

**Pennsylvania Water Resources Research Center
Annual Technical Report
FY 2012**

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). In the spirit of the Land Grant mission of the host Universities, each of the institutes emphasize the role of University research, education, and outreach in advancing pressing problems in water quality and quantity. 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 University Park campus at the Pennsylvania State University. There, PA-WRRC resides within the Penn State Institutes of Energy and the Environment (PSIEE).

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 new research programs on problems important to Pennsylvania. None of the federal funding was used to pay overhead costs, and PA-WRRC matched every dollar of its base appropriation with at least two dollars from non-federal sources.

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. This fiscal year, PA-WRRC received funding via PSIEE to coordinate additional water coordination activities on the Penn State campus, such as sponsoring 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 Program Introduction

None.

USGS Award No. G09AP00118 Long-term Responses of Stream Chemistry to Changes in Atmospheric Deposition in Mid-Appalachian Forests of Pennsylvania

Basic Information

Title:	USGS Award No. G09AP00118 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 Boyer, David Russell DeWalle

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.

PROJECT TITLE & PRINCIPAL INVESTIGATORS

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

PROBLEM & RESEARCH OBJECTIVES

This research project seeks to quantify and understand the unique long-term response of stream chemistry to reductions in atmospheric deposition that have been observed over the past three decades on five forested catchments in the Mid-Appalachian mountain region of Pennsylvania (PA). These catchments are part of the US Environmental Protection Agency's (USEPA) Long-Term Monitoring of Ecosystems (LTM) program. This network of forested, headwater catchments serves to determine status and trends in stream water quality in the eastern USA region, in response to chronic acidification via atmospheric deposition and to other vectors of change such as climatic variability.

Here, five acid-sensitive catchments in the Appalachian mountains of Pennsylvania are studied to quantify trends in surface water physical and chemical properties, in response to the effects produced by changing emissions of atmospheric pollutants on the biogeochemical cycles within the stream catchments. For forested streams of this region, the primary effects of atmospheric pollutants will be associated with acidic deposition and climate change. Responses of mid-Appalachian streams to acidic deposition involve chronic or episodic changes in the acid-base status of surface waters. Surface water acidification occurs when concentrations of strong-acid anions (sulfate and nitrate) increase relative to concentrations of base cations (calcium, magnesium, potassium, and sodium ions) in a stream. The result of this shift in acid-base status will be a depression in stream pH, possibly to a range associated with adverse effects on fish and other aquatic life. Responses of mid-Appalachian streams to climate change may be manifest in a number of ways. Increasing temperatures and shifting rainfall patterns will affect all aspects of the water cycle in these catchments. Changes in water flux through catchment soils can produce trends in surface water chemistry. Changes in episodic (storm) flow can alter chemical equilibria in streams. Changes in stream temperature can have enormous significance for freshwater organisms, and can affect temperature dependent chemical reactions.

METHODOLOGY

The five study catchments are located on the Northern Appalachian Plateau in the state of Pennsylvania. These catchments can be characterized as relatively undisturbed, mixed-hardwood forest basins. The basins are second-order streams that were not glaciated during the last major period of glaciation, and range from 5-11 km² in area, and from 701 to 893 m in maximum elevation. Benner Run and Linn Run catchments are part of state forest land administered by the Pennsylvania Department of Conservation and Natural Resources, Bureau of Forestry. Baldwin Creek, Stone Run and Roberts Run basins are located on lands managed by the Pennsylvania Game Commission. Arrangements have been made with these agencies to access these lands on a regular basis to conduct this study.

We conducted stream sampling, stream gaging, and laboratory for monthly samples from these five forested streams, which are acid-sensitive and are poorly buffered. On each stream water sample, we measured the following items:

Table 1: Summary of analytical laboratory water quality techniques.

Parameter	Methodology	Equipment
Temperature	Resistance thermometry	YSI Telethermometer
pH	EPA Electrometric (150.1)*	Beckman 360
ANC-Gran titration	EPA Titrimetric*	Radiometer automated titration unit
Specific Conductance	EPA Specific Conductance (120.1)*	YSI Conductance Meter Model 32
Sulfate, nitrate and chloride	EPA Ion Chromatography (300.0)*	Dionex Ion Chromatography Unit ICS 3000
Ammonium	Automated Phenate Method**	SEAL AQ2 Discrete Analyzer
Dissolved Metals		Perkin Elmer Atomic Absorption Spectrophotometer, Model 5100
Calcium	EPA AA Direct Aspiration (215.1)*	“
Magnesium	EPA AA Direct Aspiration (242.1)*	“
Potassium	EPA AA Direct Aspiration (258.1)*	“
Sodium	EPA AA Direct Aspiration (273.1)*	“
Aluminum – total dissolved	EPA AA Furnace (202.2)*	“
Silica	Molybdate –Reactive Silica**	SEAL AQ2 Discrete Analyzer
DOC	EPA 415.2 (low level)*	OI Analytical TOC Analyzer 1010
DIC	EPA 415.2 (low level)*	OI Analytical TOC Analyzer 1010

* Method referenced to US EPA (1983)

** Method referenced to Clesceri et al. (1998)

PRINCIPAL FINDINGS AND SIGNIFICANCE

As forested ecosystems of the eastern USA continue to adjust to dynamic changes in atmospheric deposition, long term monitoring is critical in order to understand effects on water quality. We continued measuring basic stream chemistry and stream flow in five forested streams of Pennsylvania, to further establish a record of change.

