New Jersey Water Resources Research Institute Annual Technical Report FY 2006

Introduction

The New Jersey Water Resources Research Institute supports a diverse program of research projects and information transfer activities. Under the continuing set of priorities enunciated by the Advisory Council, the available funds are split between supporting faculty in seed' projects or new research initiatives and supporting graduate students who are beginning their thesis research. Priority goes for the former to junior faculty; the goal is to help new researchers establish research programs which will have long-term investment in New Jersey water resource problems. With the latter (graduate students), the priority is to fund emerging and promising young scientists with novel ideas but little initial support to develop those ideas.

Research projects again span a wide range of topics in water resources. One of the faculty awards is supporting a effort to integrate economic impact analysis with a modeling approach to evaluating the optimal placement of BMPs for water quality improvement in an agricultural watershed in southern New Jersey. This project responds to the recent NRC report on water resources research needs that calls for an increased emphasis on the economic and social aspects of water resource management, and involves two assistant professors at two institutions. The other faculty award supported a study of the application of state-of-the-art analytic methods to separate the contributions of combined sewer flows and wastewater residuals to female hormone inputs to receiving waters.

Graduate student projects include 1) a study of spatial and temporal dimensions of nitrate removal (denitrification) in urban wetlands, which involved a comparison of soils derived from fill and from prior wetland areas within a highly urban area, as a test of the hot spots-hot moments' theory of nitrate removal; 2) a study of wildlife use of active and abandoned cranberry bogs, as an approach to managing wetland agricultural systems for better ecological quality; 3) an analysis of the distribution and potential impact of an exotic isopod in the Delaware River estuary; 4) an experimental and field-based study of the use of advanced geophysical imaging methods to characterize water movement through fractured-rock aquifers; and 5) an experimental study of the potential for using carbon nano-tubules for the removal of trichloroethylene from contaminated aquifers.

An additional project involved a collaborative effort with the Delaware, Pennsylvania and New York institutes and with the Delaware River Basin Commission to prepare an assessment of watershed health throughout the basin. The team developed a list of indicator variables and acquired data to assess the status of each variable for 21 sub-basins delineated within the Delaware River basin. The variables addressed water quality, water quantity, ecological health, and landscape structure. Numerous trends of both increasing and decreasing health were documented.

Through the information transfer program, we produced a series of well-received newsletters, updated and improved the organization of our website, and created a web log to facilitate communication within the water resource community.

Research Program

Delaware River Basin Commission State of the Basin Report

Basic Information

Title:	Delaware River Basin Commission State of the Basin Report	
Project Number:	2005NJ127O	
Start Date:	8/1/2005	
End Date:	12/31/2006	
Funding Source:	Other	
Congressional District:	N. A.	
Research Category:	Not Applicable	
Focus Category:	Management and Planning, Water Quality, Hydrology	
Descriptors:	watershed management, planning, watershed indicators	
Principal Investigators:	: Joan G. Ehrenfeld, Archil Zarnadze	

Publication

Delaware River Basin Commission State of the Basin Report

Problem and Research objectives:

The Delaware River Basin Commission (DRBC) is required by law to prepare an assessment of the status of the basin that relies on a compilation and analysis of data that broadly and comprehensively reflects the ecological and environmental health of the basin's waters and watersheds. This comprehensive assessment is also expected to generate indicators with which to establish baseline conditions and to form a basis for the future assessment of trends in the basin. In order to accomplish this goal, the DRBC contracted with the water resources research institutes in the four states in the basin (New Jersey, Pennsylvania, New York and Delaware) in order to bring the range of scientific expertise and experience available through the universities to the project. The project thus has as its goals:

1. To describe, for the general public and policy makers, the condition of water resources and water-related resources throughout the Delaware River Basin

2. To establish baseline environmental conditions in the Basin by assembling and assessing information that would characterize status and trends

3. To establish indicators in a watershed framework.

4. To determine the adequacy of current data collection and identify gaps in accounting or management,

5. Suggest improvements to data collection or management in order to expand reporting capabilities.

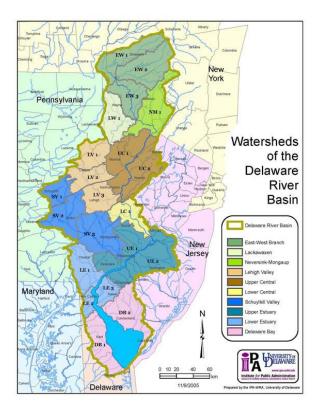
The project was based on acquiring data from a wide variety of web-based and agency-based sources, performing simple data analyses in order to display trends and current status, and using GIS capabilities to display and report the data in forms interpretable by the public as well as the scientific community.

Approach:

The water resources institutes from the four land grant universities of the states in the basin – Cornell, Delaware, Rutgers, and Penn State (institute partners) – collaborated in collecting appropriate and readily available water resource data and associated land-use and socio-economic information on a watershed basis, and worked closely with the DRBC and the Delaware Estuary Program to prepare the State of the Basin Report. The University of Delaware Water Resources Agency served as coordinator for this project.

The Basin was subdivided into 21 sub-basins; each institute was responsible for gathering and analyzing data for the sub-basins located within its state. The NJ WRRI was responsible for data collection for five of the sub-basins (Upper Central2, Lower Central 1 (half; shared with Pennsylvania), Upper Estuary 2, Lower Estuary 3, and Delaware Bay 2. Data collection for river and estuary-based indicators (e.g. fish and shellfish populations) were provided by the DRBC, and also by the Partnership for the Delaware.

Through a series of meetings, the list of indicators was refined, metrics and methods of presentation and analysis developed to ensure consistency in data reporting from the four regions, and criteria for interpretation developed.



The list of chosen indicators included the following:

- 1. Water quality: dissolved oxygen, total nitrogen, total phosphorus, total suspended sediment, metals (Cu, Pb, Zn, Hg, As), Organics (atrazine, PCBs, metalochlor), salt line (chlorides), fish consumption advisories, Sec. 303(d) designated use/impaired streams
- 2. Water quantity: water supply and demand, streamflow, groundwater quantity, flooding, dams
- 3. Living resources: macroinvertebrates, oyster beds, eastern oyster, horseshoe crab, blue crab, freshwater mussels, zebra mussels, American shad, freshwater trout, striped bass, Atlantic sturgeon, weakfish, summer flounder, Louisiana water thrush, red knots, bald eagle, black bear, amphibian, endangered species
- 4. Land use/landscape: tidal wetlands, tidal wetland buffers, total wetlands, impervious cover, land use, forest health, population, federal/state superfund sites, riparian corridor condition

Within each watershed, one or two representative streams were selected, based on the drainage area of the stream (two streams selected when no one stream accounted for >50% of the watershed), and data availability (length of the record, number of parameters for which data were available. Following is the table reporting the stream stations used to develop the NJ section of the report.

	USGS station				Drainage			
NJ Region	#	USGS station name	Data range	Counts	area (sq mi)	County	latitude	Longitude
UC 2 A	1443500	PAULINS KILL AT BLAIRSTOWN	1918 - 2005	283	126	Warren	40°58'51"	74°57'12"
UC 2 B	1457400	MUSCONETCONG RIVER At RIEGENSVILLE	1961 - 2005	208	156	Warren	40°35'33"	75°11'10"
LC 1 A	1460880	LOCKATONG CREEK AT RAVEN ROCK	1979 - 2000	23	22.9	Hunterdon	40°24'58"	75°01'04"
2017	1100000	WICKECHEOKE CREEK AT	1010 2000	20		Trantordon	10 2 100	
LC 1 B	1461300	STOCKTON	1959 - 1991	110	26.6	Hunterdon	40°24'41"	74°59'12"
UE 2 A	1464500	CROSSWICKS CREEK AT EXTONVILLE NORTH BRANCH	1908 - 2005	314	81.5	Mercer	40°08'14"	74°36'00"
UE 2 B	1467000	RANCOCAS CREEK AT PEMBERTON	1923 - 2005	243	118	Burlington	39°58'12"	74°41'04"
LE 3 A	1477510	OLDMANS CREEK AT PORCHES MILL	1975 - 2005	151	21	Salem	39°41'57"	75°20'00"
LE 3 B	1482500	SALEM RIVER AT WOODSTOWN MAURICE RIVER AT	1957 - 2005	315	14.6	Salem	39°38'38"	75°19'49"
DB 2 A	1411500	NORMA	1953 - 2005	413	112	Salem	39°29'44"	75°04'37"
DB 2 B	1411800	MAURICE R NR MILLVILLE	1968 - 2005	54	191	Cumberland	39°26'52"	75°04'21"

Overall, analysis of the water quality indicators shows that most waterways within the New Jersey section of the basin are at or better than the standard level. For only two of the gages (UE2A and LE2B) were there a majority of readings for one parameter (total P) that were above the standard. Moveover, for those indicators for which there were a small number of records above the standard (below for DO), occurrences of non-complying values were predominantly in the past (1970s or 1980s). Indicators for which there was sufficient data to suggest a temporal trend almost all show a trend towards increased water quality. Pesticides show the expected range of values with land-use, in that sub-basins with more active agriculture have higher concentrations than those with more forested land, and also show that there is a belt through the middle of the basin that has more heavily impaired waters than at the upper and lower ends. Indicators of lower water quality were clearly associated with the more intensive development and urban land-use in the Lower Central and Upper Estuary watersheds (Trenton to Camden area). Some biotic indicators (e.g., Louisiana water thrush, bald eagles) showed improving trends over the recent past, while others (e.g., oysters, red knots), showed significant declines. There were no obvious trends in water quantity data in the New Jersey sections of the basin.

A draft report integrating the data from the four states has been prepared, and a final version will be completed shortly. The project was presented as a half-day symposium at the American Water Resources Association meeting in Baltimore.

Nitrate removal in urban wetlands: examining the roles of vegetation, soils, and hydrology in the creation of hot spots' and hot moments' of denitrification

Basic Information

Title:	Nitrate removal in urban wetlands: examining the roles of vegetation, soils, and hydrology in the creation of hot spots' and hot moments' of denitrification	
Project Number:	2006NJ100B	
Start Date:	3/1/2006	
End Date:	2/28/2007	
Funding Source:	104B	
Congressional District:	6th	
Research Category:	Water Quality	
Focus Category:	Nitrate Contamination, Water Supply, Hydrology	
Descriptors:	None	
Principal Investigators:	Monica Marie Palta, Joan G. Ehrenfeld	

Publication

- 1. Palta, Monica M. and Joan G. Ehrenfeld. 2007. Nitrate removal in urban wetlands: Examining the roles of vegetation, soils, and hydrology in the creation of hot spots' and hot moments' of denitrification. 2nd Symposium of the Meadowlands Environmental Research Institute, Lyndhurst, New Jersey. (Poster presentation)
- 2. Palta, Monica M. and Joan G. Ehrenfeld. 2007. Nitrate removal in urban wetlands: Examining the roles of vegetation, soils, and hydrology in the creation of hot spots' and hot moments' of microbial activity. Poster to be presented at the 92nd Annual Meeting of the Ecological Society of America, San Jose, California. August 5-10, 2007.

Project Summary:

Problem and Research Objectives

The scale at which "hot spots" and "hot moments" of nitrogen (N) removal occur via denitrification has not been well-defined, and there has been little work relating plant biology, hydrologic regime, and soils with N removal function in floodplain restoration efforts. The role of riparian vegetation in nitrate (NO_3) removal from surface and groundwater in particular is poorly understood. Though *Phragmites australis* is identified as a noxious weed in restoration designs, the extent to which Phragmites invasion or eradication affects nutrient cycling is not known. Phragmites has substantial and deeply rooted belowground biomass and high levels of carbon (C) exudation relative to other dominant marsh plants, as well as high levels of N uptake in tidal marshes; these characteristics suggest that patches of wetland containing *Phragmites* may serve as "hotspots" of denitrification. Recent research suggests, however, that the magnitude and direction of impact of *Phragmites* on N cycling may be system-specific. Differences in hydrologic conditions and soils between wetland areas may lead to differences in N removal ability of *Phragmites*. Soil textures vary in permeability and depth of the rooting zone, affecting the availability of labile C, NO₃, and oxygen to denitrifiers in the period following a saturation (rain) event.

