western Lake Michigan and Eastern Lake Erie. Since this time, round gobies have spread rapidly to all of the Great Lakes, presumably by interbasin ballast transfer (Clapp et. al 2001). The first round goby found in the Pennsylvania waters of Lake Erie was during a trawl by the Pennsylvania Fish and Boat Commission in 1996 (Chuck Murray PFBC per. com.). Round gobies are now the dominant benthic fish in many of the tributary streams in the Pennsylvania waters of Lake Erie.

Round gobies have been found to have detrimental effects on native fish populations in the Great Lakes Region. Preliminary research has implicated them in the extirpation of the mottled sculpin (*Cottus bairdi*) and the eastern sand darter (*Ammocrypta pellucida*), and the decline of the Johnny (*Etheostoma nigrum*) and Iowa darters (*Etheostoma exile*) (Jansen and Jude 2001, Dubs and Corkum 1996, per. obs.). Round gobies have been found to prey on the eggs of log perch (*Percina caprodes*) and several other native species (Chotkowski and Marsden 1999). Under experimental conditions, they will prey on rainbow (*Etheostoma caeruleum*) and greenside darters (*Etheostoma blenniodes*) (Jude et al. 1995). It is suspected that they compete with native species for food and habitat (Jansen and Jude 2001, French and Jude 2001).

Habitat partitioning studies are “natural snapshot” experiments (Diamond 1986, van Snik Gray and Stauffer 1999). They provide information on habitat requirements of fishes as well as demonstrating habitat shifts in the presence of introduced fishes (van Snik and Stauffer 2001). Although preliminary studies suggest that round gobies are having negative effects on native fishes, no direct evidence has been documented. Habitat partitioning could give direct evidence of this effect. The purpose of this study is to examine partitioning between non-game native benthic Lake Erie stream fishes (darters, madtoms, and sculpins) and to determine if there was a shift in habitat usage of the native fishes when round gobies were present in Twenty-mile Creek.

The purposes of this project were to examine diet overlaps between Round Gobies and native benthic fishes in the deeper waters of Lake Erie, in Presque Isle Bay, and the Pennsylvania tributaries of Lake Erie and do document habitat shifts in native benthic fishes with the presence/absence of Round Gobies.

METHODOLOGY

Fishes were collected in Twenty-mile Creek from the mouth of the stream to the waterfall, just below the old railroad bridge with two 6’x 10’x 1/8th” seines to determine the fish composition

and species diversity in areas where gobies were present and absent. Additionally, we electrofished 100 meters (25-m below the sites, 50-m sites, and 25-m above the sites). All fishes collected were identified to species and released with the exception of voucher specimens for each species. Percent composition, population estimates, and Simpson diversity indices were calculated for each site.

The two sites were chosen based on physical similarities and previous investigations which indicated a similar species composition and the absence of gobies at the upstream site. The interaction habitat preference study was conducted by three skin divers who began snorkeling at the downstream end of the site and made their way slowly upstream so that the fishes would not be disturbed. Following a benthic fish observation a numbered colored flag was secured into the stream bed at the specific locality of the fish. Flag color indicated the species of fish sighted. Following the snorkeling session, the following abiotic variables were recorded at each flag: depth (cm), water velocity (m/s), substrate size, distance from shore, and distance from the origin of the site. Water velocity was measured with a digital flow meter with a bulb sensor and taken from the bottom of the stream. Depth, velocity, flow, distance from shore and distance from origin were recorded at all flags. Substrate data was taken randomly on approximately half of the fishes due to time limitations.

Substrate size was quantified using a 100 x 100 cm acrylic sheet marked with a grid of 100 5 x 5 cm squares. The center of the grid was placed over the location of the flag and the number of 5 x 5 cm squares covered by each rock was recorded. Each substrate count plot was characterized by the number of substratum falling into each of the 100 potential categories. For example, category "2" contained substratum covering a two-5 cm^2 block and category "100" contained substratum covering one hundred-5 cm^2 blocks (or 500 cm^2). The substrate index score was calculated by first multiplying the number of substratum in a particular category by the category number squared (i.e. if two substratum cover four-5 cm^2 blocks, the product is 2×4^2 or 32) and then summing the products of each category. Therefore, plots containing smaller substratum have a lower substrate index score than plots that have larger substratum.

Following the collections of fish habitat preference data, random transect data on habitat availability were collected during the months of July and August. Habitat availability was assessed by making six equally spaced transects along the length of the site. Five random points across each transect were sampled for depth, flow and width of the stream.

Electric trawls were used to collect benthic fishes in Presque Isle Bay, and backpack electro-shockers were used to collect fishes in the tributaries. Collections in the tributaries occurred downstream of any major barriers, where Round Gobies have invaded and upstream of barriers (e.g., waterfalls), where there are only indigenous benthic fishes. Sampling occurred at 20 Mile Creek, 16 Mile Creek, and Elk Creek. Although Round Gobies were found downstream of barriers at all tributaries, our efforts focused on Elk Creek due to a greater abundance of Round Gobies. At the same time the fishes were collected, collections of macrobenthos were taken using a ponar in Presque Isle Bay and D-frame kicknets and drift nets in the tributaries.

Drift nets were held in place for 15 minute sampling periods every 3 hours over a 24 hour time span. The drift nets remained on the bottom of the stream during collections and capture those

macro-invertebrates in the water column. Fish were collected using backpack electrofishing equipment at the lowest possible voltage. A seine was held downstream to collect the fish. Fish were identified, counted, photographed and preserved. Collections took place 3 times in a 24 hour period. Water velocity was recorded before the first drift sample collection and after the last drift sample collection.

Sample Processing

Stomachs were removed from all benthic fishes collected and the contents identified to the lowest possible taxon (family or genus). Macroinvertebrates collected were also enumerated and identified to the lowest possible taxon. Stomach contents of all fishes were compared to determine any trophic partitioning, which is occurring among species. These data were compared to the results of the macroinvertebrate collections and calculated electivity indicies.

PRINCIPAL FINDINGS AND SIGNIFICANCE

More individual fishes were captured by electrofishing at the upper site, Site 2, than the lower site, Site 1 (Table 1). Round gobies comprised 45% of the total fishes at the lower site. Rainbow darters comprised the second largest species composition, 35% in the bottom site and the fourth largest species composition at the top site. In contrast the fishes exceeding rainbow darters in species composition at the top site were pelagic minnows observed in large schools. In total, rainbow darters constituted the greatest percentage of benthic species composition at both sites, when round gobies were excluded from Site 1.

We chose to electrofish to estimate the number of species present because this technique is effective in capturing the greatest diversity of species (pelagic and benthic). Unfortunately, electrofishing is often biased toward pelagic fishes. We would like to note that seining efforts on Twenty-mile Creek in the past have yielded other benthic fishes not represented in Table 1, such as *Percina copelandi* and *Percina maculata*.

Diversity indices are mathematical measures of species diversity in the community. They provide information about community composition, species richness, and they also take the relative abundance of different species into account. Simpson's diversity index is a mathematical measure that characterizes species diversity in a community. The index was created by multiplying the total number of individuals of a particular species by that number minus one. These products were summed and divided into the product of the total number of fishes for that site by the total number of fishes for that site minus one. Values for the Simpson diversity index can range from a value of 1 in a community comprised of only one species to an infinite value for a community comprised of a large number of species with each represented by a single individual; therefore, the higher the Simpson's Index Score, the greater the species diversity.

The Simpson's diversity index for the top site was much higher than the bottom site (6.012 versus 3.0124). This difference is surprising considering that the lower site exposed to Lake Erie, would be expected to have more fishes present that were temporarily using the mouth of the stream. The higher diversity index for the top site could be an indication that gobies, which are present in large numbers at the bottom site, are impacting the biodiversity of the stream. It could

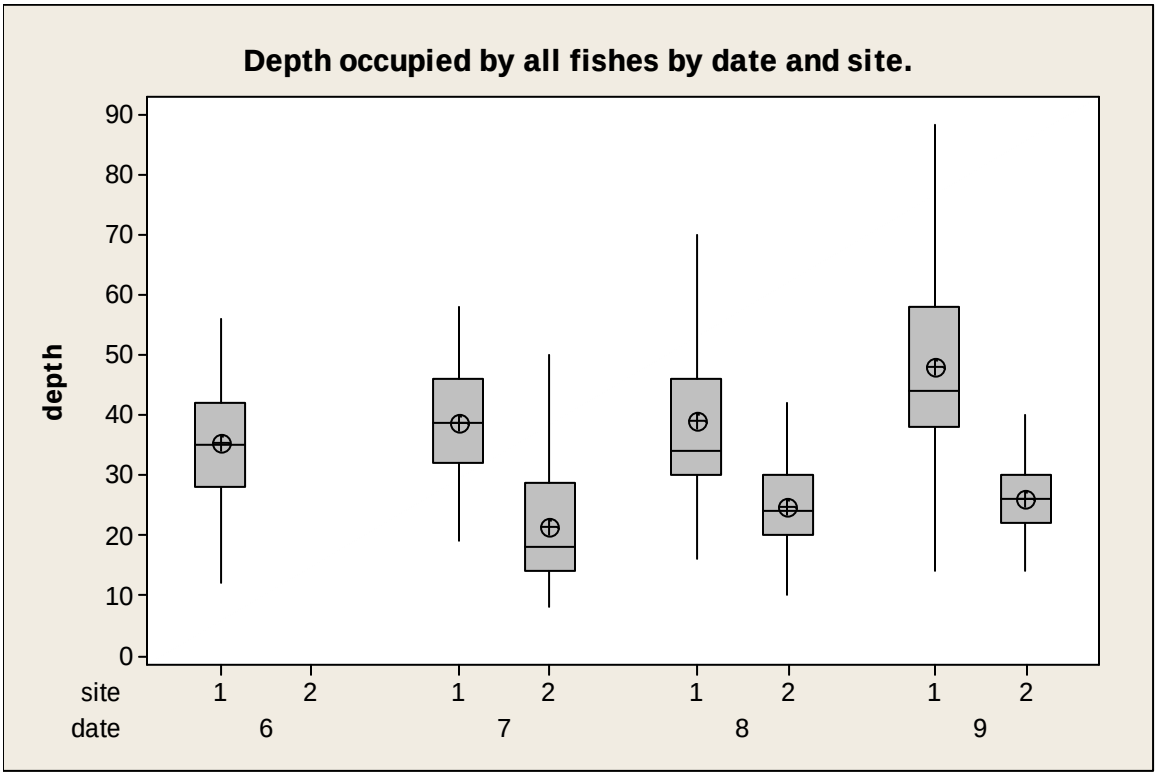
also indicate however, that the top site is better habitat for some pelagic minnows which make up a large number of the fishes sampled. When the index was calculated just including benthic fishes, the diversity index for site 1 and site 2 were more similar, 2.49 and 2.09 respectively. This indicates that benthic fish diversity is relatively the same at both sites. Additional quantitative measures, such as depth and flow, were investigated to test the comparability of the two sites.