Acid 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 (NAPAP, 1991). 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.

Similarly, nitrogen (N) retention efficiency, the percentage of N inputs from the atmosphere and other sources that are stored in catchment soils or lost to the atmosphere via denitrification, is an important characteristic of forest catchment ecosystems that controls delivery of N to receiving waters. Nitrogen budget studies in forested ecosystems reveal that retention efficiencies on relatively-undisturbed forested catchments commonly exceed 70% and may reach 90%. In these Pennsylvania catchments, N retention efficiency generally increased over the last few decades associated with declining atmospheric deposition during this period.

STUDENTS & POSTDOCS SUPPORTED

The project is related to the work of two students who helped with the project in FY2012: MS student Brendan Reed, and PhD student Lidiia Iavorivsia, from the Department of Ecosystem Science and Management at the Pennsylvania State University.

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.

2012-2013 WATER RESOURCES RESEARCH PROJECTS
THE PENNSYLVANIA WATER RESOURCES RESEARCH CENTER
Final Report

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

PRINCIPAL INVESTIGATOR(S): Holly Frederick, Visiting Assistant Professor, Wilkes University, Wilkes-Barre, PA. Holly.Frederick@wilkes.edu 570-408-4880.

ONE-SENTENCE SOUND BYTE STYLE DESCRIPTION OF THE PROJECT OR FINDINGS: This research found that consistent laboratory protocol was more significant than 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 recovery. 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 treatment 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 treatment 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

Since this was the first year of the work, no publications were generated from this grant.

PRESENTATIONS

Since this was the first year of this work, no presentations were generated from this grant.

OTHER INFORMATION TRANSFER ACTIVITIES

NOTABLE AWARDS & ACHEIVEMENTS

Since this was the first year of this work, no notable achievements have been made.

ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY

Efforts are still underway to work to develop additional funding to continue the support of this work.

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.

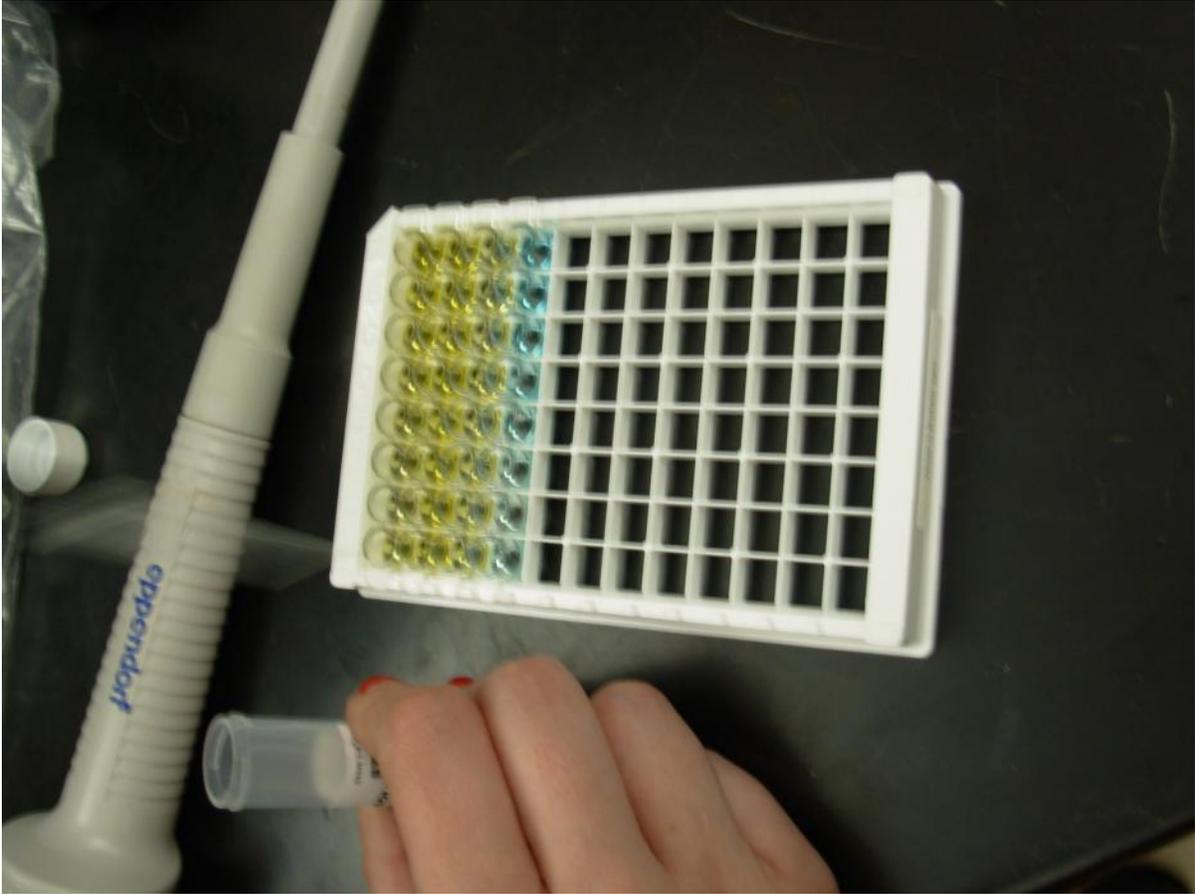


Figure 1. Wilkes University Student running Abraxis ELISA test to measure triclosan concentrations in wastewater samples.