My project took advantage of a 17 ha site (Teaneck Creek Conservancy, Bergen County) in which monospecific *Phragmites* stands are located on adjacent patches of clayey, silty, and organic soils. The presence of these adjacent patches enabled me to isolate the effects of soil type and soil-generated differences in hydrology on the spatial and temporal distribution of "hot spots" and "hot moments" of NO₃⁻ removal. My goal was to determine the temporal and spatial variability in denitrification within and among replicate areas within each of these three soil types, thus both helping to define the dimensions of "hot spots" and "hot moments" in N removal and examining the drivers behind such phenomena.

My hypotheses were (1) there will be significant differences in both spatial and temporal variability among the three soil types that will be correlated with their hydraulic properties, thus demonstrating that differences in soil texture are a source of patchiness in dentrification within wetlands; (2) further, the high water retention capacity of the clay soils will result in less within-patch variability and less variability over time than in the silty soil or peaty soil, thus resulting in larger "spots" and longer "moments" in the clays and smaller "spots" and shorter "moments" in the silt and peat; (3) finally, the dimensions of both "spots" and "moments" will be correlated with the abundance and distribution of organic matter available in the soil.

Methodology

The study took place in the Teaneck Creek watershed, a small (0.2 km²) freshwater stream system in northeastern New Jersey (NJ) that is part of the larger Hackensack River watershed. Teaneck Creek is located in a highly urbanized setting adjacent to Newark, NJ. Research hypotheses were addressed by characterizing soil properties and denitrification rates in different soil types (clayey, silty, and organic soils). Two replicate patches of each soil type were identified for sampling, and two replicate 3x3 meter plots were used in each patch (Figure 1). A "hot spot" of N removal was thus restricted to two spatial levels: between-soil patches and within-soil patch. Only the top 20 cm of the soil profile was considered in NO_3^- removal dynamics.

To identify differences in denitrification rates between soil profile types over time, soil cores were collected from each plot every day for 10 days following a saturation event (> 1" of precipitation). Cores were collected in each of three seasons when temperatures are sufficiently high enough for denitrification to occur: spring (May), summer (July), and fall (November). A "hot moment" of N removal was thus restricted to two temporal levels: within a 10-day soil wetting and drying cycle, and within a given season. In each replicate 3x3 meter plot, one core was collected every day for 10 days. These "fresh" cores were used immediately for static core, acetylene-based measurements of denitrification rate. One "incubating" core was collected on the first day of the 10 day period and immediately replaced in the ground; this core was incubated in the ground for a month prior to extracting it to determine N mineralization rate in each soil type. A KCl extraction was used to determine soil NH₄⁺ and NO₃⁻ content of fresh and incubated cores.

To characterize differences between soil types in hydraulic properties and available C, the following was characterized for each plot in the middle of the study, between summer and fall 10-day sampling periods: total organic N (TON); total organic C (TOC); plant litter biomass; soil texture (% sand, silt, clay). Percent soil moisture and percent organic matter of all soil cores collected during the study were determined concurrently with N processing. In addition, whenever possible, the redoximorphic status of the soil in each plot was measured in the field during core collection using Corning® redox combination electrode.

Linear comparative models (repeated measures PROC mixed and PROC glm) were used to determine whether significant differences existed between soil types in denitrification rate, moisture conditions, and organic matter content over time.

Principal Findings and Significance

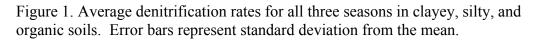
The subset of data processed and analyzed thus far largely supports the hypotheses originally proposed. Significant differences in denitrification rate were found between soil types (indicating "hot spots") and between and within seasons (indicating "hot moments"). Further, these differences do appear to be driven, at least in part, by moisture conditions, which influence nitrification rates; the latter is a key process driving denitrification. This study therefore provides important evidence that differences in soil texture are a source of patchiness in dentrification within wetlands, and that restoration projects aiming for higher levels of denitrification within wetlands must carefully consider texture and drainage of wetland soils in their design.

Highly significant (p < 0.001) differences were found between soil types over the entire time frame of the study and between seasons. Soil denitrification rates demonstrated the following pattern: organic soils < clayey soils < silty soils (all significantly different from one another at the $p \le 0.01$ level) (Figure 1). Organic soils showed very low variability in soil moisture, and initial analysis does indicate, as predicted, that clayey soils may demonstrate less variability in denitrification rates than silty soils; further analysis is needed to deconstruct these trends. Though soil moisture rates alone were not a good predictor of denitrification rate, differences in denitrification rates among soil types may be linked at least in part to soil moisture levels, since both

silty and clayey soils had significantly (p < 0.0005) lower soil moisture than the permanently saturated organic soils (Figure 2). Despite their significant differences in denitrification rates, however, silty and clayey soils had very similar soil moisture on average, and similar variability in soil moisture. This pattern was surprising, given the patterns of drainage typically found on finer (clay, poor drainage) vs. coarser (silt, good drainage) soils. A soil map currently under construction for Teaneck Creek Conservancy linking soil moisture levels to both texture and elevation will also clarify how textural patterns may drive soil moisture patterns across the site.

Differences in soil moisture may be linked to denitrification rates among soil textures due to the influence of soil moisture on rates of soil nitrification. Nitrification rates have not yet been calculated (these samples have not been analyzed yet), but soil extractable nitrate does demonstrate a weak (spring $R^2 = 0.2542$, summer $R^2 = 0.4220$) quadratic trend with denitrification rate (Figure 3), indicating that denitrification rates are highest when soil nitrate is available at intermediate levels. Since nitrification is highest under dry (aerated) conditions, this trend may indicate that, as anticipated, intermediate moisture levels in the soil (wet enough for denitrification to occur, but dry enough for some nitrification to occur, to supply the denitrifying bacteria with nitrate). Though variability is high, available nitrate does appear, on average, to be lowest in the organic soils and highest in the silty soils (Figure 4).

It was hypothesized that organic matter availability in soils would be an important driver of patterns in denitrification, but this prediction is not thus far supported by the data. Organic matter content was not a good predictor of denitrification rate, and though organic matter was significantly (p < 0.05) higher in the organic soils than in the silty or clayey soils, denitrification was lowest in the organic soils. Previous work has found that high levels of organic matter in the soil during fall are likely to promote high levels of denitrification during this same season. Soils at Teaneck showed the opposite trend: fall denitrification rates were significantly lower than either spring or summer rates (p < 0.005). Additionally, no seasonal trends were found in organic matter, is likely the most important determinant of denitrification rates in this system.



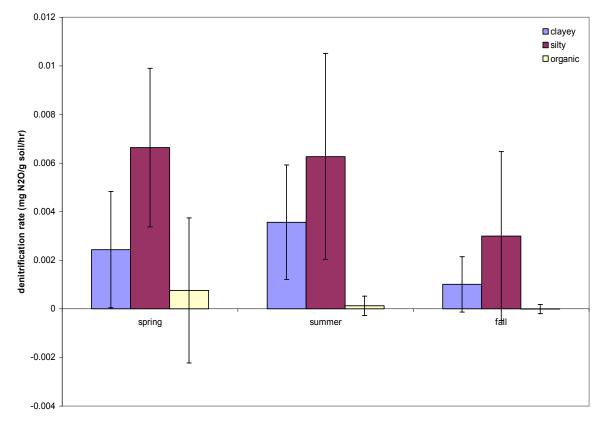


Figure 2. Soil moisture conditions over all three seasons for silty, clayey, and organic soils. Error bars represent standard deviation from the mean.

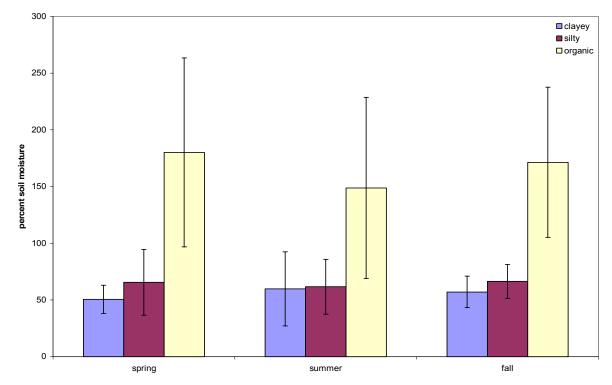
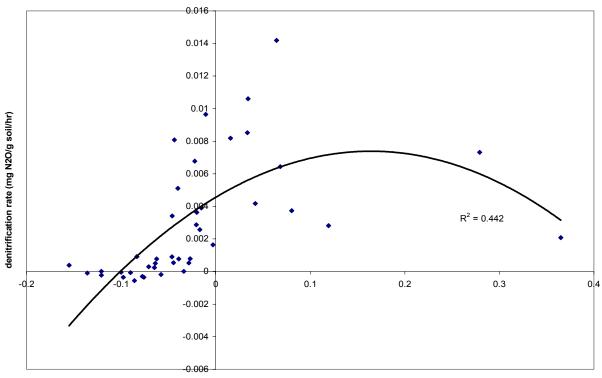


Figure 3. Summer denitrification rates vs. summer soil available nitrate for all sites.



available NO3 (ppm)

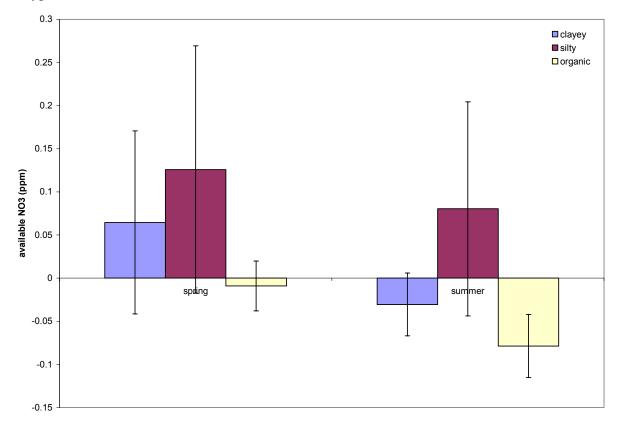


Figure 4. Average available nitrate over spring and summer seasons for each soil type.

Female Hormones in Surface Water of Central/Northern New Jersey: Impacts of Combined Sewer Overflows versus Treated Wastewater Discharge

Basic Information

Title:	Female Hormones in Surface Water of Central/Northern New Jersey: Impacts of Combined Sewer Overflows versus Treated Wastewater Discharge	
Project Number:	2006NJ101B	
Start Date:	3/1/2006	
End Date:	12/31/2007	
Funding Source:	104B	
Congressional District:	6th	
Research Category:	Water Quality	
Focus Category:	Water Quality, Water Quantity, Methods	
Descriptors:		
Principal Investigators:	Weilin Huang, Peter F. Strom	

Publication

Project Summary:

Problem and Research Objectives

We proposed to detect and quantify female hormones — a major class of endocrine disrupting chemicals (EDCs) — in the surface water of Central/Northern New Jersey. This study is especially important for densely populated Central/Northern New Jersey where treated wastewater (TWW) is a major component of surface water and combined sewer overflows (CSO) have caused substantial problems in several watersheds. More importantly, the surface aquatic ecosystems are very precious in this populous area. Yet, they are not very healthy and the surface water quality has deteriorated due to heavy contamination from extreme urbanization and industrialization. Low but constant contamination with female hormones in surface water may adversely affect the reproductive behavior of animals such as fish, posing large ecological risks. Our study would provide data on the level and the source (TWW vs. CSO) of female hormone contamination in the watersheds of Central/Northern New Jersey. It could help determine whether future effort is needed, and which source — TWW or CSO — we should pay most attention to for reducing the ecological impact of the female hormones in these watersheds.

In this study, we planned to develop analytical methods for detection and quantification of three common female hormones [17 β -estradiol (estradiol, or E2), estrone (E1), and 17 α -ethinyl estradiol (EE2)] in surface water samples using either LC-MS/MS or GC-MS. After method development, we proposed to select two to three typical surface aquatic systems that are influenced variously by TWW and/or CSO. The goal of this study was to differentiate the contributions of TWW and CSO to the female hormones detected in these aquatic systems. The study would provide much needed information for regulating the emerging pollutants and for supporting future efforts to develop water quality models and Total Maximum Daily Loads (TMDLs) for these chemicals.