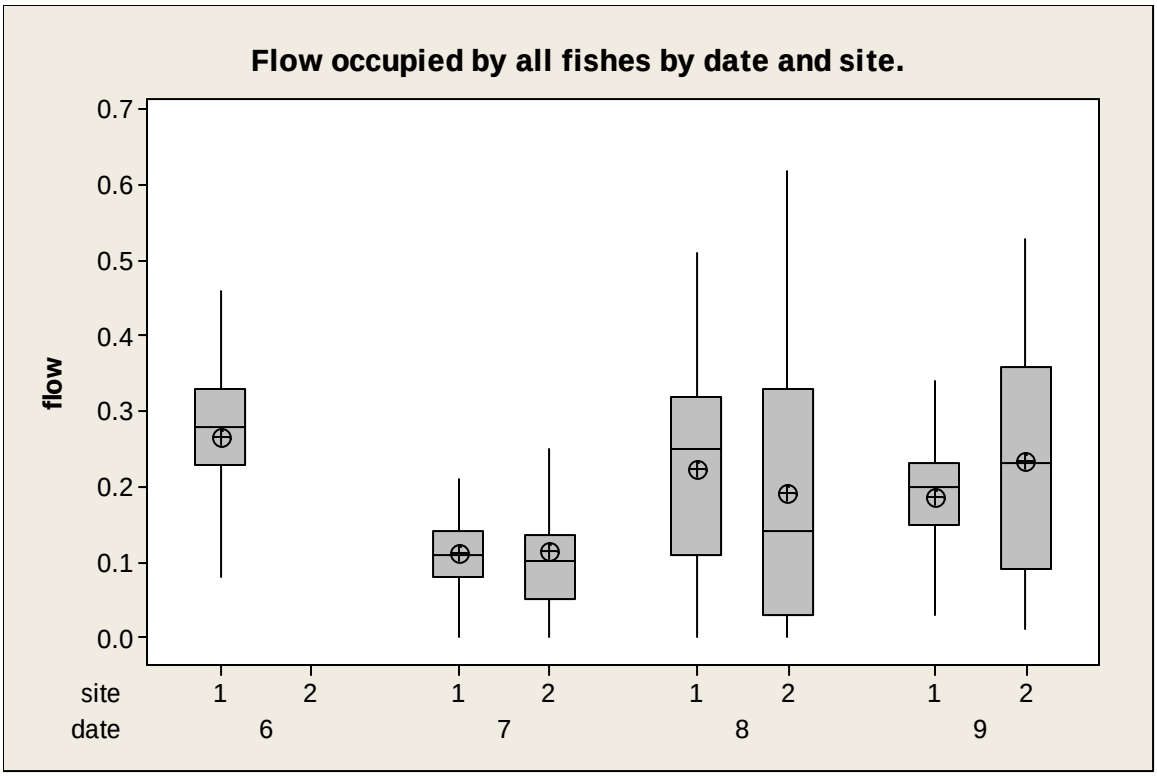
Table 1. Fish survey and species composition.

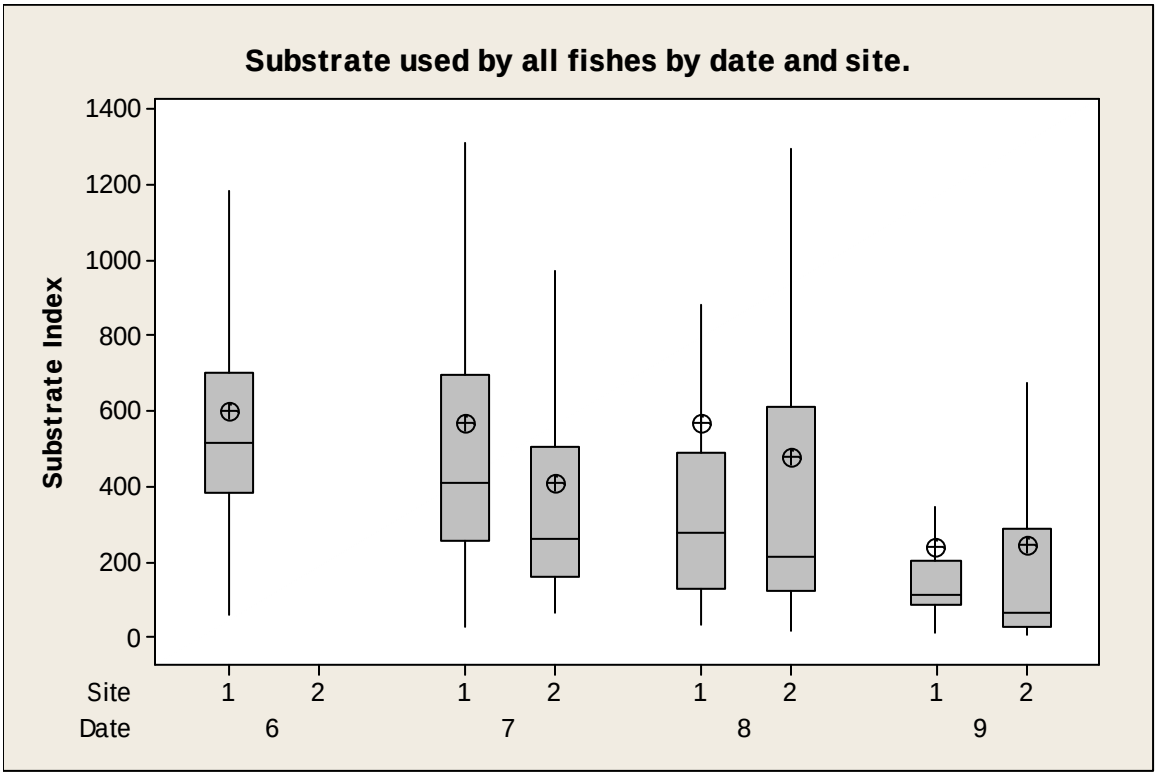
		Number of Fish		Percent Composition	
Genus	**Species**	**Site 1**	**Site 2**	**Site 1**	**Site 2**
Ambloplites	***ruprestris***	1	1	0.00	0.00
Ameiurus	***nebulosus***	0	2	0.00	0.01
Campostoma	***anomalum***	17	53	0.07	0.14
Catostomus	***commersoni***	0	8	0.00	0.02
Cottus	***bairdi***	0	11	0.00	0.03
Cyprinella	***spiloptera***	1	0	0.00	0.00
Etheostoma	***caeruleum***	88	48	0.35	0.12
Etheostoma	***flabellare***	2	6	0.01	0.02
Hypentileum	***nigricans***	1	0	0.00	0.00
Lepisosteus	***osseus***	1	0	0.00	0.00
Lepomis	***gibosus***	2	2	0.01	0.01
Lepomis	***machrochirus***	2	1	0.01	0.00
Luxilus	***cornutus***	1	0	0.00	0.00
Luxilus	***chrysocephalus***	0	22	0.00	0.06
Micropterus	***dolemuei***	7	0	0.03	0.00
Neogobius	***melanostomus***	113	0	0.45	0.00
Nocomis	***micropogon***	4	124	0.02	0.32
Notoropis	***atherinoides***	1	0	0.00	0.00
Noturus	***flavus***	3	0	0.01	0.00
Oncorhyncus	***mykiss***	4	15	0.02	0.04
Percina	***caprodes***	0	4	0.00	0.01
Pimephales	***notatus***	0	1	0.00	0.00
Rhinichthys	***atratulus***	2	59	0.01	0.15
Rhinichthys	***cataractae***	0	26	0.00	0.07
Salmo	***trutta***	0	1	0.00	0.00
Semotilus	***atromaculatus***	0	4	0.00	0.01
TOTAL		**250**	**388**		

Habitat Preferences

To analyze the effect of gobies on other benthic fishes we first examined the basic statistics of each species at each site by the depth, flow, and substrate index. Basic statistic of the overall study indicate that rainbow darters are the most abundant benthic fish found at both sites (n = 851). Round gobies were the second most abundant fishes with 127 of them being observed at the first site. Stonecats were the least abundant fishes observed in the study (n = 1) because of this they were eliminated from further statistical analysis. Rainbow darters and round gobies were found at similar mean depths (43 vs. 43.2 cm) at the first site and Logperch were found at the greatest mean depth at the second site (29.86 cm). Flows for all species were similar for the overall study with the exception of log perch which were found at the highest mean flow (0.68 m/s) at the first site. Gobies preferred the overall largest substrate size being found near substrate with a mean substrate index size of 717.7. Channel darters were found at the second largest mean substrate size (408) at the second site. Box plots of the variables were also examined to allow us to visually estimate mean differences in the variables. The box plots for all variable indicated that there were differences by date however the differences between sites was not as clear in all cases and are further examined statistically. In general, the basic statistics demonstrated that the fishes observed in this study preferred different depths and substrates in the two sites which could indicate that gobies are affecting these fishes' habitat use. To examine this more closely further statistical analysis was conducted to determine the significance of this apparent segregation between sites.




Flow occupied by all fishes by date and site.
flow
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
site
date
1
2
6
7
8
9


Substrate used by all fishes by date and site.
Substrate Index
1400
1200
1000
800
600
400
200
0
Site
Date
1
2
6
7
8
9

STUDENTS & POSTDOCS SUPPORTED
Dr. Jeanette Schnars, Director, Tom Ridge Environmental Center
Casey Bradshaw, Ph.D, Wildlife and Fisheries Science
Richard Taylor, MS, Wildlife and Fisheries Science
Shan Li, Ph.D, Wildlife and Fisheries Science
Kristin Taylor, volunteer
2012 Class WFS 454, Field Ichthyology
2012 Enviro-Camp high school students
Jackie Madzke, senior, Wildlife and Fisheries Science
C. William Hanson, Ph.D, Wildlife and Fisheries Science

PUBLICATIONS
In preparation.

NOTE:
This project is not yet completed, it is ongoing in FY 2014.

PHOTOS OF PROJECT

Round Goby in Lake Erie.

Picking macro-invertebrates from drift nets.

Seining for fish at Elk Creek.

LITERATURE CITED

Charlebois, P. M., J. E. Marsden. R. G. Goettel, R. K. Wolfe, D. J. Jude, and S. Rudnika. 1997. The round goby, *Neogobius melanostomus* (Pallas), a review of European and North American literature. Illinois-Indiana Sea Grant Program and Illinois natural History Survey Special Publication 20. Champaign.

Chotkowski, M. A. and J. E. Marsden. 1999. Round goby and mottled sculpin predation on lake trout eggs and fry: field predictions from laboratory experiments. Journal of Great Lakes Research. 25(1): 26-35.

Clapp, D. F., P. J. Schneeberger, D. J. Jude, G. Madison, and C. Pistis. 2001. Monitoring round goby expansion in Eastern and Northern Lake Michigan. Journal of Great Lakes Research. 27(3): 335-341.

Dubs, D.O.L., and Corkum, L.D. 1996. Behavioral interactions between round gobies (*Neogobius melanostomus*) and mottled sculpins (*Cottus bairdi*). Journal of Great Lakes Research. 22: 838-844.

Diamond, J. M. 1986. Overview: laboratory experiments, field experiments, and natural experiments. Pp. 3-22. In: J. Diamond and T. J. Case (ed.) Community Ecology, Harper and Row Publishers, New York.

French, J.R.P and D.J. Jude. 2001. Diet and diet overlap of nonindiginous gobies and small benthic native fishes co-inhabitating the St. Clair River, Michigan. Journal of Great Lakes Research. 27(3): 300-311.

Fuller, P. L., Nico, L. G. and J. D. Williams. 1999. Nonindigenous fishes introduced into inland waters of the United States. American Fisheries Society, Special Publication 27, Bethesda, Maryland.

Jannsen, J. and D. J. Jude, 2000. Recruitment failure of Mottled Sculpins *Cottus bairdi* in Calumet Harbor, Southern Lake Michigan, induced by the newly introduced round goby *Neogobius melanostomus*. Journal of Great Lakes Research. 27(3): 391-328.

Jude, D. J and R. H. Reider, and G. R. Smith. 1992. Establishment of Gobiidae in the Great Lakes basin. Canadian Journal of Fisheries and Aquatic Sciences. 49: 416-421.

_____, Janssen, J., and Crawford G. 1995. Ecology, distribution, and impact of the newly introduced round and tubenose gobies on the biota of the St. Claire and Detroit Rivers. 447-460 In M. Munawar, T. Edsall, and J. Leach (eds.). The Lake Huron ecosystem: ecology, fisheries and management. Amsterdam, Netherlands: Ecovision World Monogr. Ser.