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

Evaluation of Round Goby Habitat Disturbance and Impacts to Native Fish Populations.

Basic Information

Title:	Evaluation of Round Goby Habitat Disturbance and Impacts to Native Fish Populations.
Project Number:	2012PA188B
Start Date:	3/1/2012
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	5
Research Category:	Biological Sciences
Focus Category:	Invasive Species, None, None
Descriptors:	None
Principal Investigators:	Jay Stauffer, Jeanette L. Schnars

Publications

There are no publications.

PA-WRRC final report

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

ONE-SENTENCE SOUND BYTE STYLE DESCRIPTION OF THE PROJECT

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

The homogenization of the Earth's biota by the introduction and spread of non-native species is one of 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 (*Dreissnia polymorpha*), the quagga mussel (*Dreissnia bugensis*), 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.



Figure 1.
Round goby from 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 cm² block and category "100" contained substratum covering one hundred-5 cm² blocks (or 500 cm²). 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 cm² blocks, the product is 2 X 4² 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 indices.

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*.

Table 1. Fish survey and species composition.

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

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.

Site Comparability

To assess the comparability of the habitats a general linear model (GLM) was calculated to detect differences in the width, depth and flow between the two sites during the months of July and August. The data used for this comparison were taken from the random transect data. The width was different ($p < 0.05$) between the two sites; however, the width did not differ between July and August. The depth and flow did not differ between the sites. Depth was not different by date, whereas, flow was significantly different ($p < 0.05$) by date. Although flow differed by date, when the data were run separately by month with a one-way ANOVA, testing flow between sites, the flow did not differ between sites in either July or August.

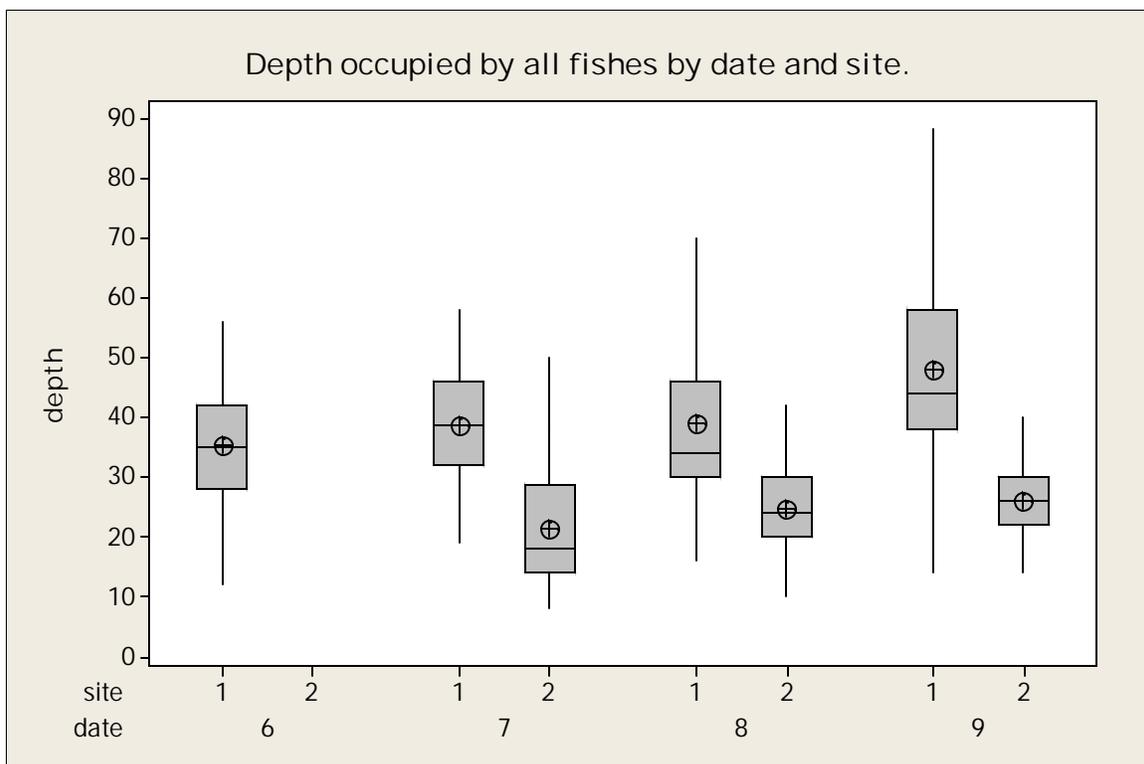
The comparability of the substrate types at the two sites was compared using a GLM. The data used for this comparison were taken from the all the substrate data collected. This is not a random set of substrate data for the site, but it is an assessment of the substrate types used by the fishes. The substrate used by the fishes was not different between sites. In contrast, this substrate was different by date. The comparability of the sites was assessed separately using one-way ANOVA by each month. The substrate data from July was different between sites ($p < 0.05$). In contrast, the substrate data in August and September was not different between sites.