The specific **objectives** of this study are to:

- 1) collect water and colloid samples from two watersheds of North/Central New Jersey during and after major storms;
- analyze the female hormones in the samples following published laboratory procedures and with liquid chromatography - mass spectrometry/mass spectrometry (LC-MS/MS) or gas chromatography-mass spectrometry (GC-MS);
- 3) quantify the loading of the hormones from different sources to the studied watersheds.

Methodology

LC-MS/MS Method Development

In the first five months of the project, we developed an LC-MS/MS method with collaboration of Dr. Zhiqiang Yu of Guangzhou Institute of Geochemistry, Chinese

Academy of Sciences. We used a liquid chromatograph with tandem mass spectrometric detection (LC-MS/MS) (Agilent). The liquid chromatographic separation was carried out at room temperature using a RP-C8 Hypersil MO5 phase ($2.1x100 \text{ mm}; 5 \mu \text{m}$) from Agilent (Waldbronn, Germany) and an RP1 guard column (2x10 mm UltraSep ES; SEPSERV, Berlin, Germany). For the separation of the analytes, a programmed gradient was applied using acetonitrile and water as solvents. The initial composition of the mobile phase was 12% acetonitrile. This level was held for five minutes and then increased within 30 minutes to 25% and within another 15 minutes to 53%. The flow rate of the mobile phase was 0.2 mL/min. The addition of buffers (ammonium acetate or ammonium hydroxide at varying concentrations) to the mobile phase caused a decrease in the responses of the analytes due to lower ionization ratios.

Reference compounds (E1, E2, and EE2) and the deuterated surrogate standard compounds 2,4-d2-17 β -estradiol (d2-E2) and 2,4,16,16-d4 Estrone (d4-E1) were used to prepare standard solutions in 2-propanol. The deuterated surrogates were used for both recovery efficiency and quantifying the concentrations of the target compounds. For method development, MiliQ water was spiked with the estrogen standards at levels of 0.1 to 50 µg/L.

Our results showed that the three estrogen compounds were separated with the instrumental conditions described above and the detection limits were about 0.5 μ g/L. These detection limits suggested that these three estrogen compounds could be detected and quantified at ng/L levels for surface water samples collected from the field.

GC-MS/MS Method Development

Because the cost of LC-MS/MS analysis is very expensive due to limited availability of the instrument, we have also developed a GC-MS method with a derivatization procedure for quantification of the three estrogen compounds. The instrument used for method development was a Waters Quattro Micro tandem quadrupole GC-MS/MS. This instrument is available to us with no cost. It uses a 60 m by 0.25 mm i.d. DB-5 (5% diphenyl dimethyl polysiloxane) capillary column with a film thickness of 0.25 mm.

For method development, we used prefiltered miliQ water which was spiked to 100 ng/L with mesterolone, the surrogate standard, and the three estrogen compounds. Mesterolone has properties similar to the other steroids but is not commonly used in human therapy, and thus should not be detected in surface water samples. The spiked filtrate was extracted through a 47-mm C-18 solid-phase extraction disc. Prior extraction, the C-18 discs had been preconditioned by rinsing them twice with 25 ml methanol followed by two rinses with 50 ml of distilled water. After extraction, the discs were rinsed twice with 25 ml of a 60:40 (v/v) water:methanol solution to selectively elute polar organic matter from the SPE discs. After this washing step, the estrogen compounds were eluted from the discs with 20 ml of a 25:75 (v/v) water:methanol solution. The eluent was then completely dried under vacuum, re-dissolved in pure methanol, and the methanol solution was transferred to a 1-ml volumetric flask. The extract was dried once again under vacuum and re-dissolved in 200 μ l of acetonitrile. Next, 50 μ l of

heptafluorobutyric anhydride, the derivatizing agent, was added, and the volumetric flask was sealed and placed in a 55°C over for 1.5 h. After completion of the derivatization reaction, the flask was cooled to room temperature, and the solvent was evaporated under a nitrogen stream. The derivatized estrogen compounds were re-dissolved in 100 μ l of iso-octane to which hexachlorobenzene (400 μ g/L) was added as an internal standard. The samples were ready for instrumental analysis.

Our results showed that the three estrogen compounds were separated on the GC-MS/MS with detection limits of ng/L, which are comparable to the LC-MS/MS method. The recovery efficiencies were 65-91% for the spiked estrogen compounds.

Principal Findings and Future Work Plan

We have completed the analytical method development and the results showed that the three estrogen compounds can be separated and quantified with both LC-MS/MS and GC-MS/MS. The detection limits of both methods for the three chemicals are comparable and are on the order of ng/L. Tests using spiked water samples indicated that 65-91% of the chemicals spiked to pure water can be recovered.

With the no-cost extension of the project, we are in the process of testing field water samples. We will take water samples from the Raritan River of New Brunswick, New Jersey. Duplicate samples (5-10 liters) will be sampled, stored in cooler with ice bags, and transported back to the lab. They will be stored immediately at 4°C for no more than 2 days. After suspended solid particles (SSP) have been settled, the supernatant (2–5 liters) will be filtered through 0.45 μ m glass fiber filters, spiked with 2.5 ng of the surrogates d2-E2 and d4-E1 for quantifying both the recovering efficiency and the concentrations of the three compounds. For the water phase, sample extraction will be performed using SPE discs that will have been preconditioned with methanol and distilled water. The water samples will be filtered with an upper limit of flowrate at 5 mL/min. Then the discs will be sequentially washed and extracted following the procedures described above. The sample extract will be transferred to acetonitrile. One half of the acetonitrile solutions will be used for direct LC-MS/MS analysis, and the other half will be used for derivatization and subsequent GS-MS/MS analysis.

After validating the two methods with the field samples, we will conduct systematic water sampling and analyze the chemicals with either or both methods, depending upon the availability of the instruments. We expect to complete the proposed work by the end of the Fall 2007 semester. A complete progress report on the results will be provided in the Spring of 2008.

Cranberry Agriculture as Wildlife Habitat in the Pine Barrens Wetland Ecosystem

Basic Information

Title:	Cranberry Agriculture as Wildlife Habitat in the Pine Barrens Wetland Ecosystem
Project Number:	2006NJ102B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	6th
Research Category:	Water Quality
Focus Category:	Wetlands, Ecology, Water Use
Descriptors:	None
Principal Investigators:	Ai Wen, David Ehrenfeld

Publication

1. Wen, Ai. 2007. The Habitat Use by Birds and Anurans of Active and Abandoned Cranberry Farms in the Pine Barrens of New Jersey. Poster to be presented at the 92nd Annual Meeting of the Ecological Society of America, San Jose, CA. August 9, 2007.

Project Summary

Objectives:

As the need for agricultural development continues to grow, it is imperative to maintain or increase the ecological function of agroecosystems while minimizing negative influences on the surrounding environment. The cranberry farms located in the Pine Barrens of New Jersey provide an excellent opportunity to study this issue. Cranberries have been cultivated in this area for about 150 years. The 3,600 acres of active farms, as well as numerous abandoned bogs, are embedded in the riverine wetlands, where a great variety of lowland plants and animals live. This is a unique opportunity to study wildlife distribution in farmland habitat as well as the response of animal communities to plant succession after agricultural abandonment.

Objective1. To study bird and frog distributions within the farm with different habitat factors (vegetation, hydrology and landscape factors).

Objective2. To study the seedbank composition in cranberry beds with different watertable depth, and their germination under different hydrological conditions.

Methodology:

1. Bird transect survey:

Since the spring 2006, I monitored the distribution of bird species along the boundary transects of two active cranberry farms (530SN, 70S) and one abandoned cranberry farm (532W). Two more abandoned farms and one more active farm were added in spring 2007. Thirteen to fifteen transects were set along each farm. Each farm was visited two to four times a month. The number of individuals of each species observed in the transects were recorded. The survey has been continued and will be finished in spring 2008.

The landscape factors have been obtained from 2002 NJ aerial photos. The habitat vegetation surveys will be finished by the end of summer 2007.

2. Anuran call survey:

During 2006, anurans were surveyed in two active farms (70S, 530SN), one newly abandoned farm (532W, 6 year abandonment) and one old abandoned farm (Pasadena, >50 years). The survey was conducted twice per month in each site. Right after sunset, I walked in the cranberry farms and stopped at different habitats (cranberry beds, ditches, reservoirs) to identify the anuran species and estimate their density by the calling intensity (level 1 to 4). Two more abandoned farms and one more active farm were added in 2007 to increase the replicates in order to compare the difference between active and abandoned farms.

In addition, anuran tadpoles were trapped with minnow traps in different habitats in each site. Traps were set right before sunset in each site and checked at the following dusk. The tadpoles were then identified and released. 3. Succession study in the abandoned cranberry farms:

In spring 2006, 25 wells were set in five beds of a newly abandoned cranberry farm to monitor water table changes. In fall 2006, 24 seed traps were set up in these beds to trap seeds dispersed by wind, aiming to compare the seed composition in these beds.

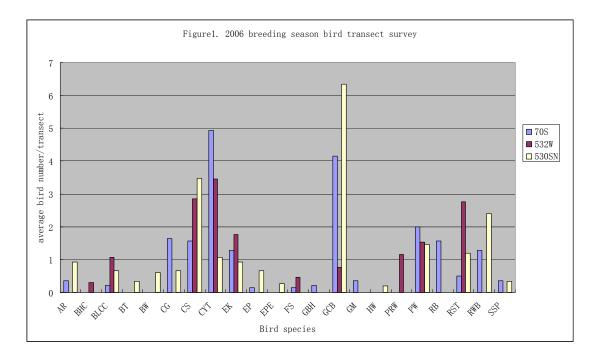
In spring 2007, soil cores were taken in eight beds (four beds with low water tables and four beds with high water tables; four cores were taken from each bed) and brought back to the greenhouse for germination. Besides regular mist spray, two out of the four cores from each bed are treated with flooding once in two weeks. The germination result will be compared between beds with high and low water tables, and dry and wet treatments. In order to examine the seedbank with different ages, each soil core was divided into three layers: top layer includes the recent cranberry plants and dead runners; middle layer includes the older layers that were covered by sanding during later years of cultivation; bottom layer is the original wetland soil from before the construction of the farm. All the layers were all treated with the same wet and dry condition to examine the germination result.

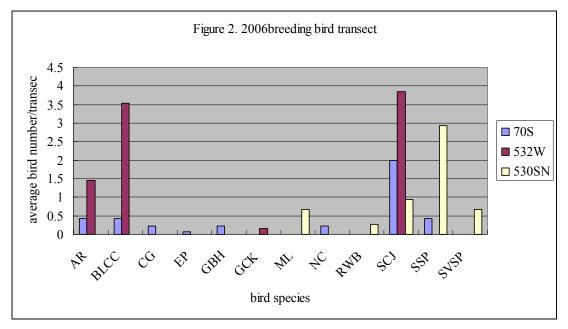
Principle findings:

1. Bird transect survey:

During 2006, a total of 115 bird species were recorded. Nine visits during the breeding season (June-August) and eight visits during the winter (December-March) were conducted at each farm. However, in order to only include bird species that are using the cranberry farms as their habitat, the data was processed with a Visual Basic program. In each transect, only bird species that were observed more than three times during the season, or observed in two consecutive visits, were considered as residents that are using the transect. Therefore, out of the 115 species, 22 species were residents during the breeding season, and 12 species were winter residents.

The bird density didn't show a significant difference among different farms during the breeding season or the winter (ANOVA, breeding P=0.74; winter P=0.55). The ANOVA analysis of each individual species shows that during the breeding season, only the Grey cat bird (GCB, *Dumetella carolinensis*) had significantly different distribution among different farms (P=0.01, Figure 1), and Rufous-sided towhee (RST, *Pipilo erythrophthalmus*) had a marginally significant difference (P=0.06, Figure 1); during winter the distribution of Carolina Chickadee (BLCC, *Parus caroinensis*) showed a marginally significant difference (P=0.06, Figure 2).