Kolar, C. S. and D. M. Lodge. 2002. Ecological Predictions and Risk Assessment for Alien Fishes in North America. Science. 289:1233-1236.

Mills. E. L., Leach, J. H, Carlton J. T., and C. L. Secor. 1993. Exotic species in the Great Lakes: a history of biotic crisis and anthropogenic introductions. Journal of Great Lakes Research. 19(1): 1-54.

Mills. E. L., Leach, J. H, Carlton J. T., and C. L. Secor. 1994. Exotic species and the integrity of the Great Lakes, lessons from the past. Bioscience 44(10): 666-676.

van Snik Gray and J. R. Stauffer Jr. 1999. Comparative microhabitat use of ecologically similar benthic fishes. Environmental Biology of Fishes 56: 443-453.

_____ and J. R. Stauffer Jr. 2001. Substrate choice by three species of darters (Teleostei: Percidae) in and artificial stream: effects of a non-native species. Copeia 1: 254-261.

_____, Janssen, J., and Crawford G. 1995. Ecology, distribution, and impact of the newly introduced round and tubenose gobies on the biota of the St. Claire and Detroit Rivers. 447-460 In M. Munawar, T. Edsall, and J. Leach (eds.). The Lake Huron ecosystem: ecology, fisheries and management. Amsterdam, Netherlands: Ecovision World Monogr. Ser.

Kolar, C. S. and D. M. Lodge. 2002. Ecological Predictions and Risk Assessment for Alien Fishes in North America. Science. 289:1233-1236.

Mills. E. L., Leach, J. H, Carlton J. T., and C. L. Secor. 1993. Exotic species in the Great Lakes: a history of biotic crisis and anthropogenic introductions. Journal of Great Lakes Research. 19(1): 1-54.

Mills. E. L., Leach, J. H, Carlton J. T., and C. L. Secor. 1994. Exotic species and the integrity of the Great Lakes, lessons from the past. Bioscience 44(10): 666-676.

Phillips, E. O., M. E. Washek, A. W. Hertle and B. M. Neible. 2003. The Round Goby (*Neogobius melanostomus*) in Pennsylvania Tributary Streams of Lake Erie. Journal of Great Lakes Research 29(1): 34-40.
Pyron, M., Ruffing, R. A. and A. L. Lambert 2003. Assessment of Fishes of the Presque Isle Bay Watershed, Lake Erie, Using an Index of Biotic Integrity. Northeastern Naturalist 11(3): 261-272.

van Snik Gray and J. R. Stauffer Jr. 1999. Comparative microhabitat use of ecologically similar benthic fishes. Environmental Biology of Fishes 56: 443-453.

_____ and J. R. Stauffer Jr. 2001. Substrate choice by three species of darters (Teleostei: Percidae) in and artificial stream: effects of a non-native species. Copeia 1: 254-261.

Information Transfer Program Introduction

USGS 104B Base Administration Project:

Information Transfer Presentations by Director Elizabeth W. Boyer during the project reporting period (March 1, 2013 through February 28, 2014)

(Invited) Boyer EW. Acid Rain in Pennsylvania. Northwestern Pennsylvania Acid Deposition Workshop, Pennsylvania Department of Environmental Protection, Warren, PA, March 2013.

(Invited). Tzilkowski SSG, B Swistock, EW Boyer, P Craig, and L Sherwin. Pennsylvanian's Opinions About the State's Water Resources. Penn State Extension Water Webinar Series, July 2013. Online URL of the presentation:
http://extension.psu.edu/natural-resources/water/webinar-series/past-webinars/pennsylvanian2019s-opinions-about-the

(Invited) Boyer EW. Women and Their Woods: Important Relations Among Forests and Water. 2013 Women and Their Woods Retreat. Penn State Cooperative Extension, Trout Run, Pennsylvania, Sepetmber 2013. Online URL of the presentation: http://bethboyerbrown.com/archives/2449.

(Invited) Boyer EW. Atmospheric Deposition in Pennsylvania: Impacts on Watersheds. Penn State Extension Water Webinar Series, September 2013. Online URL of the presentation:
http://extension.psu.edu/natural-resources/water/webinar-series/past-webinars/atmospheric-deposition-in-pennsylvania

(Invited) Boyer EW. Atmospheric mercury deposition and its accumulation in watersheds of Pennsylvania. Susquehanna River Basin Commission Water Science Forum, Harrisburg, PA, October 2013.

(Invited, Plenary Presentation) Tzilkowski SSG, B Swistock, EW Boyer, P Craig, and L Sherwin. Pennsylvanian's Opinions About the State's Water Resources. Susquehanna River Basin Commission Water Science Forum, Harrisburg, PA, October 2013. Online URL of the presentation:
http://www.srbc.net/waterscienceforum/assets/docs/Tzilkowski_PSU_Water_Science_Forum_Presentation_fs199628.

Information Transfer Activities by Director Elizabeth W. Boyer, PAWRRC Interns (Iavorivska, Tzilkowski), and others on behalf of PAWRRC during the project reporting period (March 1, 2013 through February 28, 2014)

February 2013. PAWRRC hosted Dr. Sybil Seitzinger of Stockholm, Sweden, who is the Executive Director of the International Geosphere-Biosphere Program focusing on global change. Dr. Seitzinger presented a seminar entitled "Welcome to the Antrophocene" sponsored by PAWRRC and the CarbonEarth graduate program.

March 2013. PAWRRC hosted Dr. Steve Preston, a scientist with the National Water Quality Assessment Program of the U.S. Geological Survey. He met students and faculty on campus, and presented a public seminar entitled "Spatially Explicit Modeling of Water Quality for Major River Basins of the United States."

March 2013. The U.S. Environmental Protection Agency's Science Advisory Board announced the formation of its Hydraulic Fracturing Research Advisory panel. This panel of experts will peer review EPA's draft reports for its national study on any potential impacts of hydraulic fracturing on drinking water resources. Elizabeth Boyer of PAWRRC was selected for the 31-member panel from over 140 nomninees.

March 2013. PAWRRC hosted visitor Dr. Diane McKnight, a Professor at the University of Colorado's Institute for Arctic & Alpine Research. She visited with students and faculty on campus, and gave a public seminar as part of the part of the PSIEE Water Colloquium, entitled "Climate Change and Water Quality in the Rocky Mountains: Approaches for Adapting to Too Much Summer.

March 2013. PAWRRC hosted visiting Professor David Rudolph from the Department of Earth and Atmospheric Sciences at the University of Waterloo. Dr. Rudolph was the 2013 Darcy Lecturer sponsored by the National Ground Water Association. He visited with students and faculty on campus, and gave a public seminar as part of the PSIEE Water Colloquium, entitled Managing Groundwater Beneath the Agricultural Landscape.

April 2013. Beth Boyer took a group of Penn State students and faculty on a tour of our precipitation super-station at PA42, Leading Ridge, associated with the Pennsylvania / National Atmospheric Deposition Program and the Shale Hills Susquehanna Critical Zone Observatory.

April 2013. Lidiia Iavorivska & Sarah Tzilkowski participated in an NSF EarthCube workshop to define cyberinfrastructure needs related to surface waters, held April 24-26, 2013 in Boulder, Colorado. The NSF's Directorate for Geosciences and Office of Cyberinfrastructure call for "an open, adaptable, and sustainable framework (an 'Earth-Cube') to enable transformative research and education in Earth System Science."

July 2013. Sarah Tzilkowski, Dan Lawler, Brendan Reed, Lidiia Iavorivska, Beth Boyer, and Mike Brown hosted young visitors from Penn State University's Hort Woods Center elementary age summer program (ages 6-9) for a tour of the Water Quality Lab in 329 Forest Resources Building, discussing the water cycle and water quality analyses.

August 2013. Sarah Tzilkowski, Dan Lawler, Brendan Reed, Lidiia Iavorivska Beth Boyer, and Mike Brown hosted young visitors from Penn State University's Bennett Family Center pre-school (ages 3-5) for an intro to the Water Cycle, and tours of the Water Quality Lab and Green Roof in the Forest Resources Building.

September 2013. Sarah Tzilkowski, Dan Lawler, Brendan Reed, Lidiia Iavorivska, Beth Boyer, and Mike Brown participated on behalf of the Pennsylvania Water Resources Research Center, in Pennsylvania Forest Fest held at the Penn State Arboretum. They talked about forested watersheds and helped to spread the word about water resources in Pennsylvania.

September 2013. Brendan Reed, Lysle Sherwin, and Beth Boyer participated in Penns Valley Conservation Association's "CrickFest" Creek Festival), helping Penn State Cooperative Extension to spread the word about a free Drinking Water Testing Clinic. Interested residents who rely on a private well, spring, or cistern for their drinking water were given test kits and instructions to receive free, basic water testing conducted by a water quality lab at Penn State University. Test results including coliform bacteria, E. coli bacteria, pH, total dissolved solids, arsenic, and nitrate were later provided to the homeowners, along with information about how to interpret the results.

December 2013. Beth Boyer of PA-WRRC served on Penn State University's small Water Task Force Committee, and helping to develop a new strategic plan for Water at Penn State. Read the draft plan here: http://www.psiee.psu.edu/news/2013_news/aug_2013/waterTaskForceDraftReport.pdf

Pennsylvania Water Resources Sustainability Surveys

Basic Information

Title:	Pennsylvania Water Resources Sustainability Surveys
Project Number:	2012PA184B
Start Date:	3/1/2012
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	5
Research Category:	Social Sciences
Focus Category:	Management and Planning, Education, None
Descriptors:	None
Principal Investigators:	Bryan Reed Swistock, Elizabeth W. Boyer, Patricia Craig, Lysle Sherwin

Publications

There are no publications.

PA WRRC Final Report

Project Title
Pennsylvania Water Resources Sustainability Survey

Principal Investigators

Bryan Swistock	Senior Extension Associate, Penn State University, brs@psu.edu, 814-863-0194
Elizabeth W. Boyer	Director, Pennsylvania Water Resources Research Center and Associate Professor, Pennsylvania State University, ewb100@psu.edu, 814-865-8830
Patty Craig	Assistant Director, Pennsylvania Water Resources Research Center, and Director of Communications, Penn State Institutes of Energy & the Environment
Lysle Sherwin	Senior research associate, Pennsylvania Water Resources Research Center

One-sentence description of the project
More than 1,700 Pennsylvania residents expressed opinions on water resource topics ranging from priority water issues, efficacy of management tools, allocation of funds, and personal home drinking water quality through either an on-line or hard copy survey.

Problem & Research Objectives
Concerns over water resources in Pennsylvania have been growing in recent years, in response to severe droughts and floods, a growing population, increasing demands for water, and the need to understand how changes in land-use and climate will affect water quantity and quality. Such concerns led to the passage of the state's Water Resources Planning Act and an initial state water plan in 2002. This and other activities have highlighted the vast diversity of water stakeholders in the state, each of whom has various perspectives on priorities for water. For example, Pennsylvania currently lacks a holistic approach to its water management. The state's drinking water, water used for industrial and agricultural purposes, and lake and river water are monitored and managed by independent agencies and stakeholders. Questions remain about how much water is used relative to how much is being replenished. A primary objective of the PA-WRRC is to plan, facilitate, and conduct research to aid in the resolution of State and regional water problems. Toward those goals, a necessary first step is to articulate the breadth of water issues facing the state, and to prioritize them.

This was accomplished by administering a broad survey of stakeholders to describe their perceptions and knowledge of water issues. Specifically, the objective of this public opinion survey was to examine the public's awareness, attitudes, and concerns about water issues and the strategies to protect water resources; and to better understand residents' opinions and knowledge. This effort engaged a diversity of citizens, from various age groups, educational levels, land management settings (and environmental settings (e.g., urban vs. rural), industrial setting (e.g., agriculture, natural gas drilling); and socio-economic status.