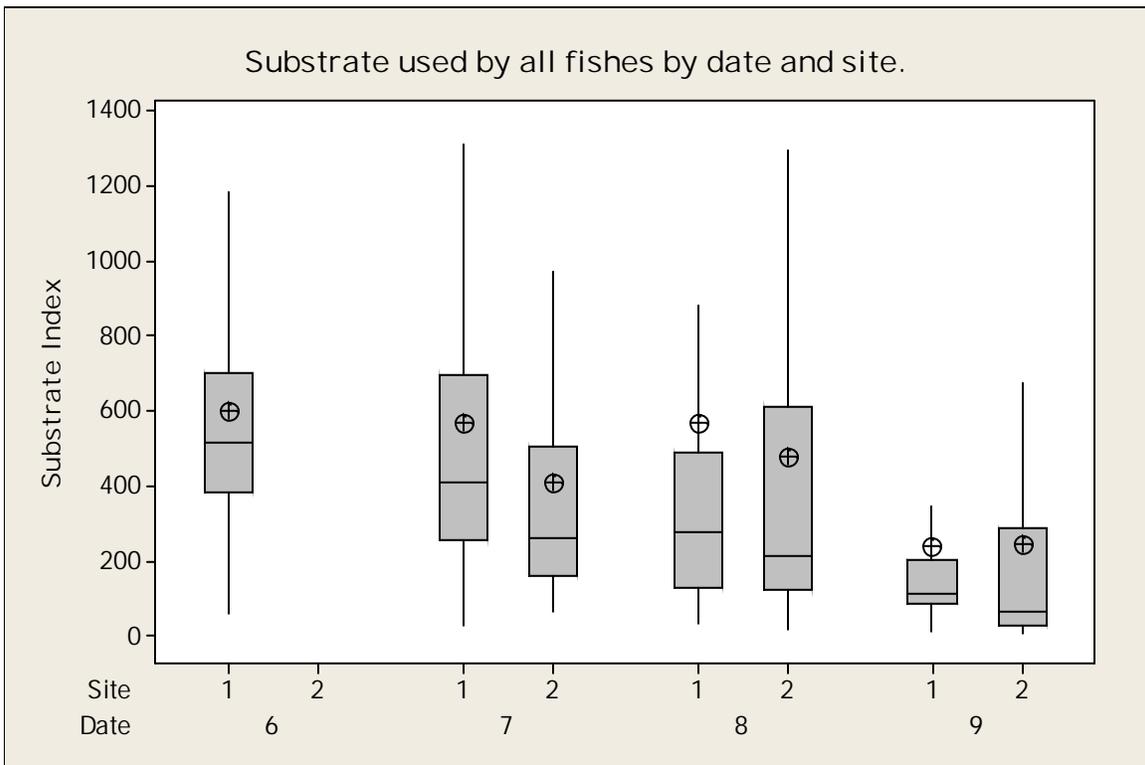
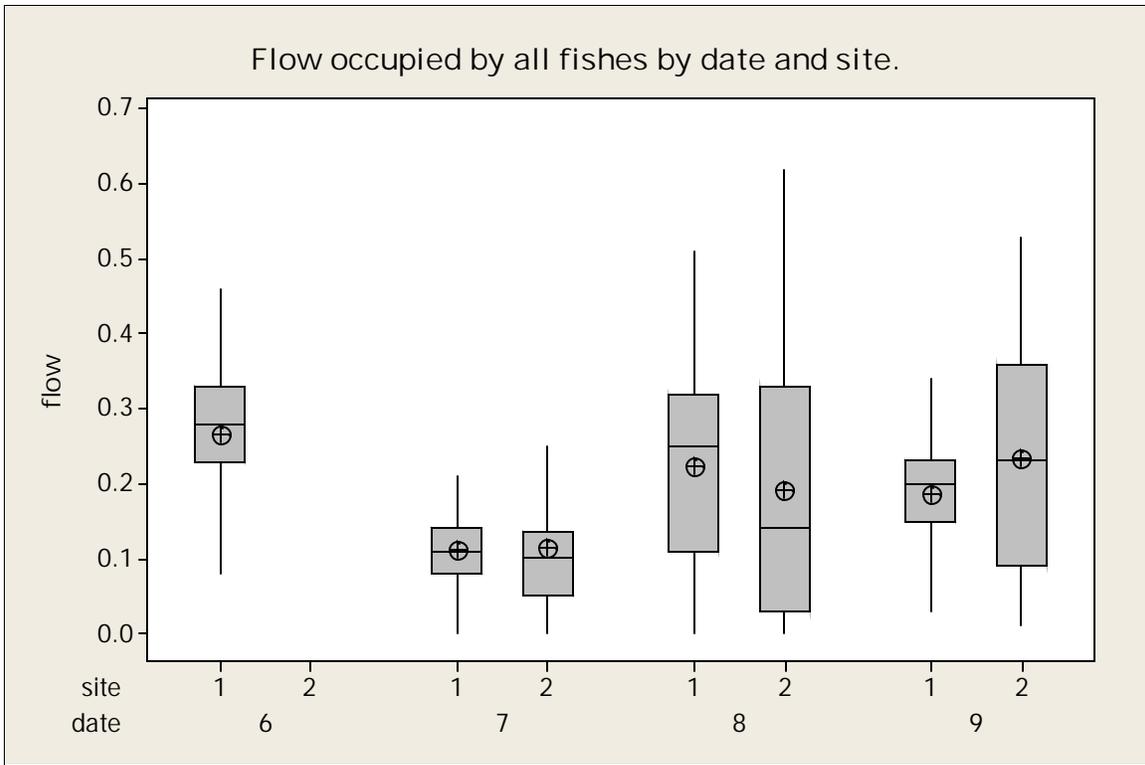
In summary, we believe the two sites are comparable because the depth, flow, and substrate did not differ between sites in a given month. Although width was significantly different between sites, we are not concerned with the effects of this variable on the habitat preferences of the fishes because the other abiotic variables are more important to fish.

behavior and they did not differ. Due to differences in the two sites across months, the habitat preferences of the fishes will be evaluated individually for each month when possible.