Therefore, birds' distribution among various farms doesn't show a significant difference in general. In each season, however, some transects did support significantly higher densities of certain species. I hypothesize this can be explained by the difference in habitat factors for each transect. I am therefore conducting a vegetation survey in each transect to obtain the number and coverage of evergreen trees, deciduous trees, evergreen shrubs, deciduous shrubs, berry-producing shrubs and grass/sedges. Also, the landscape factor of the coverage of human residence, agricultural land, coniferous forests, wetlands, and barren lands will be obtained from 2002 NJ aerial photos. These factors together with the bird density will be analyzed with Canonical Correlation Analysis (CCA) to explain different bird species distributions in each transect. As a result, instead of using individual farms as replicates to monitor bird distributions, the boundary sections of these farms will be treated as replicates to evaluate the critical factors that determine bird habitat preferences.

The survey results of 2006 have demonstrated the difficulty of comparing bird distributions among different sites presumably because of the significant differences among each transect. Therefore, in order to compare the habitat function of active and abandoned cranberry farms, I have been surveying transects with similar vegetation types in three active and three newly abandoned farms. In each farm, three boundary transects and three dike transects were selected. I expect in this way I can eliminate the difference caused by transect variation, therefore each farm will then be treated as a replicate for either active or abandoned farm to compare the bird communities' composition.

2. Anuran survey

Eight species have been recorded by the call survey¹. They are listed following the sequence of their call phenology: northern *spring peeper (Hyla crucifer crucifer) (SP), wood frog (Rana sylvatica) (WF), *carpenter frog (Rana virgatipes) (CARP), *southern leopard frog (Rana utricularia) (SLF), *Fowler's toad (Bufo woodhousei fowleri) (FT), *Pine Barrens treefrog (Hyla andersoni) (PBT), *green frog (Rana clamitans melanota) (GF), and grey treefrog (Hyla versicolor) (GTF). Species marked with an asterisk are believed to be the most common Pine Barrens species (Zampella and Bunnell, 2000). However, the survey result shows the distribution of these species is not even in the surveyed sites. Grey treefrog was only heard in the abandoned DeMarco site (accumulate intensity 5), where they could find an old artificial water pool to hold non-acidic water. The Pine Barrens treefrog and spring peeper have been only heard once in the two active bogs, but they were abundant in the Pasadena site. Fowler's toad, however, was found to be very abundant from May to early June in the active site 70S (the accumulate intensity was 26.0), but was never heard in the old abandoned Pasadena site, and only once intensively heard in the DeMarco site (accumulate intensity 4.2). In terms of the microhabitats they are using, PBT and SP were only heard in the surrounding canopies; FT was only heard along the roadside in the active site 70S and does not go into the bogs, but in the DeMarco site it was heard in the abandoned bogs. Similarly, CARP, the most abundant species throughout the season in all of the sites, was found in all kinds of microhabitats in both abandoned sites, but was only heard calling in the reservoirs or surrounding ditches in the active site. GF, on the other hand, was most frequently heard within the cranberry beds of the active farms. Interestingly, the tadpoles of CARP were trapped frequently both in the ditches and in the cranberry beds. This shows that the adult CARP doesn't use the beds for breeding, but the larvae like the narrow ditches in the beds for foraging. Overall, the two abandoned sites have the highest anuran diversity (all eight species have been recorded in the DeMarco site, and 6 out of 8 have been heard in Pasadena) and density. In both active sites, although five species have been recorded, the two widely distributed Pine Barren species (Pine Barrens treefrog and spring peeper), were rarely heard.

¹ 1. Northern cricket frog (Acris crepitans crepitans) has been heard twice in August, but the call cannot be verified by visual evidence. Therefore it is not included in the result.

A quantitative comparison of the distribution of anurans in active and abandoned farms will be completed by the end of 2007. Survey results from the three active and three abandoned farms will be used to compare changes in anuran composition and density before and after abandonment. Because of anurans' restricted mobility and the differences in behavior among species, each anuran species' distribution will be compared respectively between the active and abandoned farms by two-way nested ANOVA.

3. Succession study in abandoned cranberry farms:

From April to August 2006, the water table fluctuations within five cranberry beds were monitored. They have shown significant differences between beds (ANOVA P<0.001), and multiple comparisons with Bonferroni correction shows the water table of three beds are significantly different from the other two.

The seed traps unfortunately failed to examine the wind dispersed seeds because of the extremely high wind intensity in the open farm. Only seeds with long glumes can be captured and remained on the trap. Therefore, instead seed traps, soil cores were dug this spring to study the seed dispersal and seedbank.

References:

Zampella, R.A. and J.F. Bunnell. 2000. Distribution of Anurans in Two River System of a Coastal Plain Watershed. Journal of Herpetology, 34(2): 210-221.

The Potential Impact of the Asian Isopod, Synidotea laevidorsalis (Miers 1881), on the Delaware Bay, USA

Basic Information

Title:	The Potential Impact of the Asian Isopod, Synidotea laevidorsalis (Miers 1881), on the Delaware Bay, USA	
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Publication

- Boyd, S. and D. Bushek. 2007. Rapid Ecological Assessment of a Non-Indigenous Isopod in Delaware Bay. Annual New Jersey Academy of Sciences Meeting, 2007. Kean University, Union, NJ. April 21, 2007.
- 2. Boyd, S. An Ecological Assessment of the Non-Indigenous Isopod, Synidotea laticauda, in Delaware Bay. Masters Thesis. Rutgers, The State University of New Jersey, New Brunswick, NJ. In Prep.

Project Summary

i. Problem and Research Objective

The non-indigenous isopod *Synidotea laticauda¹* was first documented in Delaware Bay in 1999 and recent data indicates extremely high seasonal abundances (Bushek and Boyd 2006). These observations suggest a potentially strong impact on the local ecosystem. To better understand the extent of any impact and the potential for further spread we need to know how *S. laticauda* is distributed in Delaware Bay and how its niche characteristics are likely to influence further establishment. These questions fall under the research goals of the NJWRRI. Specifically, they address the integrity of a New Jersey aquatic ecosystem impacted by a new exotic species. Because its arrival to the Northeast coast is relatively recent, there is a general lack of scientific knowledge about the impact this isopod may have on local ecosystems. This study is the first to address issues relating to the presence of *S. laticauda* in Delaware Bay, and was conducted during its establishment rather than after the fact.

Specific Objectives and Hypotheses

- 1. Catalogue the distribution and abundance of *S. laticauda* with respect to environmental parameters of the isopod
- 2. Determine environmental tolerances to temperature and salinity as a mechanism for identifying potential limits to its aquatic distribution
- 3. Identify potential food resources for S. laticauda in Delaware Bay
- 4. Identify potential predators of S. laticauda in Delaware Bay^2

ii. Methodology Implemented

Distribution

A presence-absence survey was conducted June through September 2006 to establish the distribution of *S. laticauda* throughout Delaware Bay and along the Atlantic coast of New Jersey. Survey sites included marinas, bridges, and beaches, as well as sites accessible only by boat, such as buoy lines and channel markers deployed by local fishermen, researchers and government agencies. Geographic coordinates along with water temperature and salinity were recorded for each site. Local topography and biota were noted and photographed when possible.

Thirty-five sites were surveyed along the New Jersey coastline of Delaware Bay from Pennsville Township (39° 38' 20 N, 75° 32' 48 W) to Douglass Park (38° 58' 05 N, 74° 57' 45

¹ During the course of this research the taxonomic classification of the species investigated was changed from *S. laevidorsalis* to *S. laticauda*

² Objective not initially identified as part of this study but was added during the course of the investigation

W). Twelve sites along the Delaware coastline were surveyed between Fort Delaware Park (39° 34' 17 N, 75° 35' 25 W) and Indian Bay (38° 34 50 N, 75 ° 05' 12 W). The Atlantic coast of New Jersey was surveyed at 23 sites between Liberty State Park (40° 43' 34 N, 74° 03' 31 W) and Cape May (38° 56' 43 N, 74° 53' 53 W). Thirty-six navigational channel markers were surveyed by boat on September 16, 2006 between Tuckerton (39° 30' 12 N, 74° 20' 36 W) and Cape May, NJ (48° 58' 15 N, 74° 51' 48 W) along a 150 km stretch of the Intracoastal Waterway. Finally, the Haskin Shellfish Research Laboratory (HSRL) monitors monthly oyster recruitment on Delaware Bay shellfish beds and technicians involved in this project reported appearances of *S. laticauda* on their sampling equipment.

Acute Exposure to Temperature and Salinity

A 48 h acute temperature-salinity challenge assessed the ability of *S. laticauda* to survive an array of temperature and salinity regimes associated with Delaware Bay. Isopods were collected from the Maurice River (39° 13' 58" N, 75° 01' 57" W) and acclimated without food for 72 h in a 10-L aerated aquarium containing room temperature ($18-23^{\circ}C$) river water (20 psu). Twenty liter batches of 5, 15, 20, 25, 30, and 35 psu water were prepared by adjusting water from the Maurice River (18 psu) with Instant Ocean® or de-ionized water and then filtering the water to 1µm. Untreated HSRL well water was used for a salinity of 0. For each salinity treatment, 200 ml of water was added to 15 Carolina culture dishes and divided between five temperature chambers set at 5, 12, 25, 30, and 35 °C. Six isopods were added to each culture dish and survival monitored for 48 h at 4 h intervals. Death was defined according to criteria modified from Kivivuori and Lahdes (1996). Specifically, isopods exhibiting no movement following three prods with a metal probe were scored as dead. Movement included any voluntary swimming, movement of antennae and perepods, or the beating of pleopods (Kensley and Schotte 1989).

Identification of Available Food Resources

Single-choice *in vitro* feeding trials were conducted at HSRL June through August 2006 to identify potential food resources being exploited by *S. laticauda* in Delaware Bay. Isopods were collected from the Maurice River (39° 13' 58" N, 75° 01' 57" W) and acclimated without food for 72 h in a 10-L aerated aquarium containing room temperature (18-23°C) artificial seawater (25 psu). Eleven commonly occurring aquatic biota were collected from the Maurice River and split among three Carolina culture dishes, each containing 200 ml of artificial seawater. Four isopods were added to two of the three cultures dishes while the third dish was used as a control. Qualitative observations were recorded periodically over 48 h and included the condition of the prey item as well as the level of isopod activity.

Predation Pressure

Gut content analysis assessed whether trophic interactions exist between *Synidotea laticauda* and eight species of fish present in Delaware Bay. Fish were collected June through August, either from a multi-species trap deployed in the Maurice and Nantuxent Rivers or were provided by New Jersey State Biologist and recreational fishermen. Fish collected from the multi-species

trap, as well as those provided by state biologist, were anesthetized in ice water before a scalpel was used to remove the stomach. Recreational fishermen provided filleted fish carcasses which allowed the easy removal of the exposed stomachs. Individual fork length and weight of each fish was recorded when possible. Stomachs were placed in labeled plastic bags and stored at - 25°C. In January 2007, stomachs were thawed overnight at room temperature and the entire contents examined under a dissecting microscope for evidence of *S. laticauda*. The distinctive concave shape of the *S. laticauda* telson was used to positively identify the presence of the isopod.

iii. Principle findings and significance

Synidotea laticauda was documented along portions of both the New Jersey and Delaware coastlines of Delaware Bay. However, they were only present in areas where the salinity was between 2 and 20 psu and were generally associated with anthropogenic structures, particularly marinas. Isopods were not observed along the Atlantic coast of New Jersey. At the present time it is unlikely that the northern range of *S. laticauda* in the bay will expand into freshwater portions of the estuary. Temperature-salinity challenges found that isopods died quickly in the freshwater treatments. However, isopods were able to survive in salinities of 30 and 35 psu. This tolerance may allow isopods to expand their range farther south into portions of the bay where higher salinities are prevalent. Temperature-salinity trials also found that *S. laticauda* were capable of surviving in water temperatures typical for Delaware Bay. Although lethargic, isopods experienced very little mortality at 5°C; however, high mortality (> 65 %) was experienced above 30°C. The normal upper temperature limit for Delaware Bay is 28°C (Sharp 1988) and appears to be close to upper limit for this isopod, but is not likely to be limiting, although isopods trapped in tidal pools and shallow waters during summer may not survive the increased temperatures these areas experience.