Methodology

A 5-member team of Penn State faculty, staff, and a doctoral student affiliated with Cooperative Extension, PA WRRC, and the Department of Ecosystem Science and Management was organized by the PI in summer 2012 to develop and conduct a public opinion survey focused on specific topics within the overall theme of water resource sustainability. The required human subjects research approval was obtained, research team members completed training in survey protocols, and a pilot version of the survey was distributed in late summer 2012 at Ag Progress Days, Grange Fair, and a watershed association festival (all held in Centre County) to solicit feedback from respondents on survey content and format. Initial responses to the survey at these events resulted in minor modifications in the phrasing of survey questions. The resulting 22-question survey was reformatted for online distribution using SurveyMonkey and was released for public input in October 2012.

The research team distributed announcements inviting citizen participation of the open survey through various e-mail list serves in their professional networks including the academic community and Cooperative Extension staff at large, county conservation district watershed specialists, statewide NGOs such as the Pennsylvania Organization for Watersheds and Rivers, watershed community based associations, other environmental or natural resource conservation organizations, Sea Grant regional programs, and water resource professionals in the public and private sectors. The open survey announcements requested recipients to forward the URL to access the on-line survey to their own personal list serves. On January 29th a press release generated by College of Ag Sciences Communications was posted on the “Penn State Live” news network which is distributed to several thousand subscribers statewide.

Before collection of response data for processing, responses from the pilot paper surveys were manually entered into the online survey. Only questions that were worded similarly to questions online were entered. Once all paper surveys were manually entered, the results from the survey were downloaded from the Survey Monkey server on May 2nd, 2013. Response statistics were calculated in Microsoft Excel. Zip code data were used to identify where survey takers were from. Using a geo-referenced zip code database, zip code responses were imported into ArcGIS.

Principal Findings

Demographics

Every county in Pennsylvania was represented by survey participants (Figure 1). Basic demographic questions were included in the survey, including zip code, sex, year born, and education level. Of the survey participants, over 60% were male. Age of the participants ranged from 90 years to 19 years, with a median age of 53. Overall respondents to the survey were well-educated with a majority (74%) having completed a 4-year or graduate degree program at the time of completing the survey.

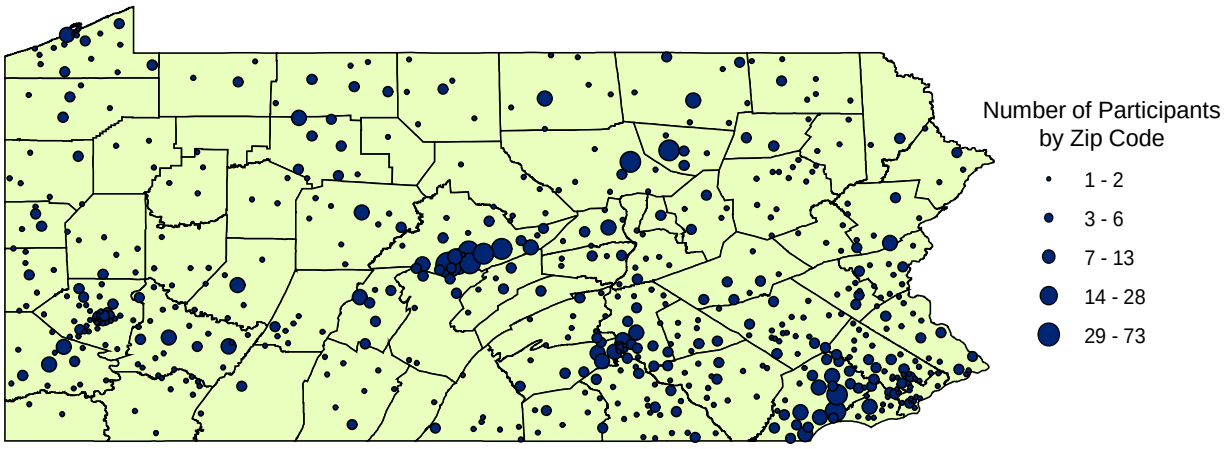


Figure 1. Map representing the number of survey participants by their zip code across Pennsylvania. Every county in Pennsylvania was represented the survey participants.

Question Responses

In response to the question: "How has the quality of rivers, streams and groundwater in your area changed in your lifetime" less than 20% of the participants stated that the water quality in Pennsylvania has not changed (Figure 2). Most people (34%) thought Pennsylvania's waters have improved, however only slightly less than that (31%) stated that the waters in Pennsylvania have gotten worse over their lifetime. Generally those who selected "Unsure" or "Same" were younger, with median ages of 43 and 46, respectively. The median age of those who thought Pennsylvania's waters have gotten worse was 55, while the median age of participants who selected "Better" was 56.

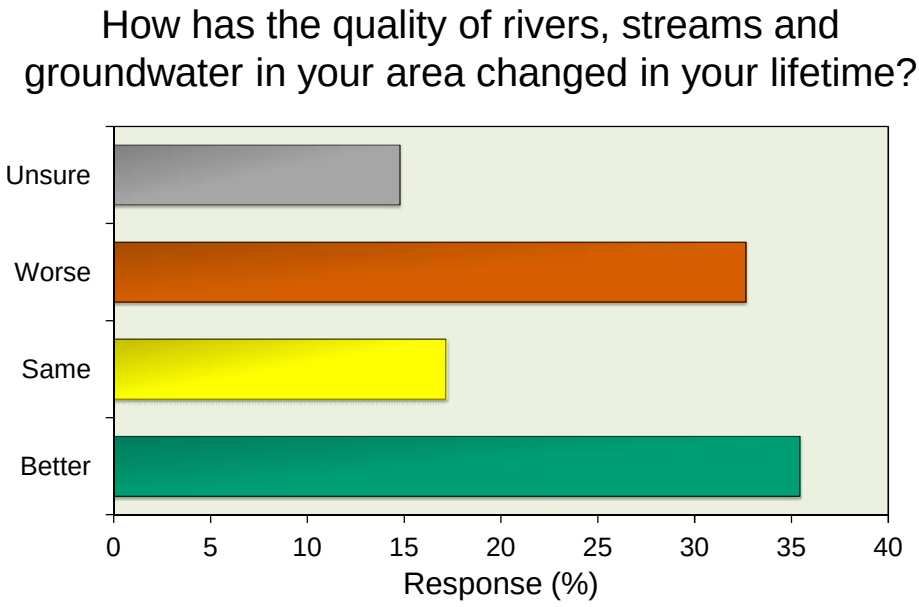


Figure 2. Bar chart representing percent response to the question "How has the quality of rivers, streams, and groundwater in your area changed in your lifetime?"

Survey participants were also asked: “From the list below, select the 3 most important issues facing Pennsylvania’s waters where significant research, education, or funding should be directed” (Figure **3**). Of the choices given, chemical pollution (i.e., salt, oil, pesticides, metals, hazardous waste, pharmaceuticals, frac water, etc.) was selected more than any other issue, with over 1200 selections. Following chemical pollution, nutrient and sediment pollution (i.e., phosphorous, nitrogen, fertilizers, manure, erosion, etc.) and stormwater and wastewater (i.e., septic systems, sewage, urban runoff, etc.) received 832 and 809 selections respectively.

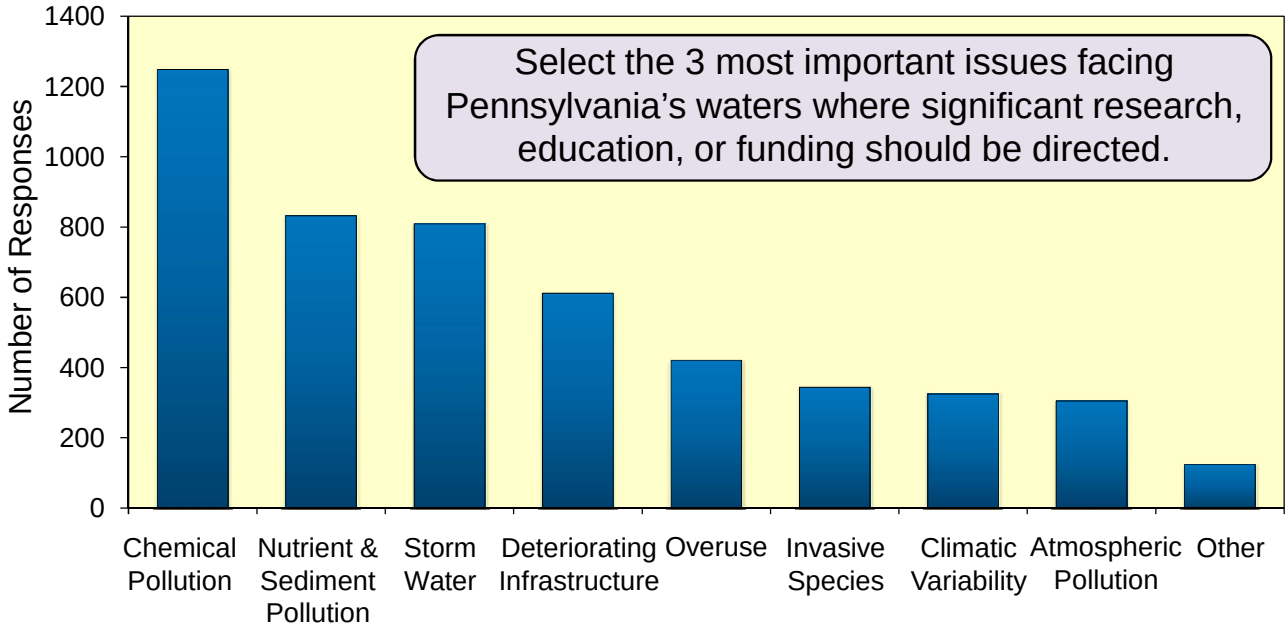


Figure 3. Column chart depicting the number of responses for each important issue facing Pennsylvania’s waters.

At the end of the survey participants were asked to express any additional comments or concerns. Responses reflected participant’s answers to the water-issues question, voicing concern for chemical pollution, particularly fracking for natural gas in the Marcellus shale. Of the 700 survey participants that included a comment, over 200 people mentioned the words: gas, frac, or Marcellus. The majority of these participants were concerned about the natural gas industry in Pennsylvania and the potential negative impacts it may have on Pennsylvania’s waters. Only a few comments (<10) were in favor of the natural gas industry and voiced concern about the negative economic impacts if extraction of natural gas from Marcellus shale was no longer allowed or heavily regulated. Example comments are given in Table 1.

Table 1. Example comments that mention Marcellus shale, fracking, or natural gas. Majority of comments voiced concern about effects of natural gas extraction from Marcellus shale and fracking water.

Comment	Sex	Age	Education
Much more research must be done into the water impacts of shale gas extraction.	M	65	4-Year College Degree (BA, BS, etc.)
Am concerned about fracking accidents, and who would take responsibility. Strong laws/regulations/fines need to be in place for accountability.	F	59	4-Year College Degree (BA, BS, etc.)
Please work to ban hydraulic fracturing. I personally know so many people in PA who have lost their water quality to gas extraction. It is too big a risk, and the industry is treating PA as a canary in the coal mine.	F	27	4-Year College Degree (BA, BS, etc.)
I believe the fracking is not controlled or monitored sufficiently nor or the penalties severe enough for those companies that fail regulations or contaminate ground and/or well water.	M	59	Some college
I don't think gas companies should be allowed to drill wells on private property for the use of fracking.	F	62	High School/GED
We need to do a much better job of protecting our water from any and all threats from urbanization/industry, with a HUGE focus on making sure that industry (such as fracking) is allowed to continue. In other words, we need to make sure we can create jobs and a better economy while at the same time protecting PAs nature.	M	23	4-Year College Degree (BA, BS, etc.)