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 statistics 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.





This analysis indicated that there were mean differences in all variables by the month in which they were examined. The relationship between the sites and the variables was not clear in this analysis. Because the main purpose of this study was to determine if there was a shift in habitat use between the two sites (site 1 where gobies are present and site 2 where they are absent) and the month in which they were observed appears to influence this use, we further analyzed the data by looking at the individual species of fish by each site look. Because we only had data for site 1 during June the data for this month was eliminated from these analyses.

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
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Jackie Madzke, senior, Wildlife and Fisheries Science
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PUBLICATIONS

Two in preparation

PRESENTATIONS

Round Gobies Impact on native benthic fishes – Environthon Camp final presentation; Tom Ridge Center, Erie, PA

Diet overlap between Round Gobies and native benthic fishes in Lake Erie Tributaries – Casey Bradshaw, Tom Ridge Annual Scientific Meeting

OTHER INFORMATION TRANSFER ACTIVITIES

First Record of the Tubenose Goby in Pennsylvania.

ADDITIONAL FUNDING ACQUIRED USING USGS GRANT AS SEED MONEY

Additional monies requested from Coastal Zone Management to continue studies

PHOTOS OF PROJECT



Picking macro-invertebrates from drift nets.



Seining for fish at Elk Creek.

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_____ 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.

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

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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 developed 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 tested¹. 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 nation²⁻⁵. 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 its 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 years⁷. 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 environment⁸.

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 vancomycin⁹. The amount of resistant bacteria found in water systems has increased throughout the United States¹⁰. 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 all¹¹.

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 sufficient⁸. 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 carbons¹⁵. 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 Zhang²¹, 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

Titration experiments 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 pK_a '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 Nakai¹⁷, 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 $\mu\text{mol/g}$ for the ionic compound as compared to Q_e values between 10 and 40 $\mu\text{mol/g}$ 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 ($pK_a=6.0$) 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

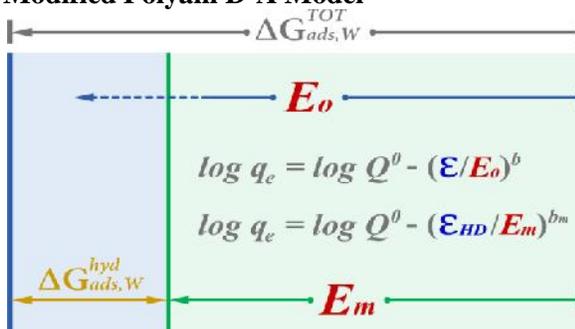
PHOTOS OF PROJECT

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



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Information Transfer Program Introduction

None.

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 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.

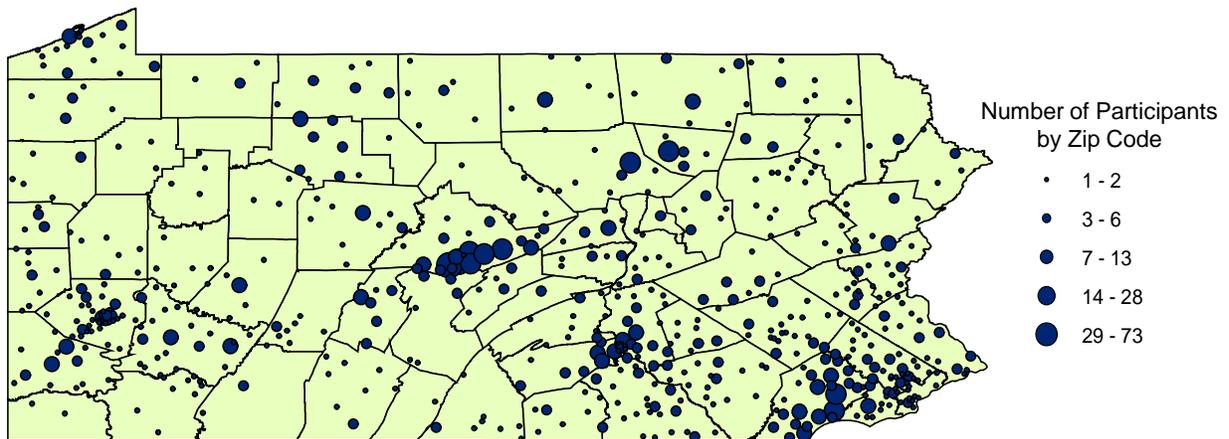


Figure 1. Map representing the number of survey participants by their zip code across Pennsylvania. Every county in Pennsylvania was represented the survey participants.

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.