Several trophic interactions between *S. laticauda* and the biota of Delaware Bay were identified through this study. Single-choice feeding trials identified nine different native fauna and flora that were readily consumed and establish *S. laticauda* as an omnivore capable of exploiting multiple food resources within the Bay. Gut content analysis of fish collected from the Maurice and Nantuxent Rivers indicate that at least four predatory species may consume *S. laticauda*, although the isopod did not appear to be an important component of their diets.

References

Bushek, D and Boyd, S. 2005. The Potential Impact of the Asian Isopod, Synidotea laevidorsalis (Miers 1881), on the Delaware Bay, USA. Biological Invasions. 8: 697-702.

Kensley, B., and Schotte, M. 1989. Guide to the Marine Isopod Crustaceans of the Caribbean. Smithsonian Institution Press, Washington. pp 308.

Kivivuori, L. A. and Lahdes, E. O. 1996. How to measure the thermal death of *Daphina*? A comparison of different heat tests and effects of heat injury. Journal of Thermal Biology. 21:305-311.

Sharp, J. H. 1988. Dynamics, pp. 43-53. In: T. L. Bryant, and J. R. Rennock, eds. The Delaware Estuary: Rediscovering a Forgotten Resource. The Philadelphia Press, Inc, Burlington New Jersey.

Integrated Assessment of Economic and Water Quality Impacts of Agricultural Best Management Practices in Upper Cohansey River Watershed

Basic Information

Title:	Integrated Assessment of Economic and Water Quality Impacts of Agricultural Best Management Practices in Upper Cohansey River Watershed
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Focus Category:	Water Quality, Economics, Models
Descriptors:	
Principal Investigators:	Zeyuan Qiu, Christopher Obropta

Publication

- 1. Qiu, Z., M.T. Walter, and C. Hall. 2007. Managing Variable Source Pollution in Agricultural Watersheds. Journal of Soil and Water Conservation, 62(3): 115-122.
- 2. Qiu, Z. 2006. An Integrated Framework for Targeting Best Management Practices in an Agricultural Watershed. Journal of Soil and Water Conservation, 61(3):197 (Abstract).
- 3. Qiu, Z. 2006. An Integrated Framework for Targeting Best Management Practices in an Agricultural Watershed. The 61st Annual International Conference of Soil and Water Conservation Society, Keystone, Colorado, July 22-26, 2006. (Oral Presentation)
- 4. Qiu, Z. 2006. Identifying Critical Source Areas in Watersheds for Riparian Buffer Restoration. The 2006 Conference of the Mid-Atlantic Sections of the American Water Resources Association: Stream Restoration and Protection in the Mid-Atlantic Region, NJ School of Conservation, Montclair State University, Branchville, New Jersey, June 14-16, 2006. (Oral Presentation)

Project Summary:

Problem and Research Objectives

The lack of understanding regarding agricultural best management practices (BMP) effectiveness in improving water quality on a watershed scale is not unique to New Jersey. In the past several decades, many BMPs and land management practices have been developed and implemented to reduce water contamination risk associated with nonpoint sources such as agriculture and urban stormwater runoff. An extensive body of literature exists that describes those conservation practices aimed at protecting water quality; i.e., the chemical, physical, and biological integrity of a water body. Billions of dollars have been spent on implementing land use management and conservation practices for improving water quality. However, water quality degradation from nonpoint sources like agriculture remains a major environmental problem in many parts of the United States. Since much of this work was conducted at the plot- or field-scale, there is little documentation on the effectiveness of these practices in actually restoring water quality. Inferences drawn from plot- and field-scale studies are limited in that they cannot capture the complexities and interactions of conservation practices as applied within various locations throughout a watershed (NRC, 1999; Robertson, et al., 2004).

Research that evaluates the interactions among management practices and their biophysical setting on water quality at the watershed scale is a national priority. As the U.S. shifts heavily toward performance-based environmental policy, federal agencies have put great efforts on assessing the effects of conservation practices at watershed scales. The Conservation Effects Assessment Project (CEAP) began in 2003 as a multi-agency effort to quantify the environmental benefits of conservation practices used by private landowners participating in U.S. Department of Agriculture (USDA) conservation programs. So far the CEAP watersheds are mostly located in the big agricultural states. This research will make contribution to the National CEAP Program by assessing the water quality impacts of conservation practices in suburban settings like New Jersey.

Understanding the economic and water quality impacts of agricultural BMPs is becoming increasingly important for achieving the desired water quality standards in watersheds in suburban settings. It is generally perceived that the water pollutant load reductions from traditional point sources such as industrial and municipal wastewater treatment plants have reached their potential due to stringent regulation and technological innovation in the last three decades. Additional reduction from such point sources will incur much higher abatement costs. On the other hand, the agro-environmental policy has been adopting a "softer carrot" approach through cost-sharing and subsidies for reducing agricultural water pollution. It is also perceived that pollution reduction from agricultural sources has lower abatement costs and the additional pollution reduction that is needed to attain water quality standards in watersheds with mixed land uses in suburban settings should come primarily from agricultural sources. This research will provide essential information to evaluate the potential of achieving water quality improvement through reducing agricultural water pollution and facilitate discussions on water quality trading between point and nonpoint (such as agricultural) sources in suburban settings. The goal of this research is to provide a science-based information analysis to policy makers who want to maximize the water quality benefits while minimizing economic costs when implementing multiple conservation practices in a watershed. The supporting objectives are (1) to estimate the economic and water quality impacts of various agricultural BMPs being implemented in the Neshanic River watershed. The working hypothesis of this objective is that there is a poor understanding of the costs and water quality benefits of BMPs being implemented; and a detailed information on costs and benefits of BMPs is essential to understand the linkages between BMPs and water quality effects in a watershed scale; and (2) to evaluate the potential of controlling agricultural pollution to achieving locally defined water quality goals through optimal placement of BMPs in the watershed by integrating the results of the estimated costs and water quality benefits in the first objective is that spatial variability of natural resource conditions in a watershed has profound impacts on the water quality of conservation practices at the watershed scale.

Methodology

Literature review has been conducted on hydrological theories, agro-environmental policies, effectiveness of agricultural BMPs, and modeling to develop innovative ways of managing agricultural nonpoint source pollution. Empirical evaluation of agricultural BMPs in the Neshanic River watershed went two directions. The first is to identify the critical source areas for the placement of conservation buffers, one of the most popular agricultural BMPs by integrating hydrological modeling with geographic information systems to improve its effectiveness. The second is to apply a watershed-scale water quality simulation model Soil and Water Assessment Tool (SWAT) and economic models to evaluate the placement of conservation buffers and other BMPs in the watershed.

The study area is the 31 square miles of Neshanic River watershed in the Raritan River Basin in Hunterdon County, New Jersey. It is comprised of Walnut Brook, First, Second and Third Neshanic River, and the Neshanic River main branch immediately above the Back Brook entrance into the Neshanic River. The Neshanic River is a tributary to the South Branch of the Raritan River, which drains into the Atlantic Ocean. Based upon numerous monitoring sources, including the New Jersey Department of Environmental Protection (NJDEP) Ambient Biomonitoring Network, the NJDEP/USGS water quality monitoring network, and the Metal Recon Program, the Neshanic River and its branches are impaired for aquatic life, phosphorus, total suspended solids (TSS) and copper, and is listed in Sublist 5 of the New Jersey 2004 Integrated Water Quality Monitoring and Assessment Report. A Total Maximum Daily Load (TMDL) for fecal coliform has been approved and adopted for the Neshanic River. This TMDL requires 87% reductions in fecal coliform loads from medium/high density residential, low density/rural residential, commercial, industrial, mixed urban/other urban, forest, and agricultural lands. A TMDL for the total phosphorus in the Neshanic River is nearly completed. The watershed is also experiencing the increasing occurrences of no/low base water flow in the Neshanic River in the late summer (Reiser, 2004). Compared to other areas, the watershed is one of the

worst in terms of the overall water quality in the Raritan River Basin. The Neshanic River had either the highest concentrations of constituents or the highest frequency of not meeting water quality standards for 13 of the 17 constituents. This non-trout river has over 40% of its drainage area in agricultural land use, which is the highest percentage in the entire Raritan River Basin.

After four years of comprehensive water resource characterization and assessment in the Raritan River Basin, the Watershed Protection Unit at the New Jersey Water Supply Authority developed the Raritan River Basin Management Plan in 2003. According to the Plan, riparian buffer restoration is the number one priority for restoring the water quality in the Basin. The Raritan Watershed Agricultural Committee (RWAC) is a group of proactive agricultural producers and agency personnel in seven counties in the Raritan River Basin that addresses potential water quality impacts of agriculture. Neshanic River watershed was recognized by RWAC as one of the priority watersheds to implement the riparian buffer restoration because of its poor water quality and the high percentage of agricultural lands compared to other watersheds in the Basin. Riparian buffer restoration as a much-needed BMP on agricultural lands can be implemented through the New Jersey Conservation Reserve Enhancement Program (CREP). New Jersey CREP covers 100 percent of the implementation costs of installing riparian buffers and offers land rental payments to landowners who take their lands out of agricultural production and install riparian buffers for 15 years. Clearly identifying the critical source areas for riparian buffer restoration would significantly improve the efficiency of CREP and the water quality in the watershed.

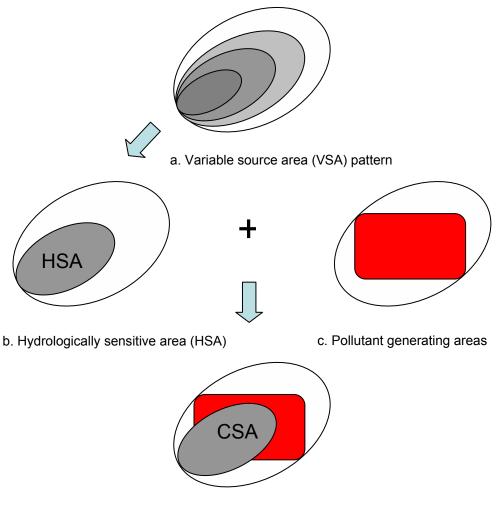
Critical source areas are the intersection of hydrologically sensitive areas and pollutant generating areas in landscapes. Identification of critical source areas is based on the concept of variable source area hydrology. Since the early 1960s, researchers have repeatedly noted saturation excess processes as a more physically realistic runoff process than Hortonian infiltration excess process. The earliest study by the U.S. Forest Service (1961) suggested that runoff was generated primarily from discrete saturated areas within forested watersheds. Other early studies refined the saturation excess runoff theory and identified inconsistencies between field observations and the Hortonian infiltration excess runoff theory (Betson, 1964; Tennessee Valley Authority, 1965; Amerman, 1965; Ragan, 1967; Hewlett and Nutter, 1970; Dunne, 1970; Dunne et al., 1975). Hewlett and Hibbert (1967) are generally credited with the term "variable source areas" (VSAs), implying the extent of saturated runoff source areas varies with a watershed's moisture state. Dunne and Black (1970a, b) are generally credited with the definitive field experiment describing VSA mechanisms, especially for watersheds where shallow, transient interflow is common. According to the VSA hydrology, runoff is generated from saturated areas in landscapes where soil saturation capacity is exceeded and is controlled by the development, expansion and contraction of these saturated areas.

The VSA hydrology concept has evolved over the past 40 years to incorporate the suite of hydrological processes leading to the development and expansion of saturated zones in the landscape. Some of the prominent locations for VSAs are along valley floors and other topographically converging areas, shallow water table areas, the lower portions of

hillsides especially where the topographic slope flattens, and places where a shallow restrictive layer underlies the soil. The source of the water saturating the landscape can be the baseflow, groundwater reservoir, or shallow, transient subsurface flow over a near-surface restrictive layer commonly called interflow. Many researchers have shown that the distribution and extent of the saturated areas are often closely related to the pattern of stream channels, i.e., the locations where groundwater re-emerges on the surface (e.g., Dunne and Black, 1970a, b; Beven and Kirkby, 1979). Recently, shallow interflow has been shown to be an important control on VSA dynamics, especially in the northeastern U.S. (Moore and Thompson, 1996; Frankenberger et al., 1999; Ogden and Watts, 2000; Srinivasan et al., 2002). Besides the humid northeastern U.S., the VSA hydrological process is acknowledged in Canada (Dickinson et al., 1987 and 1990) and other parts of the U.S., including the Midwest claypan soil region (Schmitt, 1999), the mountainous West (e.g., Idaho - Boll et al., 1998; Brooks et al., 2000), and the South (e.g., Florida - Tatiana et al., 2003).