In a series of four questions survey participants were asked to rate the efficacy of the following management tools for protecting and improving Pennsylvania's water resources (Figure 4):

- Voluntary efforts (such as water conservation, less fertilizer use, eco-friendly living).
- Educational programs (such as information from schools & universities, watershed groups, Cooperative Extension, government and non-governmental sources).
- Regulations and enforcement (such as Clean Water Act, Clean Streams Law, zoning).
- Incentives (such as cost sharing, tax breaks, or payments for conservation).

For each management tool, the majority (>60%) of participants selected “moderately effective”. When analyzing the response rate of “effective” vs. “not effective” the survey participants voted “Incentives” as the least effective, which received the highest “not effective” rating of 20% and the lowest “effective” rating at 18.2%. Regulations and Enforcement received the highest “effective” response rate (26.7%). By adding up the positive selections (i.e., both effective and moderately effective selections) educational programs were voted as the most effective with a total of 88.6% of the participants. Regulations and enforcement was a close second to educational programs with 87.3% of the vote.

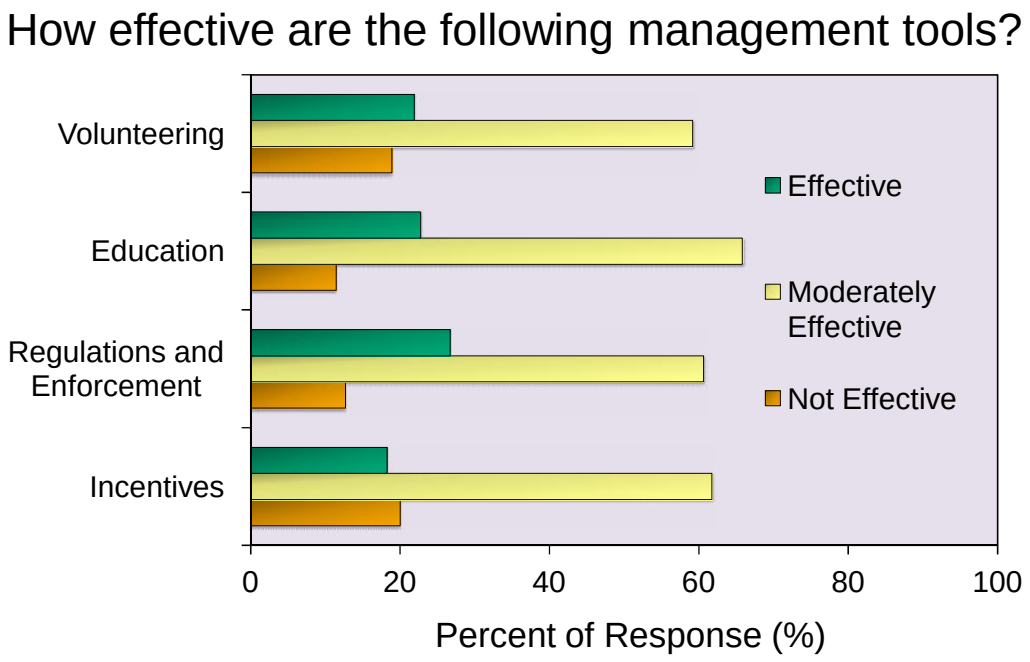


Figure 4. Bar chart showing how participants rated the efficiency of management tool sin water resources.

Survey participants were asked how funds should be spent for water resources (Figure 5). The first question asked: “With funds ($) available for water resources in Pennsylvania, how shouldthe funds be balanced between: improving polluted & impaired waters versus protecting healthy & good quality waters”. Three choices were available for fund distribution: Most money to improving, most money to protecting, or an even distribution with 50% of funds for improving and 50% for protecting. Participants clearly thought funds should be distributed evenly between protecting healthy waters in Pennsylvania and improving polluted and impaired waters, with over 1100 participants (67%) selecting this option (Figure 5-a). When asked how funds should be distributed between a targeted distribution (i.e., addressing the most important and severe problems, regardless of location) and an equal distribution (i.e., providing the same funding to towns and counties across the state), over 58% of the participants stated that most money should follow a targeted distribution (Figure 5-b).

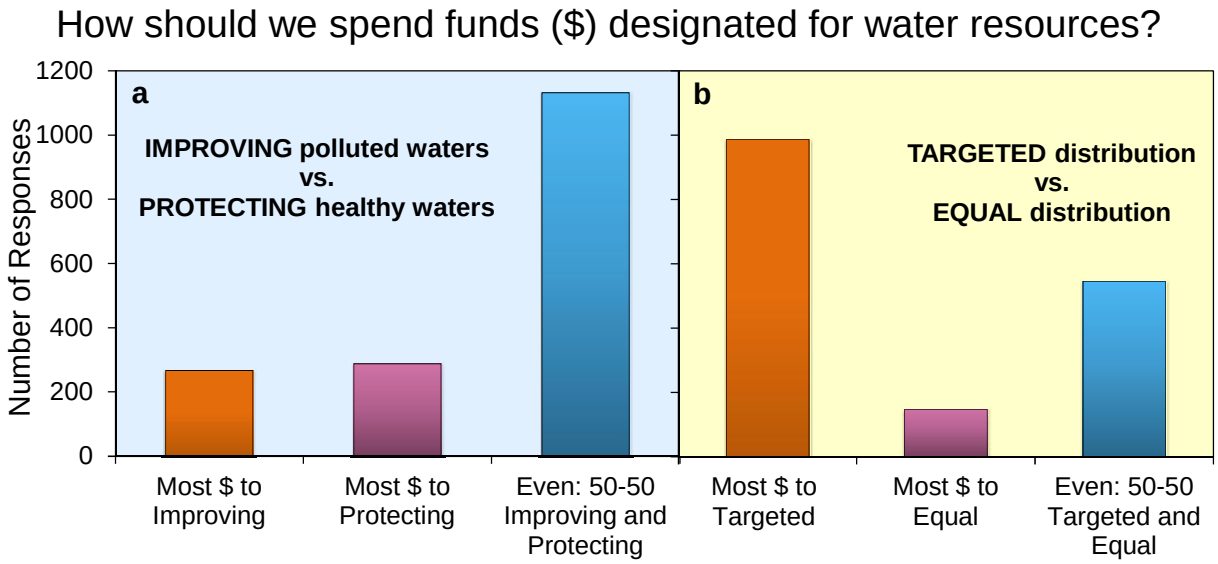


Figure 5. Column chart depicting the distribution of funds designated for water resources. Participants were asked how money should be spent between (a) Improving polluted waters vs. Protecting healthy waters, and should money be allocated using a (b) Targeted distribution of funds vs. an Equal distribution of funds.

Lastly, survey participants were asked six questions regarding their home drinking water (Figure 6). More than half of the survey respondents utilized public as opposed to private drinking water supplies in their home. The percentage of respondents using private water supplies (42%) is nearly double the overall percentage for Pennsylvania indicating that the survey was answered by a more rural audience.

While only 26% of respondents rated their drinking water as “excellent”, 68% felt that their water was “fair” or “good” and 5% felt their drinking water quality was “poor”. Given these opinions of water quality, it was not surprising that nearly one-third had installed some type of drinking water treatment device in their home and about one third used at least some bottled water as a drinking water source. The majority of respondents had never tested their drinking water quality presumably because most were using public water supplies which are already tested.

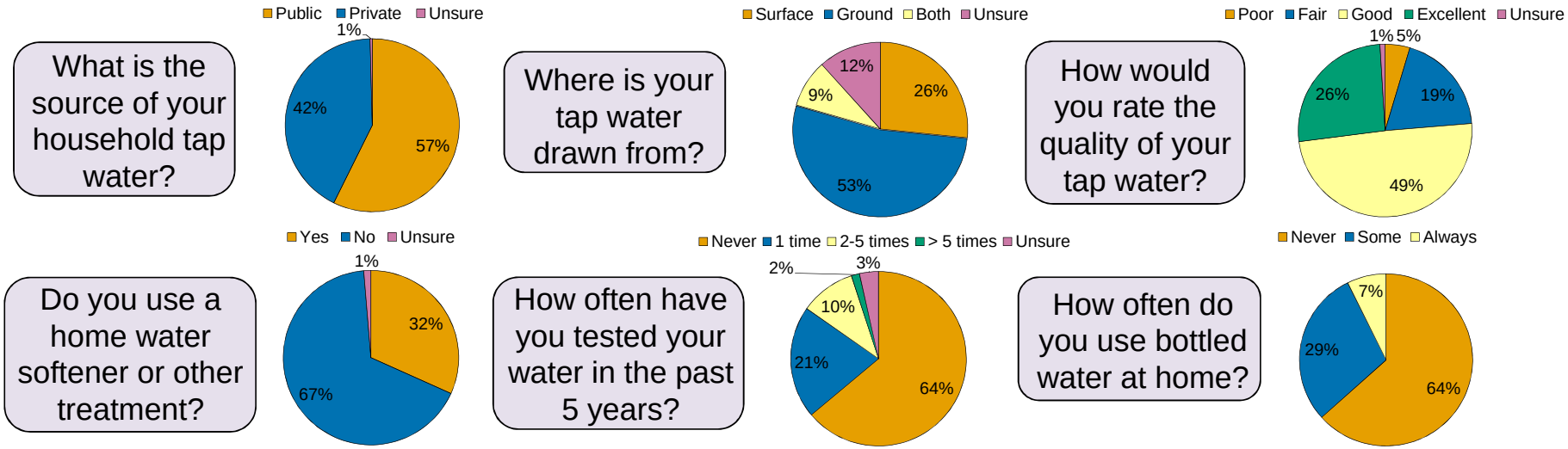


Figure 6. Pie charts of various characteristics of survey participants home drinking water. Participants were asked the source of their water, where is it drawn from, how they would rate their drinking water, if they use a water softener, if they have tested their water in the past five years, and how often they used bottled water at home.

Significance
The deep concern felt by Pennsylvanians about Marcellus Shale development impacts on water resources, perhaps not surprisingly given the media attention over the recent years, was reflected in the top ranking of the Chemical pollution issue and the high number of survey takers adding specific comments on shale fracking. Nonetheless, it is significant that a majority of Pennsylvanians felt that the quality of rivers and streams had improved or at least stayed the same during their lifetime. A case can be made that citizen awareness has been heightened by the success of various educational programming efforts and the endorsement of education as the most effective management tool, thus creating a better informed, more pro-active citizenry-a vitally important element to be empowered in addressing the complex and challenging issues faced by Pennsylvanians going forward.

Students Supported
Sarah Tzilkowski, PhD candidate advised by Elizabeth Boyer, Associate Professor of Water Resources, Department of Ecosystem Science & Management

Publications
None to date

Presentations
Poster "A Survey of Pennsylvanians and Their Water" at Pennsylvania Groundwater Symposium *Emerging Issues in a Changing Landscape,* May 8, 2013 Penn State University.

Other information transfer
- News release – Penn State College of Agricultural Sciences (June 2013)
- Pennsylvania Water Resources Research Center website
- Penn State Water Resources Extension website
- Penn State Water Resources Extension webinar – July 2013

Awards
None

Additional funding
None

Photos

Figure 7. Photo of survey takers at Crickfest on September 2nd, 2012.