How has the quality of rivers, streams and groundwater in your area changed in your lifetime?

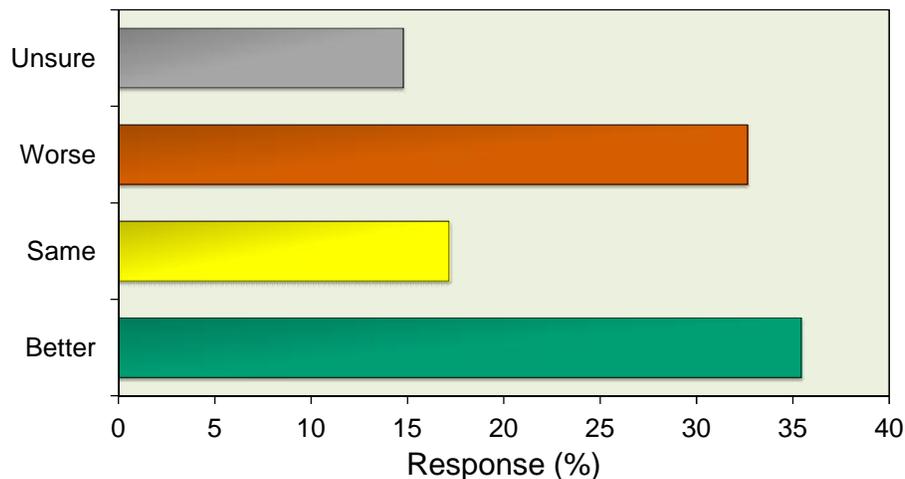


Figure 2. Bar chart representing percent response to the question “How has the quality of rivers, streams, and groundwater in your area changed in your lifetime?”

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.

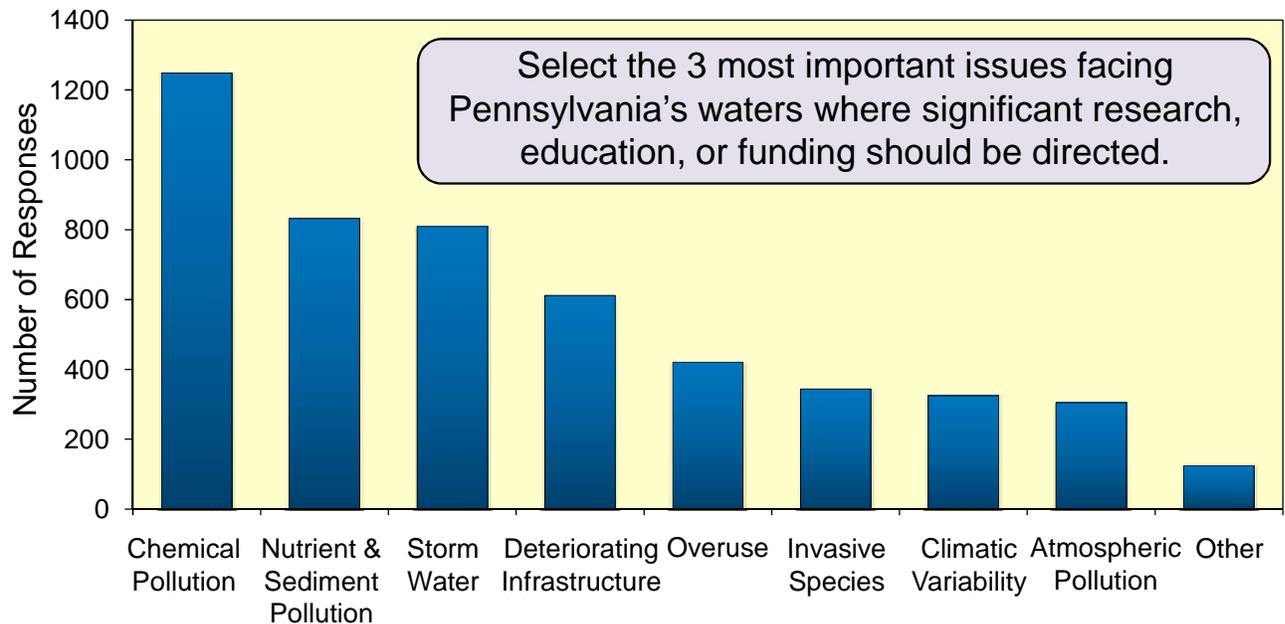


Figure 3. Column chart depicting the number of responses for each important issue facing Pennsylvania’s waters.

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.

How effective are the following management tools?