The pollutant generating areas are the areas in landscapes that have been actively used by people for production and consumption, such as agricultural production, residential development, and industrial and commercial uses. The hydrologically sensitive areas are the areas that actively contribute to generation of runoff and water pollutants in landscapes.

Figure 1: the relationships among VSAs, HSAs and CSAs



d. Critical source area (CSA)

Figure 1 presents a procedure that identifies the critical source areas for riparian buffer restoration in a watershed with three steps: (1) identifying the VSA patterns in the watershed using a modeling technique; (2) delineating the hydrologically sensitive areas (HSA) from the identified VSA patterns based on a typical weather condition; and (3) identifying the critical source areas (CSA) of a watershed by overlapping the identified HSA and critical land use layers.

Various models can be used to identify the VSA patterns in a watershed. In this application, a modified topographic index model will be used to identify VSA patterns. As demonstrated by Agnew et al. (2005), the topographic index model can simulate the VSA patterns as the SMR does in the Catskill mountain watersheds. A watershed can be divided into small 10-meter or 30-meter grids. A topographic index can be calculated for each of the grids. The topographic index measures the relative likelihood of being

saturated for each grid during a storm. In general, the higher the index, the more likely the grid is saturated in a storm. Specifically, the topographic index is defined as

(1)
$$\lambda = \ln\left(\frac{\alpha}{\tan(\beta)K_sD}\right)$$

where λ is the derived topographic index, α is the upslope contributing area per unit contour length in meters, $\tan(\beta)$ is the local surface topographic slope, *Ks* is the mean saturated hydraulic conductivity of the soil in meters per day, and *D* is the soil depth in meters. α and $\tan(\beta)$ can be derived from a digital elevation model, and *Ks* and *D* can be found in the USDA Natural Resource Conservation Service (NRCS) soil survey data.

Incorporating VSA hydrology into water quality management implies that soil and water conservation efforts should be concentrated on these small but hydrologically sensitive parts of a watershed. Given natural conditions, such as topography, soil, land use/cover and hydrology in landscapes, a series of VSA patterns corresponding to dynamic rainfall events will be identified in the watershed (Qiu, 2003; and Gérard-Marchant et al., 2003). The identified VSA patterns could vary from 1 percent to over 50 percent of the watershed. However, water resource managers usually prefer well-defined, static HSAs for targeting water conservation practices such as conservation buffers. After identifying the VSA patterns in the watershed, a set of criteria can be developed to delineate HSAs from identified VSAs. For example, a typical rainfall event can be used to delineate the HSAs. Since the modified topographic index model is used to simulate the VSA patterns, the calculated topographic index is used to delineate HSAs. For example, a grid is considered to be a part of the HSAs when the topographic index of the grid is greater than a reference number.

Walter et al. (2000) defined CSAs based on HSAs in an agricultural setting. For an agricultural field in the Catskill Mountain region of New York State in which dairy manure is spread, CSAs were defined as the intersection of the HSAs and the manure spread areas in the field. The idea of identifying CSAs can be extended to other settings. In general, CSAs are the intersections of the HSAs and the pollutant generating areas in watersheds. The pollutant generating areas are the areas in landscapes that have been actively used by people for production and consumption, such as agriculture, residential development, and industrial and commercial uses. CSAs can be identified by overlaying the identified HSAs in Step 2 with existing land use and zoning maps. The identified critical areas provide the basis for targeting the conservation buffers.

Three spatial datasets were used to delineate the critical source areas in the watershed: a digital elevation model (DEM), a soil data and a recent land use/cover. The 10-meter resolution DEM was developed by the NJDEP and was downloaded from its website (<u>http://www.state.nj.us/dep/gis/</u>). The Natural Resources Conservation Service (NRCS) Soil Survey Geographic (SSURGO) soil data was used in this application. Since the study area is entirely located within the Hunterdon County, the digital SSURGO soil databases for Hunterdon County was downloaded from the NRCS Soil Data Mart website (<u>http://soildatamart.nrcs.usda.gov/</u>). The land use/cover data, compiled from the aerial photographs taken in the spring of 2002, were downloaded from NJDEP website.

The DEM and SSURGO soil data are used to derive the topographic index for identifying the VSAs pattern in the watershed. The data are processed using ArcGIS 9.1 in three steps to obtain the VSAs pattern. First, the DEM was processed using an open source

ArcGIS extension TauDEM (Torboton, 2005) to obtain a wetness index grid, $\ln(\frac{\alpha}{\tan(\beta)})$,

where the variables were defined as above. Second, the soil depth (D) and the mean saturated hydraulic conductivity (Ks) were extracted for each soil type from the soil data. Their product (Ks*D) was calculated and linked to the spatial soil boundary layer. The soil layer was converted into a grid layer based on the value of KsD. When extracting the D and Ks, the physical properties of each soil type in the soil database were evaluated to determine whether there was a restrictive layer or bedrock in the soil. For example, a significant drop in Ks could imply the existence of a restrictive layer. If there is a restrictive layer, the soil depth to the restrictive layer was extracted and the mean of the saturated hydraulic conductivities in different soil layers above the restrictive layer was calculated. Third, the Raster Calculator in ArcGIS 9.1 was used to manipulate the two raster layers obtained in the first two steps and to calculate the topographic index based on equation (1). The higher the index, the higher likelihood the grid gets saturated during a storm.

A reference level of the topographic index is selected to classify the HSAs in the watershed from the VSAs pattern. Not all areas within HSAs are subject to conservation buffer restoration. In general, restoration is not a concern for HSAs in forests, already established wetlands, and riparian buffers. Buffer restoration should focus on the parts of the HSAs where land use activities, such as agricultural production and urban development, have the potential to degrade stream water quality. Identified HSAs were overlapped with the 2002 land use/cover to identify the critical source areas for riparian buffer restoration in the watershed. Specifically, HSAs were defined as areas where the topographic index is greater than 10. CSAs are those HSAs for which the land use types are agriculture, barren land and urban. All data were processed and analyzed using ArcGIS 9.1.

Besides the conservation buffers, we are also investigating the other types of BMPs implemented in the watershed such nutrient management, pest management, and tillage management. Due to the restriction in the Privacy Act and Freedom of Information Act, the Natural Resource Conservation Service New Jersey Office did not release any information on BMPs being implemented in the watershed. I have been interviewing farmers, NRCS and the Rutgers Cooperative Extension personnel and conducting field visits and interviews with farmers.

Principal Findings and Significance

Agricultural runoff is a major contaminant source threatening water quality in streams, lakes, and public drinking water reservoirs. Agricultural pollution control practices and programs are traditionally based on the assumption that overland flow is only generated when rainfall intensities exceed soil infiltration capacity. Our research review challenges

this assumption, noting that overland flow associated with agricultural pollutant transport is often physically consistent with the variable source area (VSA) hydrology concept, for which overland flow is generated in parts of the landscape where the soil saturates to the surface. Incorporation of VSA hydrology into watershed management practices reconceptualizes nonpoint source pollution as "variable source pollution," in which pollution control efforts can be focused on relatively small hydrologically-sensitive areas, recognizing that the extent of these areas will vary throughout the year. There are substantial technical, economic, social, and institutional barriers to implementing strategies for managing variable source pollution partially because of massive institutional inertia of existing agroenvironmental policies, programs and best management practices. Substantial research is needed to quantify the water quality risks associated with variable source pollution, expand the capacity to identify the critical management areas, and eliminate the institutional barriers for managing variable source pollution in agricultural watersheds.

Following the procedure laid out in Figure 1, the topographic index, hydrologically sensitive areas and critical source areas were derived. The resulting topographic indices in the watershed range from 2 to 25. The higher topographic indices imply a higher likelihood that runoff is generated during a storm event. Table 1 presents the area distribution of the topographic indices in the watershed. The majority of the watershed has topographic indices of 6, 7, 8, 9, and 10. The area corresponding to each index is over 10 percent of the watershed. Only 4.6 percent of the watershed has topographic indices greater than 12. Figure 2 presents the spatial distribution of the topographic index, i.e. the VSA patterns, in the watershed. Several observations can be made based on Figure 2. First, the majority of the grids with the highest topographic indices (above 19 as indicated by the reddish colors) tend to be located along the existing stream network. This is not a surprise because the streams and their riparian areas are VSAs. Second, some of the grids with the highest topographic indices are distributed outside of the existing streams and their riparian areas. Third, a majority of the grids with next highest indices (between 12 and 18 as indicated by the yellowish colors) are outside of the existing streams and riparian areas, in the upland contributing areas. The spatial distribution of topographic indices indicates that conservation buffers for improving water quality should be located beyond the riparian areas of the existing streams.

Topographic Index	Number of Grids	Area	Distribution	
		(hectares)	(%)	
2 3	106	1.06	0.01	
	1,456	14.56	0.18	
4	10,555	105.55	1.32	
5	40,025	400.25	5.00	
6	86,417	864.17	10.78	
7	144,738	1,447.38	18.06	
8	161,046	1,610.46	20.10	
9	141,879	1,418.79	17.71	
10	100,497	1,004.97	12.54	
11	52,787	527.87	6.59	
12	24,891	248.91	3.11	
13	12,476	124.76	1.56	
14	7,191	71.91	0.90	
15	4,593	45.93	0.57	
16	3,196	31.96	0.40	
17	2,300	23.00	0.29	
18	1,800	18.00	0.22	
19	1,771	17.71	0.22	
20	1,528	15.28	0.19	
21	958	9.58	0.12	
22	509	5.09	0.06	
23	395	3.95	0.05	
24	153	1.53	0.02	
25	8	0.08	0.00	
Total	801,275	8,013	100	

Table 1: The distribution of area in Neshanic River Watershed according to topographic index

The HSA is determined by evaluating the VSA patterns using different reference numbers in topographic index. It was decided that the grids with topographic indices greater than 10 were considered to be HSAs. A separate GIS layer on HSAs was created by selecting the grids with topographic indices greater than 10 using ArcGIS 9.1. The resulting HSAs cover around 1,146 hectares and make up 14.3 percent of the watershed. CSAs were identified by overlaying the HSAs with topographic indices greater than 10 with the 2002 land use/cover layer for the watershed developed from aerial photographs. There are six broad categories of land uses in the watershed: agriculture; urban; forest; barren; wetlands; and water. The pollutant generating areas are the areas with agriculture, urban and barren land uses.

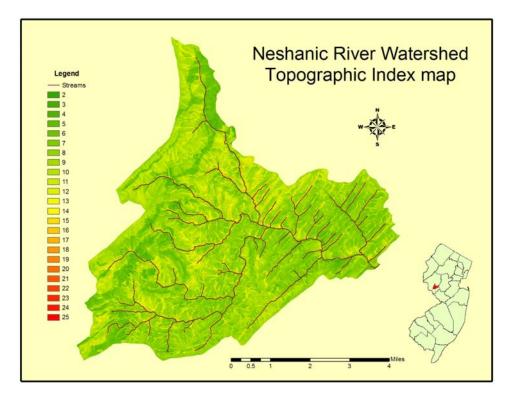


Figure 2. Derived topographic index map in Neshanic River Watershed

Figure 3. Derived hydrologically sensitive areas and critical source areas in Neshanic River Watershed

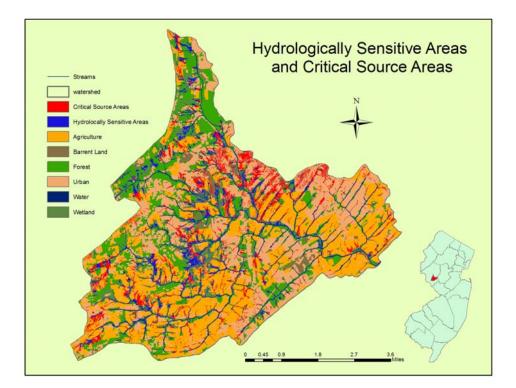


Figure 3 presents the location of the identified CSAs as indicated by the red areas. The total area of the identified CSAs is 654 hectares. As shown in Figure 3, the CSAs are scattered around the watershed. Many of them are located in the upland areas and are not necessarily in close proximity of streams in the watershed. This occurs because many parts of the riparian areas of streams are usually covered by dense forest and wetlands, as shown in Figure 3 and as observed in many other watersheds.