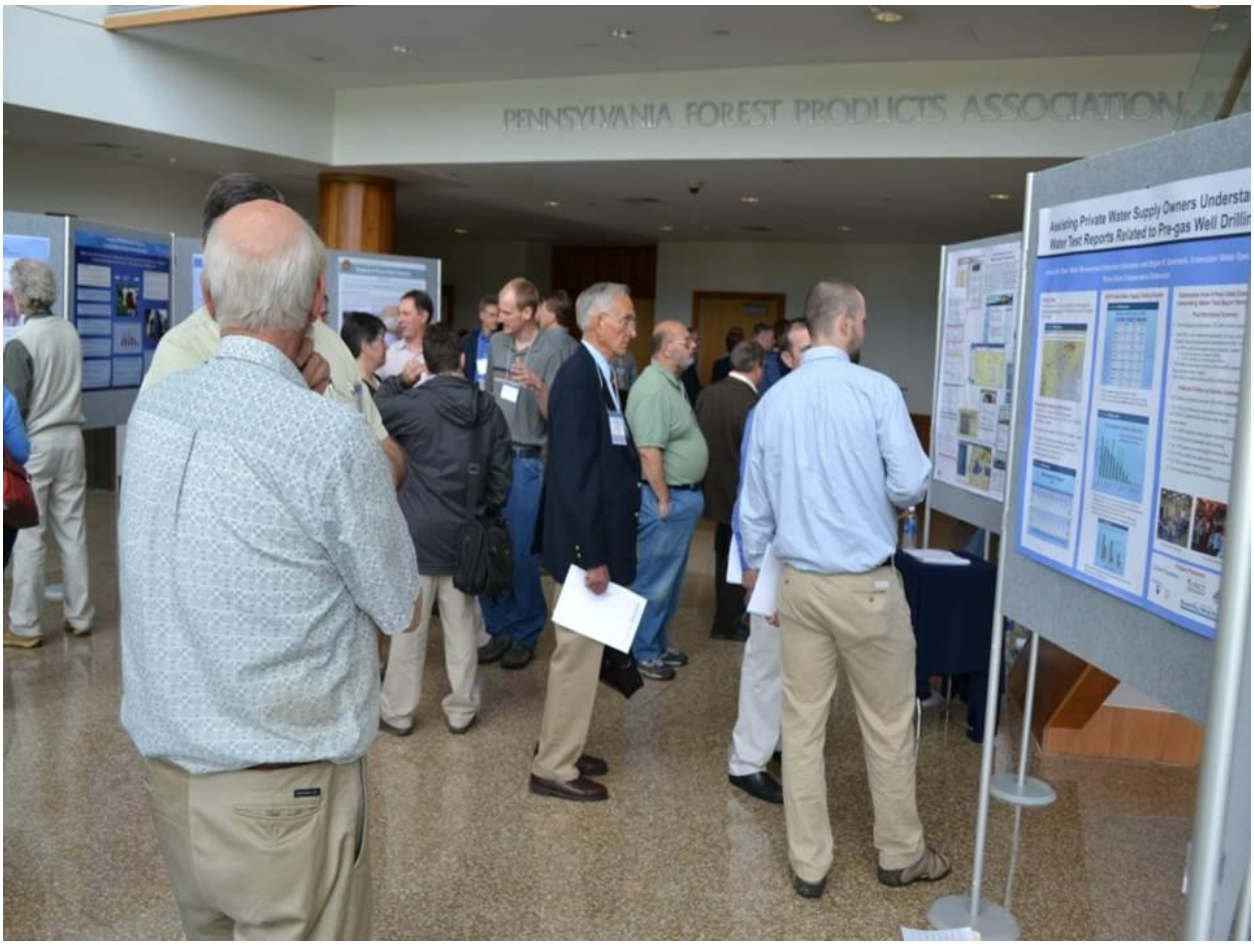


Figure 8. Lysle Sherwin presents a poster on the survey at the Pennsylvania Groundwater Symposium on May 8, 2013 at Penn State University.

Instrumenting Nature: Bringing real-time data into the K-12 curriculum

Basic Information

Title:	Instrumenting Nature: Bringing real-time data into the K-12 curriculum
Project Number:	2012PA185B
Start Date:	3/1/2012
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	5
Research Category:	Climate and Hydrologic Processes
Focus Category:	Education, Wetlands, Hydrology
Descriptors:	None
Principal Investigators:	Charles Andrew Cole

Publications

There are no publications.

PROJECT TITLE & PRINCIPAL INVESTIGATOR

Instrumenting Nature: Bringing real-time data into the K-12 curriculum

Charles Andrew Cole, Ph.D., Associate Professor of Landscape Architecture and Ecology, The Pennsylvania State University. cac13@psu.edu; 814-865-5735.

ONE-SENTENCE SOUND BYTE STYLE DESCRIPTION OF THE PROJECT OR FINDINGS

This project was developed to help integrate digital weather and soil moisture data from schoolyard wetlands into the K-12 curriculum in the State College Area School District

PROBLEM & RESEARCH OBJECTIVES

School children have diminishing opportunities for hands-on learning given current budgetary constraints. Any activity that can connect a student with a real-life experience is therefore increasingly important. This project seeks to virtually connect a local wetland (Millbrook Marsh) with several local schoolyard wetlands for K-12 student projects. Local school children frequent Millbrook Marsh several times during their K-12 years. Thus, they are generally familiar with the site but not necessarily with the ecological details. This project will tie in data from a site that they have visited to sites at or near their schools.

Schoolyard wetlands themselves are becoming more common in K-12 settings as schools try to increase hands-on learning opportunities for their young students. Such wetlands can vary from natural wetlands nearby or adjacent to a school to wetlands that are created on school property for educational purposes. These wetlands, whatever their type, provide students with an opportunity to study wetland ecology, as well as other disciplines, such as wildlife biology and meteorology, as well as math and writing. Equally important is the opportunity for young students to begin to understand the process of science and learn what it means to be a scientist. In State College, Park Forest Elementary (PFE) developed their first schoolyard wetland in the State College Area School District (SCASD) in late spring 2009, with assistance from Environmental Concern, Inc., with funding from the National Oceanographic and Atmospheric Administration (NOAA). The site – affectionately named “The Penguin Puddle” after the schools’ mascot - has proven to be extremely popular with the students, especially as many had helped to plant the wetland. The wetland is being used in classroom exercises as well as part of the school’s nature journal writing. The success of the wetland has encouraged other elementary schools within the district to develop their own sites. Two schools (Ferguson Township Elementary and Mount Nittany Elementary) have recently been built (both finished in 2011) with schoolyard wetlands and I will be instrumenting both schools similarly to the PFE wetland. A third school (Radio Park Elementary) desires a

wetland to be built (and the SCASD will construct it) thus allowing for the District to have four instrumented wetland sites and access to the data for curricula at all levels.

The objective of this project is to develop real-time data from a regional natural wetland so as to enhance the development of an existing schoolyard wetland project within the State College Area School District. This will allow teachers and students to interact with real-time data across a wide spectrum of the K-12 curriculum. Four schools are under development, with two additional schools possible (Gray's Woods, Easterly Parkway) at some point in the future. These schools will become the initial schools whose data will populate a web site to be developed that will highlight schoolyard wetlands within the region and across Pennsylvania. The concept is to have schools with access to real-time weather and wetland data for wetlands, even if they do not have such a site at their own school (and inspire such schools to perhaps create their own schoolyard wetland). The ability to compare their schoolyard wetland with a local natural site is critical for any analyses the kids will do on their wetlands.

METHODOLOGY

Millbrook Marsh (Figure 1) had a Davis Vantage Pro 2 weather station installed on a tripod adjacent to the new environmental education building. This unit comes with a console which picks up the Vantage Pro's signal wirelessly. The console is then connected to a Windows-based pc for uploading the data to the web where kids can then see real-time weather data (rainfall, temperature, barometric pressure, wind speed, humidity, among others).

Additionally, I installed a Davis soil moisture sensor within Millbrook Marsh: the Farm 12 groundwater-fed wetland (Cole et al. 2008). This will transmit its data wirelessly to the same console that picks up the weather data. Both will then be uploaded to the internet which will be available at the education building.

PRINCIPAL FINDINGS AND SIGNIFICANCE

As of November 2, 2012, there is a functioning weather station at the Millbrook Marsh Nature Reserve. This is an important site as the district brings hundreds of children there each year to learn about wetlands.

Additionally, the funds from the Stuckeman Collaborative Design Research Fund were used primarily to purchase weather monitoring equipment for several elementary schools within the SCASD. I placed a weather station at Park Forest Elementary (PFE) and I have instrumented the Ferguson Township School (FTE). A fourth school (Radio Park Elementary (RPE)) will build a wetland in the spring of 2013 and I installed the weather station at the location of the proposed wetland during the summer of 2012.

At this point, there are two stations that are functioning and transmitting data to an on-line site for viewing by anyone (PFE, MMNC). I have had technical troubles getting FTE connected and the SCASD IT personnel are trying to troubleshoot the issue. RPE will be on-line shortly.

Park Forest Elementary (top left); Ferguson Township Elementary (top right); Radio Park Elementary (bottom left); Millbrook Marsh Nature Center (bottom right).

STUDENTS & POSTDOCS SUPPORTED

Trevor Weaver, MLA

PUBLICATIONS

None as of yet

PRESENTATIONS

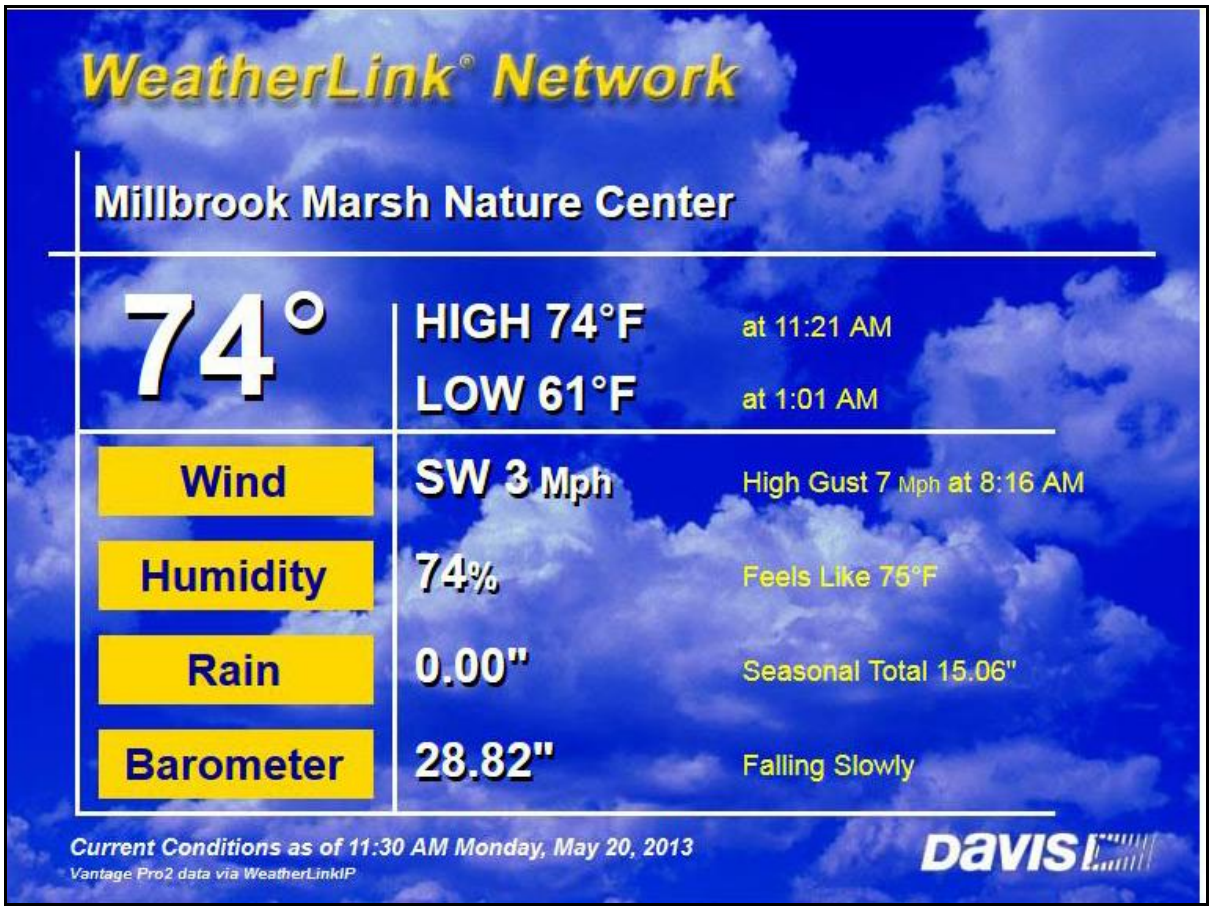
None as of yet

ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY

None as of yet

PHOTOS OF PROJECT

Weather station at Millbrook Marsh Nature Center – fall 2012.