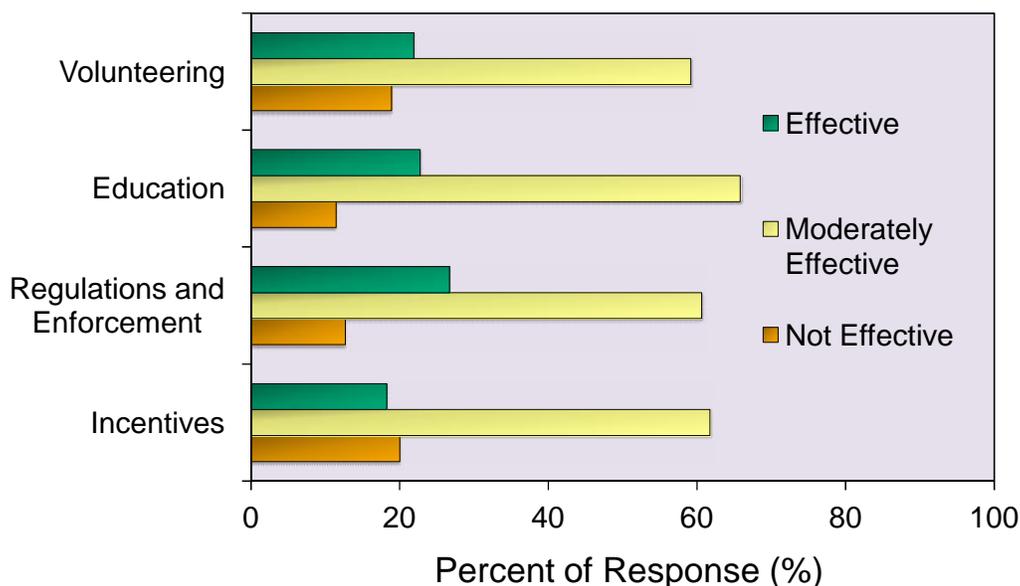


Figure 4. Bar chart showing how participants rated the efficiency of management tool sin water resources.

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).

How should we spend funds (\$) designated for water resources?

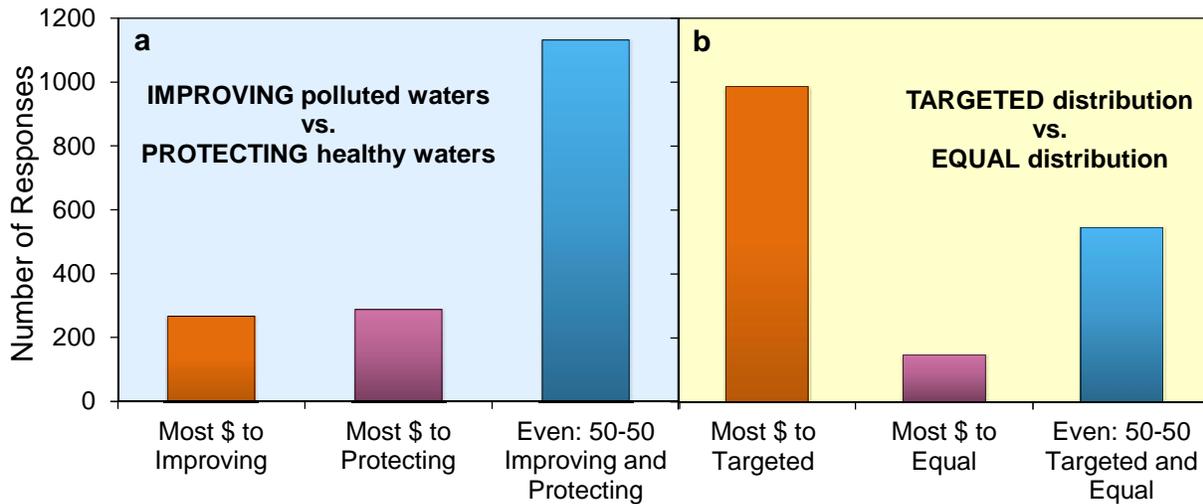


Figure 5. Column chart depicting the distribution of funds designated for water resources. Participants were asked how money should be spent between (a) Improving polluted waters vs. Protecting healthy waters, and should money be allocated using a (b) Targeted distribution of funds vs. an Equal distribution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

Tell Us about Your Home Drinking Water

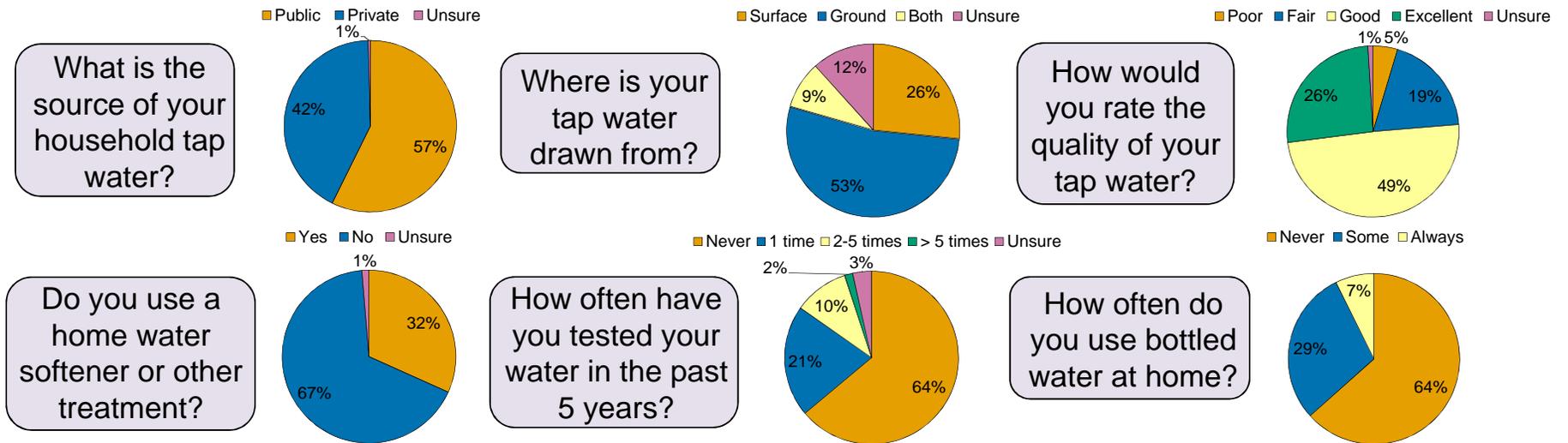


Figure 6. Pie charts of various characteristics of survey participants home drinking water. Participants were asked the source of their water, where is it drawn from, how they would rate their drinking water, if they use a water softener, if they have tested their water in the past five years, and how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

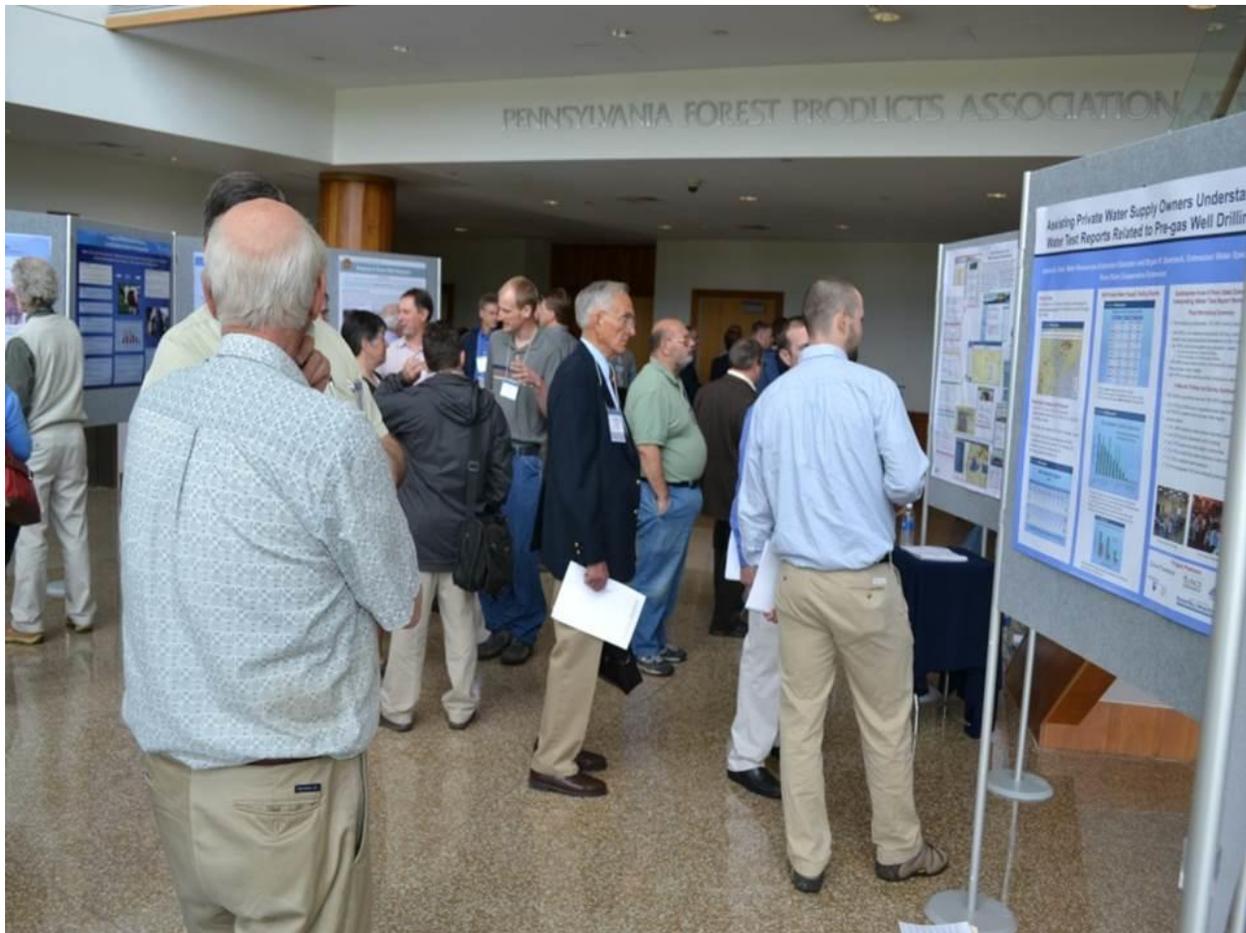


Figure 8. Lysle Sherwin presents a poster on the survey at the Pennsylvania Groundwater Symposium on May 8, 2013 at Penn State University.

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.

WeatherLink® Network

Millbrook Marsh Nature Center

74°

HIGH 74°F

at 11:21 AM

LOW 61°F

at 1:01 AM

Wind

SW 3 Mph

High Gust 7 Mph at 8:16 AM

Humidity

74%

Feels Like 75°F

Rain

0.00"

Seasonal Total 15.06"

Barometer

28.82"

Falling Slowly

Current Conditions as of 11:30 AM Monday, May 20, 2013
Vantage Pro2 data via WeatherLinkIP

DAVIS

Screen capture from Millbrook Marsh weather station

USGS Summer Intern Program

None.

Notable Awards and Achievements