Screen capture from Millbrook Marsh weather station

Toward Mitigating Effects of Elevated Temperatures on Aquatic Ecosystems: Monitoring Thermal Impacts to Halfmoon Creek

Basic Information

Title:	Toward Mitigating Effects of Elevated Temperatures on Aquatic Ecosystems: Monitoring Thermal Impacts to Halfmoon Creek
Project Number:	2013PA207B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	5
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Surface Water, Water Quality
Descriptors:	None
Principal Investigators:	Lysle Sherwin

Publications

There are no publications.

PA-WRRC ANNUAL REPORT
USGS 104B FINAL PROJECT REPORT

PROJECT TITLE & PRINCIPAL INVESTIGATOR

Toward Mitigating Effects of Elevated Temperatures on Aquatic Ecosystems: Monitoring Thermal Impacts to Halfmoon Creek and Penns Creek, Central Pennsylvania

Lysle S. Sherwin, Research Associate, Department of Ecosystem Science and Management, Pennsylvania State University.

PRINCIPAL FINDINGS AND SIGNIFICANCE

This information-transfer project was intended to identify specific stream segments impacted by elevated water temperatures for implementation of riparian buffers and in-stream fish habitat improvement. Initial baseline data were collected and provided to the cooperating local stakeholder groups (watershed associations).

Seven HOBO stream temperature loggers were deployed in streams of the **Halfmoon Creek Watershed** on June 22, 2013 through May 2, 2014; recording hourly temperatures from the mouth upstream approximately six miles to the village of Centennial, aiming to provide initial background data on stream temperature magnitudes and variability. Data showed lowering of summertime daily peak temperatures and average daily temperature from the uppermost station in the watershed to the lowest station at the mouth, most likely caused by increasingly greater inflows of groundwater to summer base flow. Data are being used to identify and priority sites for stream restoration. Similarly, seventeen HOBO stream temperature loggers were deployed in portions of the upper **Penns Creek watershed**, and are now in the fourth year of continuous temperature monitoring. The stream temperature data have been utilized to identify stream buffer and restoration priority sites and to support four successful grant applications and two in review to private foundations and state agency grant programs for implementation projects to mitigate elevated stream temperatures in the watershed.

STUDENTS INVOLVED

Brendan Reed, MS Student in Forest Resources, Pennsylvania State University, Department of Environmental Science and Management

KEY OUTREACH ACTIVITIES

March 2013. Excerpt from Penns Valley Conservation Winter 2013 Newsletter featuring Penns Creek Watershed temperature monitoring project.

Summer 2012 Stream Temperature Monitoring

--By Lysle Sherwin--
PSU Ecosystem Science and Management

Preliminary summer 2012 data from the cooperative Penns Creek watershed stream temperature monitoring project are again confirming the importance of cold groundwater inputs and riparian buffers to the health of Penns Creek and tributaries large and small. Begun in 2009 by PVCA and the Center for Watershed Stewardship, the monitoring network at 11 locations was expanded last summer adding three temperature loggers at the Coburn Park confluence of Penns and Elk Creek and three in the Muddy Creek watershed of Georges Valley. The stream temperature findings are being used to identify "hot spots" to prioritize buffer project sites being funded and implemented by PVCA and many partners through the "Young Forest" initiative and to monitor effectiveness of those projects in mitigating elevated summer water temperatures impacting stream ecosystems.

July 7 in the late afternoon recorded the highest peak water temperature at almost all monitoring sites during the period from end of June to early October when hourly temperatures were recorded. At Coburn, Penns Creek temperature was 78.5 degrees F, which exceeded the accepted stress threshold for brown trout of 76 degrees F, although the temperature dropped below the stress threshold by midnight it was certainly not in the optimum temperature range for trout. Only 100 yards away at the mouth of Elk Creek at the same time, the high temperature recorded July 7 for the entire summer was 66.5 F – a full twelve degrees colder than Penns Creek. Overnight Elk Creek temperature dropped to 59.8 F just about perfect for trout. Cold groundwater-rich inputs from Elk Creek and its tributary Pine Creek are obviously critical to maintenance of the nationally renowned Class A Wild Trout fishery in Penns Creek gorge below Coburn.

A newly installed logger at Laurel Run, a well-forested mountain tributary of Muddy Creek recorded a peak temperature for the summer of

Continued on p. 11

Temperature Monitoring, Continued from p. 8

71.2 degrees F only briefly on July 7. Generally, Laurel Run maintained a temperature regime supportive of a native brook trout population with average daytime temperatures below the 70 degree stress threshold of brook trout which evolved in colder environments than brown trout. That's the good news-below Laurel Run in the valley section of Muddy Creek the stream warms quickly. At Harter Road only a mile below Laurel Run the stream temperature gained over 6 degrees peaking at 77.6 F on July 7, and a mile further at the mouth of Muddy Creek reached 81.6 degrees – the highest temperature recorded at any monitoring location last summer.

For this reason, lower Muddy Creek is the focus of several riparian habitat buffers PVCA will be working on in 2013 enabled by a $10,000 commitment of organizational funds and a recent grant by the Foundation for PA Watersheds and proposed grants currently in review by two other funding sources. PVCA members are encouraged to contact George Kelly, Watershed Committee chair at *gkelly4@verizon.net* to volunteer to help planting new buffers and maintaining existing buffers or to assist in operating the temperature monitoring system set to be activated again in June 2013.

August 2013. Excerpt from Penns Valley Conservation Summer 2013 Newsletter featuring Penns Creek Watershed temperature monitoring project.

Stream Temperature Monitoring Expanded

--By Lysle Sherwin--
PSU Ecosystem Science and Management

Now in its fourth season, the summer stream temperature monitoring program has been expanded from 17 to 24 sites in the upper Penns Creek watershed above Coburn. The new locations target coldwater tributaries at Vonada Gap and Synagogue Gap in the Muddy Creek watershed, Kettle Run near Zerby, and sites upstream and downstream of a stream restoration and buffer planting project to be constructed this fall at the Martinec farm on Penns Creek about two miles upstream of Spring Mills.

The Muddy Creek locations will provide stream temperature data on coldwater inputs from tributaries entering a critical reach of lower Muddy Creek experiencing peak temperature increases on the order of 2-3 degrees F per stream mile. The Martinec farm sites will provide a baseline to compare "before and after" conditions following a restoration project in an important trout spawning nursery water. Kettle Run will be surveyed by PA Fish and Boat Commission biologists this summer to verify the presence and abundance of native brook trout. Physical habitat and water quality does appear to be impaired by siltation from an extensive network of dirt and gravel roads in the Kettle Run watershed.

The additional temperature loggers were obtained at no cost with assistance by Jason Detar, PAFBC regional fisheries biologist from a completed research project. Remaining battery life of the used equipment valued at $800 is sufficient for several years of data collection programmed to record hourly samples 24/7 from June to September. The data from all 24 sites are being shared with PAFBC for their long term monitoring of Penns Creek which includes electrofishing a number of sites this year in the watershed to assess wild trout populations and trends.

August 2013. Contributions to Pennsylvania Growing Greener Grants in the Halfmoon Creek and Penns Creek Watersheds.

Excerpt from Cenre County Conservation District Conservation Update 2013, Summer Edition. Online URL: **http://centrecountypa.gov/DocumentCenter/View/1248**

Centre County Receives Growing Greener Grants

On February 19, the Pennsylvania Department of Environmental Protection announced that the Commonwealth of Pennsylvania will invest more than $18.7 million in watershed protection projects. This funding, awarded to non-profit organizations and government entities, will improve watersheds in forty counties by addressing stormwater runoff and acid mine drainage, by implementing Best Management Practices on farms and by supporting environmental education programs. *Four Centre County organizations received a total of $429,385 from the state's Growing Greener program.*

The Centre County Conservation District received $89,250 to contract with a plan writer to develop Manure Management and Ag Erosion and Sediment Control Plans. The focus will be on farms in the Halfmoon Creek watershed. This funding will provide a valuable service to farmers, enabling them to move into compliance. ClearWater Conservancy received $185,000 to fund stream restoration and agricultural projects in the Halfmoon Creek watershed.

Wildlife for Everyone Endowment Foundation, working with Lysle Sherwin, received $60,427 to mitigate a site in the Halfmoon Creek watershed. This project is a continuation of a previous restoration. Halfmoon Creek watershed was targeted for these funds because DEP has designated sections of the stream as impaired. DEP's intent is to help to eliminate those impairments.

The Penns Valley Conservation Association received $94,708 to implement Agricultural Best Management Practices on two neighboring farms, one English and one Amish, located outside Millheim on Elk Creek.

The District's Agricultural Conservation Technician and the Watershed Specialist will contribute significant in kind assistance in the implementation of all of these projects.

For more information about Growing Greener or to see the complete list of grant recipients, email GrowingGreener@pa.gov; call 717-705-4500; or visit DEP's website at

www.dep.state.pa.us, keyword: Growing Greener.

September 2013. Information Transfer about upper Penns Creek Watershed at Creek Festival. Lysle Sherwin and Elizabeth Boyer of the Pennsylvania Water Resources Research Center participated in the Penns Valley Conservation Association's CrickFest (Creek Festival), discussing stream temperature and other aspects of water quality and watershed health within the upper Penns Creek Watershed.

Lysle Sherwin discusses temperature variations within the upper Penns Creek Watershed at the Penns Valley Conservation Association's "Crickfest" (Creek Festival).

September 2013. Information Transfer about groundwater supplied drinking water quality in the upper Penns Creek Watershed at Creek Festival. Lysle Sherwin and Brendan Reed of the Pennsylvania Water Resources Research Center participated in the Penns Valley Conservation Association's CrickFest (Creek Festival), helping the Pennsylvania Water Resources Research Center and Penn State Cooperative Extension to spread the word about groundwater quality via a free Drinking Water Testing Clinic. 90 interested residents living within the Penns Creek watershed who rely on a private well, spring, or cistern for their drinking water were given test kits and instructions to receive free, detailed water testing conducted by a water quality lab at Penn State University. Several months later, the test results including coliform bacteria, E. coli bacteria, pH, total dissolved solids, arsenic, and nitrate were provided at no charge to the homeowners, along with information about how to interpret the results.

Brendan Reed hands out kits for free groundwater quality testing at the Penns Valley Conservation Association's "Crickfest" (Creek Festival).

February 2014. The Upper Penns Valley Young Forest Initiative and the Muddy Creek Stream Restoration Project.

Excerpt from Penns Valley Conservation Winter 2014 Newsletter:
Online URL: http://www.pennsvalley.com/newsletters/2014%20winter.pdf

The Upper Penns Valley Young Forest Initiative and the Muddy Creek Stream Restoration Project launched in 2010 as a holistic framework integrating water quality and aquatic and terrestrial fish and wildlife habitat improvement goals while engaging and stimulating a broader, more proactive stewardship of resources by watershed landowners. Summer water temperatures increase by as much as 7 degrees over the 1.7 mile reach and often exceed the stress threshold for trout survival due to inadequate buffer canopy cover, especially in the Myers/Marquardt (the two participating landowners) reach. Likewise, sedimentation loads from unstable stream channel profiles reduce trout spawning success and recruitment of juveniles needed to sustain its Class A Wild Trout capability and the High Quality Cold Water Fishery "Special Protection" regulatory designation.

Lylse Sherwin of the Pennsylvania Water Resources Research Center in collaboration with the Penns Valley Conservation Association implemented the planting of 7,000 trees along Muddy Creek and other areas within the Upper Penns Creek Watershed. Temperature monitoring along stream reaches of Penns Creek identified reaches of the watershed along Muddy Creek as a priority for restoration. See YouTube Video produced by the Penns Valley Conservation Association, including an appearance by Lysle Sherwin, online at: https://www.youtube.com/watch?v=IIp724eCmNQ.

Excerpt from Penns Valley Conservation Winter 2014 Newsletter:
Online URL: http://www.pennsvalley.com/newsletters/2014%20winter.pdf

Trout Spawning in Muddy Creek "Nursery Water"

-- By Lysle Sherwin, Watershed Committee --

Watershed Committee members George Kelly, chair, Tom Doman, Lysle Sherwin, and Lisa Williams walked, and waded, Muddy Creek on November 21 from the Lower Georges Valley Road bridge upstream 1.5 miles counting trout nests (called "redds") to assess trout spawning activity in the stream as a measure of the watershed's capacity to sustain a naturally reproducing wild trout population. This stream section, which traverses the properties of Jerry and Carol Myers, Mike Marquardt, and Jennifer Tucker and Gerry Lange, is a focal point for PVCA's stream restoration and riparian "young forest" habitat improvement projects (see articles by Art Gover and Andrea Ferich in this issue).

Penns Creek's trout spawn in the autumn, starting with brook trout in September-October followed by more abundant brown trout spawning peaking in late November and into December. The later spawning is a real competitive advantage for brown trout since suitable habitat is very limited in all our streams. Using the tail and vigorous body movement, the female excavates a shallow depression in the small gravel of shoals and riffles to make the redd, thereby dislodging and destroying fertilized eggs deposited there by earlier spawners, whether brookies or other browns. Recent stocking of a fall spawning rainbow trout of hatchery origin to Penns Creek has introduced another competitor with the potential to impact the reproductive success of the other species.

An average three-year-old female in the 13-15 inch size class releases from 500 to 1,000 eggs. Fertilization by the milt of attending males occurs immediately on release of eggs which settle into the spaces around the gravel where highly oxygenated flowing water helps prevent fine silt from smothering the eggs. The female continues releasing eggs and moving gravel, which settles over the eggs in a slightly elevated loose mound of clean gravel--a

Stream survey along Muddy Creek.

characteristic of a successful redd. Depending on water temperature, which must stay between 35 and 55 degrees F for eggs to survive, the eggs hatch in 4-10 weeks--usually from late February to March. Now called "sac fry" nourished by the egg yolk, the fry live in and around the redd gravel. When the yolk is used up, typically by late April, the less than one-inch fish called "swim up fry" leave the gravel to begin feeding on plankton and microscopic stream life. The fry are fed upon by many predators, including adults of their own species. Safe habitat niches like overhanging streambank vegetation over shallows, which afford food and protection from predators, are vital at this life stage. By early summer the fry become fingerlings referred to as "young of the year" and will supplement their plankton diet by rising to feed on small insects on the surface--just like the grown-ups do sometimes.

The November count at Muddy Creek found a total of 65 redds in about 1.5 miles of stream (43 per mile), many occupied with actively spawning fish. The group observed a good number of juvenile fish not part of the spawning population of resident adults and several larger than average fish which may be residents or migrants moving up from Penns Creek to spawn in Muddy Creek and its tributaries. All fish that could be identified to species were brown trout.

Making comparisons of redd counts from one stream to another, or even sections of the same stream, is risky--like comparing apples and oranges as the saying goes. Some reaches of Muddy Creek were devoid of redds, but have

Continued on p. 9

Trout Spawning, Continued from p. 6

excellent deep pool and large cobble/boulder habitat. As noted, spawning habitat is extremely limited naturally, and where one redd was found, we found multiple nests frequently overlapping and clustered in a small area.

A 2009 redd survey of upper Penns Creek by the Center for Watershed Stewardship students found 173 redds in a similar length of stream (115/mile), but the survey section average width was larger than Muddy Creek and is lower gradient with more suitable gravel and small cobble spawning substrate. The Penns Creek survey area also has approximately two and a half times higher density of resident adult fish based on electrofishing biomass data (40 kg/ha in Muddy Creek vs 100+kg/ha on Penns Creek).

The bottom line: Muddy Creek has a very healthy wild fish population with great potential to respond to the ongoing stream restoration efforts to improve all important physical fish habitat types and to mitigate sediment and temperature degradation of the coldwater ecosystem.

Excerpt from the Young Forest Project, Mid-Atlantic Region, Georges Valley Cooperative Project, Central Pennsylvania:
Online URL: http://www.youngforest.org/demo/georges-valley-cooperative-project-central-pennsylvania

Landowners Team Up in a Keystone State Watershed

What happens when a bunch of **landowners** decide to help the American woodcock, a bird whose numbers have fallen as its young-forest habitat has dwindled? Add a **local conservation group** and a university-based **watershed center**, and good things can happen fast. In central Pennsylvania, this sort of team approach may provide a blueprint for similar projects throughout the East.

Lysle Sherwin heads the Center for Watershed Stewardship in **Penn State University's Department of Ecosystem Science and Management**. He worked with a local conservation association to enlist wildlife-minded landowners in Georges Valley, a 13.3-square-mile watershed near the town of Spring Mills.

Lysle Sherwin (left), George Kelly, and Lisa Williams inspect a young aspen planted in a field along Muddy Creek. (Plastic tubing protects against deer browsing.)/C.Fergus

Sherwin notes that **landowner-to-landowner networking** is essential for this kind of effort to succeed. He says, "The property owners in Georges Valley are a mix of longtime residents, including families who have farmed the land for generations, along with more-recent move-ins who like living in a rural setting. Hunting, fishing, and watching wildlife are strong local traditions."

First It Was for Fish

The project started as an effort to improve streams by reforesting their banks and cooling their waters to help **cold-water-loving trout** – in particular, those in Penns Creek, a famous fishery fed by many tributaries, including Muddy Creek, which drains Georges Valley. The Upper Penns Creek Watershed Project drew in Penn State landscape architecture graduate students Jake Powell and Drew Siglin, who wanted to study "the complex dynamics of human communities and social networks among disparate residents in a watershed."

One such resident is Lisa Williams, a woodcock biologist for the Pennsylvania Game Commission. She immediately saw the value to woodcock of **creating young forest on the fringes of Muddy Creek**. "The birds will feed and rear their young in the thickets that shade the waterway," she says. "They'll use nearby more-open habitats for spring courtship and nighttime roosting." Other wildlife will also thrive, including birds such as brown thrashers, indigo buntings, and whip-poor-wills, and reptiles like box and wood turtles – animals whose numbers, like those of the woodcock, have been falling as less and less young forest covers the landscape.

In spring 2011, Williams ran a woodcock singing-route survey in Georges Valley. She heard **13 males singing along a two-mile stretch**. "That told us that a breeding population was already in place," she says, "one that would fill any new habitat that landowners created."

The Penn State watershed specialists and members of the Penns Valley Conservation Association reached out to local residents through **letters and brochures**, **site tours, and a panel discussion** featuring representatives of federal and state conservation agencies that offer programs to help landowners create and restore wildlife habitat.

The Georges Valley effort may offer a broader application. "We realized that if we could figure out the critical pieces in creating a watershed-wide project like this one," says Sherwin, "we could then pick it up and move it to other areas."

Key to gaining local acceptance were public meetings, including panel discussions with conservation professionals./J. Powell

In the Landowners' Words

Ask landowner Jerry Myers why he got involved, and he'll point to the **wildlife-management plan** that the Pennsylvania Game Commission developed for his farm through the agency's Private Landowner Assistance Program. In spring 2012, workers planted 500 alder and other native shrubs on 1.5 acres of wet pasture. "That patch hadn't been used for 10 years," Myers says, "not since we sold our beef cattle. It's an area I don't need to mow now."

This newly planted streamside buffer on the Bierly farm will lower the temperature of stream tributary while providing habitat for wildlife./C Fergus

Doug Bierly, a township supervisor, also cites the fact that he won't be mowing a pasture that his family no longer needs for their horses. The Bierlys opted for a **streamside buffer** of aspen and black gum trees, along with shrubs such as redbud, silky and flowering dogwood, and crabapple – all prime wildlife plants. The U.S. Fish and Wildlife Service put in 500 trees and shrubs on 4 acres. Says Bierly, "I've noticed a definite increase in birdlife since the plantings went in."

Ray Grove has been controlling non-native invasive shrubs and planting native shrubs on his land with help from the Wildlife Habitat Incentives Program (WHIP) of the federal Natural Resources Conservation Service. Other Georges Valley landowners have enrolled in the Fish and Wildlife Service's Wetlands Conservation Program.

On Hill Crystal Farm, owned by Jennifer Tucker and Gerry Lang, machines removed unwanted invasive shrubs and scarified the soil, promoting **root sprouting of aspen trees** already growing along Muddy Creek. Conservationists also planted 230 aspen seedlings, quick-growing trees that will transform an old field into an patch of young forest. Says Tucker, "We were motivated by the fact that early successional forest is becoming an endangered habitat, something we didn't realize until Lisa Williams explained it to us. We've been impressed with the professionalism of all the folks involved in the project, from the biologists to the people operating the machinery."

Says Game Commission biologist Williams, "The Muddy Creek watershed will produce more local woodcock, and migrating woodcock will stop and rest in places where they'll find **food combined with cover** to protect them from predators. Just think what could happen if projects like this were replicated up and down the Atlantic Flyway, one of the corridors that woodcock follow as they shift between northern breeding grounds and southern wintering areas." (For more information about woodcock, see **timberdoodle.org**.)

Says George Kelly, who chairs the Watershed Committee of the Penns Valley Conservation Association, "Enthusiasm for making young forest and native shrub habitat is growing in Georges Valley, and it's spreading to neighboring Penns Valley." There, landowner David Martinec plans to convert a whopping **52 acres of his 100-acre family farm** to wildlife habitat, with help from the Natural Resources Conservation Service and the Game Commission.

Woodcock, like this nesting hen, will seek out the new young forest fostered in the Penns Valley watershed./C. Fergus

Conservationists outside the area are watching carefully, wondering if this kind of group approach – which seeks to join cooperating agencies and local landowners – can translate into **landscape-scale efforts** that will help young-forest wildlife in other regions.

Lysle Sherwin of Penn State's Center for Watershed Stewardship is optimistic. "People want to do the right thing for wildlife," he says. "If we can help them find the best way to do it, good things will happen."

How to Visit

Contact Lysle Sherwin, Director, Center for Water Stewardship, Department of Ecosystem Science and Management, Pennsylvania State University, 301B Forest Resources Laboratory, **lss9@psu.edu**, 814-865-5736. Pennsylvania Game Commission woodcock biologist Lisa Williams can be reached at **liswilliam@pa.gov**, 814-422-8243.

Funding and Partners

Penns Valley Conservation Association, Pennsylvania State University, Pennsylvania Game Commission, Natural Resources Conservation Service, U.S. Fish and Wildlife Service, Woodcock Limited of Pennsylvania, Wildlife Management Institute

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	0	2
Masters	5	0	0	1	6
Ph.D.	9	0	0	0	9
Post-Doc.	0	0	0	0	0
Total	16	0	0	1	17

Notable Awards and Achievements