The locations of the CSAs have several implications. First, conservation programs should encourage landowners to install and construct conservation buffers in CSAs. For example, CREP can provide higher incentives to farmers who enroll their lands in CSAs located in agricultural areas. In suburban settings, various land use planning tools and ordinances can be adopted to protect and preserve CSAs from development. For example, conservation easements, which preserve open space, can be targeted to CSAs. Second, conventional riparian preservation as implemented in New Jersey is not efficient and effective in protecting the identified CSAs because many of them are located in upland areas.

The science-based GIS procedure discussed here is a powerful screening tool for identifying potential sites for buffer restoration and construction. Contrary to the conventional wisdom that states buffers should always be in the riparian areas in the existing stream corridors, the CSA map shows that many upland areas should be also targeted for buffer restoration because of their active role in generating runoff. The procedure described here is applicable to both small and large watersheds and can be further extended to rank the identified potential sites based on conservation priorities, data and funding availability.

Although placing conservation buffers within CSAs has the potential to improve the efficiency and effectiveness of the conservation buffer programs, it is challenging to achieve such placement under the existing buffer programs for several reasons. First, the proposed approach is based on a targeting criterion, whereas most existing buffer programs result in conservation buffer placement that reflects the voluntary nature of the program, i.e., buffers are placed where landowners voluntarily agree to place them. Second, since priority is given to placing conservation buffers in CSAs, the approach raises equity concerns among the stakeholders, i.e., priority for buffer placement is given to stakeholders who own land in CSAs. Third, the proposed approach could require constructing conservation buffers in only parts of a field, which can create monitoring and implementation difficulties. In addition, there are limited technical guidelines available for a partial-field buffer approach. Farmers may resist this approach if it adversely affects the economies of scale of farming operations. Fourth, local conservation practices are usually administered by different agencies, which can pose substantial barriers to acquiring the resources and coordinating the efforts needed to implement a CSA-based buffer program.

Empirical evaluation of SWAT modeling in the watershed has been slowed down due to the lack of cooperation from the NRCS New Jersey Office. The SWAT has been compiled and evaluated in the watershed. We are still in the process of finalizing the farming practices and alternative BMPs in watershed by working with farmers, NRCS field offices and agrochemical businesses. By plugging the information into the model, we will calibrate the model and evaluate the placement strategies for BMPs to achieve the watershed management goals.

Cited Literature

- Agnew, L.J., M.T. Walter, A. Lembo, P. Gérard-Marchant, T.S. Steenhuis. 2006. Identifying hydrologically sensitive areas: Bridging science and application. J. Envir. Mgt. 78: 64-76.
- Amerman, C.R. 1965. Use of unit-source watershed data for runoff prediction. *Water Resour. Res.* 1(4): 499-508.
- Arnold, J. G., J.R. Williams, R. Srinivasan, K.W. King, R.H. Griggs. *SWAT: Soil and Water Assessment Tool*. Temple, Texas: USDA Agricultural Research Service, 1994.
- Arnold, J.G., J.D. Atwood, V.W. Benson, R. Srinivasan and J.R. Williams. 1998. Potential Environmental and Economic Impacts of Implementing National Conservation Buffer Initiative Sedimentation Control Measures. USDA, NRCS, Resource Assessments Division Working Paper, Temple, TX.
- Betson, R.P. 1964. What is Watershed Runoff? *Journal of Geophysical Research* 69(8):1541-1552.
- Beven K.J. and M.J. Kirkby. 1979. A physically based variable contributing area model of basin hydrology. *Hydrol. Sci. Bull.* 24(1): 43-69.
- Boll, J., C.O. Stockle, S.K. Young, E.S. Brooks, J.E. Hammel, C.R. Campbell, and P.A. McDaniel. 1998. Progress toward development of a GIS based water quality management tool for small rural watersheds: modification and application of a distributed model. ASAE presentation paper. ASAE Annual International Meeting. July 12-16, 1998. Disney's Coronado Springs Resort, Orlando FL. Paper 982230. pp.20.
- Brooks, E.S., P.A. McDaniel, and J. Boll. 2000. Hydrologic modeling in watersheds of the eastern Palouse: Estimation of subsurface flow contributions. Presented at the 2000 PNW-ASAE Regional Meeting. Water, Energy, and the Environment: Critical Agricultural and Biological Engineering Challenges in the 21st Century sponsored by ASEA and CSAE. Sept 21-23, Richland WA. Paper 2000-10. pp. 11
- Dickinson, W.T., R.P. Rudra & G.J. Wall. 1987. Identification of soil erosion and fluvial sediment processes. Hydrological Processes 1: 11-124.
- Dickinson, W.T., R.P. Rudra & G.J. Wall. 1990. Targeting remedial measures to control non-point source pollution. Am Wat. Res. Bull. 26(3): 499-507.
- Dunne, T. 1970. *Runoff production in humid areas*. U.S. Department of Agriculture Publication ARS-41-160. pp. 108.
- Dunne, T. and R.D. Black. 1970a. An Experimental Investigation of Runoff Production in Permeable Soils. Water Resource Research 6(2):179-191.
- Dunne, T. and R.D. Black. 1970b. Partial Area Contributions to Storm Runoff in a Small New England Watershed. Water Resource Research 6(5):1296-1311.
- Dunne, T., T.R. Moore, and C.H. Taylor. 1975. Recognition and prediction of runoff producing zones in humid regions. *Hydrol. Sci. Bull.* 20(3): 305-327.

- Frankenberger, J.R., E.S. Brooks, M.T. Walter, M.F. Walter, T.S. Steenhuis. 1999. A GIS-based Variable Source Area Hydrology Model. Hydrological Processes 13:805-822.
- Gérard-Marchant, P., W.D. Hively and T. Steenhuis. 2003. Distributed modeling of total dissolved phosphorus loading on a small farm watershed. In: Pfeffer, M.J., D.J. Van Abs, and K.N. Brooks (Editors), Watershed Management for Water Supply Systems. AWRA's 2003 International Congress. American Water Resources Association, Middleburg, Virginia, TPS-03-2, CD-ROM.
- Hewlett, J.D. and Hibbert, A.R. 1967. Factors affecting the response of small watersheds to precipitation in humid regions. *In* W.E. Sopper and H.W. Lull (eds.) *Forest Hydrology*. Pergamon Press, Oxford. pp. 275-290.
- Hewlett, J.D. and Troendle, C.A. 1975. Non-point and Diffused Water Sources: A Variable Sources Area Problem. Pages 21-46 in the Proceedings of the Symposium on Watershed Management, American Society of Civil Engineers.
- Hewlett, J.D. and W.L. Nutter. 1970. The varying source area of streamflow from upland basins. Proc. of the Symposium on Interdisciplinary Aspects of Watershed Management. held in Bozeman, MT. August 3-6, 1970. pp. 65-83. ASCE. New York.

Moore R.D. and J.C. Thompson. 1996. Are water table variations in a shallow forest soil consistent with the TOPMODEL concept? *Water Resour. Res.* 32 (3): 663-669.

- National Research Council (NRC). 1999. New Strategies for America's Watersheds. Washington, D.C.: National Academy Press.
- Ogden F.L. and B.A. Watts BA. 2000. Saturated area formation on nonconvergent hillslope topography with shallow soils: A numerical investigation. *Water Resour. Res.* 36(7): 1795-1804.
- Qiu, Z. 2003. A VSA-based strategy for placing conservation buffers in agricultural watersheds. Environmental Management 32(3): 299-311.
- Ragan, R.M. 1967. An experimental investigation of partial area contribution. Int. Ass. Sci. Hydrol. Proc. Berne Symposium.
- Reiser, R.G. 2004. Evaluation of Streamflow, Water Quality and Permitted and nonpermitted Loads and Yields in the Raritan River Basin, New Jersey, Water Years 1991-98. Water-Resources Investigations Report 03-4207, U.S. Geological Survey, West Trenton, New Jersey.
- Robertson, G.P., J.C. Broome, E.A. Chornesky, J.R. Frankenberger, P. Johnson, M. Lippson, J.A. Miranowski, E.D. Ownes, D. Pimentel, and L.A. Thrupp. 2004. Rethinking the vision for environmental research in US agriculture. BioScience. 54(1): 61-65.
- Schmitt, S.J. 1999. *Application of a flow source mixing model and remote sensing to the hydrology and water quality of two small watersheds in Northern Missouri*. M.S. Thesis. The School of Natural Resources, University of Missouri, Columbia, MO.
- Srinivasan M.S., W.J. Gburek, and J.M. Hamlett. 2002. Dynamics of stormflow generation - A hillslope-scale field study in east-central Pennsylvania, USA. *Hydrol.Proc.* 16(3): 649-665.
- Tatiana H., M. Nachabe, M. Ross, and J. Obeysekera. 2003. Modeling runoff from variable source in humid, shallow water table environments. *Journal of the American Water Resources Association* 39(1):75-85.

- Tennessee Valley Authority. 1965. Area-stream factor correlation, a pilot study in the Elk River Basin. International Association of Scientific Hydrology Bulletin 10(2):22-37.
- Torboton, D.G. 2005. Terrain Analysis Using Digital Elevation Models (TauDEM). Accessible at <u>http://hydrology.neng.usu.edu/taudem/</u>.
- U.S. Forest Service. 1961. *Some ideas about storm runoff and baseflow*. Annual Report. Southeastern Forest Experiment Station. pp. 61-66.
- Walter, M.T., M.F. Walter, E.S. Brooks, T.S. Steenhuis, J. Boll, and K. 2000. Weiler. Hydrologically sensitive areas: variable source area hydrology implications for water quality risk assessment. Journal of Soil and Water Conservation 55(3):277-284.

Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands

Basic Information

Title:	Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands
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End Date:	2/28/2007
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Congressional District:	6th
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Focus Category:	Groundwater, Methods, Water Quality
Descriptors:	None
Principal Investigators:	DeBonne N. Wishart, Lee D. Slater

Publication

- 1. Wishart, D.N., L.D. Slater, and A.E. Gates. 2006. Self potential improves characterization of hydraulically-active fractures from azimuthal geoelectrical measurements. Geophysics Research Letters, 33: L17314, doi:1029/2006GL027092.
- Wishart, D. N. and L. D. Slater. 2007. Advancements in Fracture anisotropy characterization of the New Jersey Highlands bedrock using Azimuthal Geoelectric Methods. American Geophysical Union, Spring Meeting 2007, Acapulco, Mexico, May 22-25, 2007 (Oral presentation). Eos. Trans. AGU, 88(23), Jt. Assem. Suppl., Abstract NS53A-07.
- 3. Wishart, D. N., L. D. Slater, and A. E. Gates. 2006. Azimuthal geoelectric characterization of fracture flow in the New Jersey Highlands bedrock. Geological Society of America 2006 Philadelphia Annual Meeting, October 22 25, 2006 (Oral presentation). GSA Abstracts with Programs, 38(7):26.
- 4. Wishart, D. N. and L. D. Slater. 2006. Hydraulic and electric anisotropy characterization of the New Jersey Highlands fractured bedrock in: Environmental Geology of the Highlands, Field Guide and Proceedings, S. Macaoay and W. Montgomery (Eds). Geological Association of New Jersey, XXIII Annual Conference and Field Trip, October 13 -14, 2006, Ramapo College, New Jersey. (Oral presentation)
- 5. Wishart, D. N. and L. D. Slater. 2006. Geoelectric characterization of fracture flow in the North and Central New Jersey Highlands bedrock. Pennsylvania Water Resources Symposium, Camp Hill, Pennsylvania, October 11, 2006.
- Wishart, D. N. and L. D. Slater. 2006. Geoelectric characterization of fracture flow in the New Jersey Highlands bedrock. 18th Annual Electromagnetic Induction (EMI) Workshop, University of Barcelona, El Vendrell, Spain, September 17 23, 2006. (Poster presentation)
- Slater, L. D. and D. N. Wishart. 2006. Geoelectric characterization of hydraulic anisotropy in fractured rock aquifer model: the advantages of natural' (self) potential over induced' electric potentials. Society of Exploration Geophysicists (SEG) Hydrogeophysics Workshop, Vancouver, British Columbia, July 31August 2, 2006.
- 8. Wishart, D., L. D. Slater, and A. G. Bolden. 2005. An integrated geoelectric assessment of fracture and anisotropy characterization of the North New Jersey Highlands bedrock. American Geophysical Union Fall 2005 Meeting, San Francisco, California, December 59, 2005. (Poster presentation)
- 9. Wishart, D. N. Anisotropy Characterization of fracture-dominated media using azimuthal geoelectric methods. Ph.D. Dissertation. Rutgers, The State University of New Jersey, Newark, NJ. 250 p. (In prep)

Problem Statement

Global population growth and increasing demand for new, viable groundwater resources has necessitated the exploration and development of fractured-rock aquifers. Groundwater pollution from paint sludge and gas stations impacts Ringwood, one of the communities in the north New Jersey Highlands. This poses a serious threat to the region's most important watershed. State authorities fear the contamination will work its way into the drinking water supply of 2.5 million people in Bergen, Passaic, and Essex counties.¹ The Federal Government aims to preserve environmentally sensitive areas of the New Jersey Highlands² that include highly fractured rocks. The recently enacted New Jersey Highlands Water Protection and Planning Act (2004) aimed at preventing urban sprawl in the North Jersey Highlands is also in accordance with the New Jersey Department of Environmental Protection (NJDEP) water quality initiative to protect water resources in these areas.^{3,4} Fractures serving some communities as the principal sources of clean groundwater also act as hydraulic conductors that form potential pathways for transport of contaminants in the groundwater system or, if mineralized, may act as barriers that prevent fluid flow. Groundwater flow through a fracture network is strongly influenced by the geometry of fractures, thus impacting the transport of contaminants and the design of groundwater remediation efforts. The potential exists for contaminants to migrate at high velocities in these fractures. Information on the presence, extent, intensity, and direction of fracturing is vital to the design of groundwater remediation strategies. Importantly, increasing our understanding of the properties influencing groundwater flow through fractured-rock aguifers has great implications for our world today and in the future. Geophysical techniques applied to fracture characterization and fluid flow analysis may be used to locate, identify, and predict the behavior of hydraulicallysignificant fractures in the subsurface.

Geophysical methods provide rapid, helpful, and cost-effective techniques that are increasingly used to non-invasively investigate water resources and water quality.^{11, 12, 16, 18, 19} Azimuthal electrical measurements have aided in the hydrogeologic characterization of fractured rock aquifers for over three decades.^{6, 20} Electrical current and groundwater are both channeled through fractures in rock (the rock itself is electrically insulating and impermeable to flow of water) such that it is assumed that the principal direction of groundwater flow may be inferred from the measured electrical anisotropy under favorable conditions.²³ The direction of maximum apparent resistivity measured with collinear azimuthal resistivity arrays is parallel to the principal fracture strike orientation. ^{14, 20, 21, 22} Unfortunately, the resistivity measurement is not a unique proxy measure of a water bearing fracture as other features, particularly clay minerals, are also electrically conductive.^{7, 17} The method therefore can fail when geological features other than fractures cause the subsurface to exhibit anisotropy and/or heterogeneity.

Project Research Objectives

This project initiates hydrogeophysical research in the New Jersey Highlands directed towards improving water resources management and reducing aquifer vulnerability in the region. Rather than relying solely on traditional collinear (symmetric) azimuthal resistivity surveys alone to characterize fracture anisotropy as was done in previous investigations, asymmetric azimuthal arrays of ASP and ARS measurements are coupled with hydrologic measurements to characterize fractures at the laboratory and extended to the field scale. Two-thirds of the research completed has allows us to (1) improve the effectiveness of electrical geophysical methods in the hydrogeologic characterization of fractured bedrock aquifers, (2) devise a method to delineate hydraulically-active fractures, (3) extend bench-scale laboratory research to the field sites, and (4) apply methods to improve understanding of fracture geometry in the north New Jersey Highlands

(NJH). The complex fracture geometry in the bedrock of the NJH region encourages the application of such integrated geophysical methods that are sensitive to hydraulic anisotropy, the direction of groundwater flow, and heterogeneity. Interestingly, the program of research investigates how integrated geoelectric measurements can be used to distinguish hydraulicallyconductive fractures and to infer direction (and possibly rates) of groundwater flow based on the electrokinetic phenomena associated with "streaming' or self potential (SP), illustrated in Figure 1. The third and final experiment for the completion of the project will involve the use of electric geophysical methods used in earlier experiments to characterize fractures created in a clay formation by the Pneumatic Fracturing Technology® (an engineering application) that serves two principal functions: (1) to enhance fluid flow and (2) reduce transport limitations that are inherent at many remediation sites. The Pneumatic Fracturing Technology® patented in 1992 (Schuring, 1992) has emerged as one of the most cost effective methods for enhanced remediation of contaminated groundwater and soils over the last decade. The objective of this study is to investigate the relationship between fracture propagation pressure and the simultaneous injection of a liquid by capitalizing on the *in situ* electrokinetics to increase the capability to detect the advance of injectate/contaminant through hydraulically-conductive fractures.

A successful demonstration of the concepts outlined here to a real-world problem (water resources and water quality in the NJ Highlands) will pave the way for submission of a research proposal to the Hydrologic Sciences Division of the National Science Foundation. The proceeds of the New Jersey Water Resources Research Institute (NJWRRI) have provided a remarkable opportunity to collect significant data to justify the NSF proposal. There is ample scope to expand this work into an NSF proposal as the next logical step is to model and interpret the integrated geophysical signals in terms of the physical and chemical characteristics of the fractures (aperture width; fracture surface chemistry; hydraulic gradient; flow velocity, etc.).

METHODOLOGY

Electric geophysical investigations were undertaken to characterize hydraulic and electric anisotropy in the laboratory on (1) a fracture block model and (2) pneumatic-fractured compressed clay sediments, and (3) above fractured crystalline bedrock at field sites throughout the north New Jersey Highlands Province. We examined the potential for geophysical characterization of fractured rock anisotropy by combining asymmetric configurations of azimuthal self potential (ASP) and azimuthal resistivity surveys (ARS).

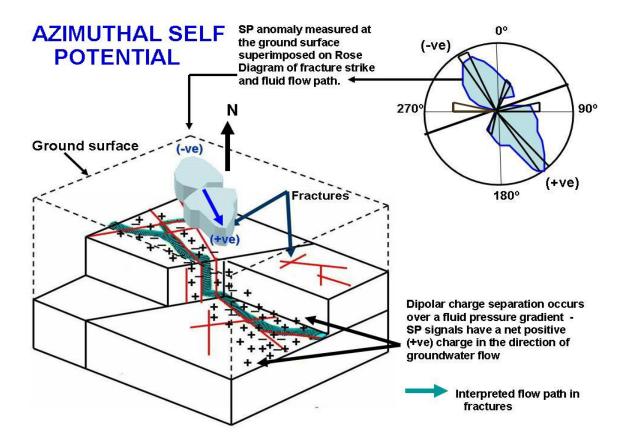
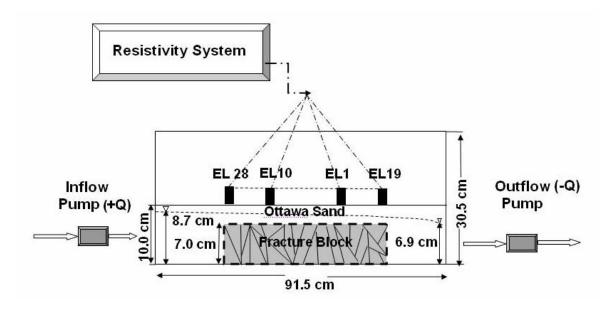


Figure 1. Schematic of the streaming potentials (electrokinetic effect) during flow along interconnected (dense) fractures over a hydraulic-pressure gradient in the bedrock.

Laboratory Investigations

Fractured Aquifer System (FAS)

ASP and ARS measurements were performed on a Plexiglas® fracture block model (50.0 cm long x 39.0 cm wide) cemented to the base of a sand-filled rectangular glass tank 91.5 cm x 61.0 cm x 30.5 cm, shown in Figures 2(a) - (b). The fracture block is a replica of the Wisconsin Niagaran Dolomite Formation fracture study.⁹ The fracture block is considered an anisotropic medium due to the preferential alignment of fractures of varying lengths and widths along three azimuths. In order to establish a uniform surface with good electrical contact, the FAS was filled with Ottawa Sand to a level 3 cm above the block (i.e. 10 cm deep in the surrounding area). The tank was then saturated with a 0.01 M NaCl electrolytic solution. A steady-state flow through the FAS was established using variable flow pumps connected to the inflow and outflow chamber via a single tube at each end of the glass tank (Figure 2). Azimuthal self potential and azimuthal resistivity measurements were made using asymmetric arrays so that anisotropy and heterogeneity could be distinguished.⁶ A mobile asymmetric dipole method was used to acquire ASP measurements with two custom-made non-polarizable PbCl-PbCl₂ miniature electrodes⁶ constructed in our laboratory were kept at a fixed distance from each other and rotated simultaneously at 20° degree segments to record electric potential (φ) as a function of azimuth. Electrodes were connected to a precision multimeter (input impedance >10 MOhm). SP values were recorded for no-flow conditions and at five flow rates: O = 0.50 mL/min, 0.65 mL/min, 0.80mL/min, 1.20 mL/min, and 1.40 mL/min.



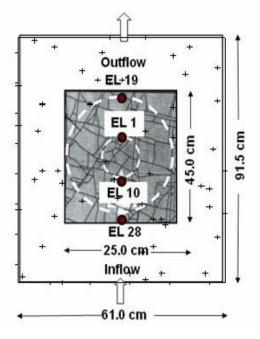


FIGURE 2(a): Schematic side view of the experimental tank holding the FAS and a fracture block which is a replica of the Wisconsin Niagaran Dolomite Formation fracture study⁹ (1985) (EL defines electrode) and (b) Plan view with black crosses indicating the locations where hydraulic head was measured at flow rate of 1.40 ml/min. White circles indicate circumferences of inner and outer electrode rings making up asymmetric azimuthal self potential and azimuthal resistivity arrays.

Pneumatic-Fractured Aquifer System (PFAS)

The Pneumatically Fractured Aquifer System (PFAS) consists of a 1.0 m x 1.0 m x 1.0 m clay-filled, square, bullet-resistant glass tank, illustrated in Figure 3. The tank is being packed with clay and compressed to a level 0.9 m and sealed by 0.1 m thick layer of bentonite. A 3.0 inch diameter clear Lexan® tube inserted in the center of the tank and connected to a sealable portal in the base of the tank facilitates optical imaging of the pneumatic-induced fractures propagated in the formation. Compressed nitrogen (N_2) gas is to be supplied from two cylinders with a flow rate of 5 psi and injected into the formation through two 0.50 inch diameter Schedule 40 PVC tubes, each attached to nozzles situated to the depth of the anticipated fracture interval at 0.25 m (indicated by dashed line in Figure 3). Both injector tubes are positioned at 71.0 cm diameter from the optical imaging port along a diagonal length of the tank. The parameters associated with fracture propagation and deformation (fracture initiation pressure and maintenance pressures) will be measured and recorded digitally. Eight electronic biaxial tiltmeters will be placed on the soil surface to (1) assure intimate contact with the tamped ground surface, (2) sense the surface deformation caused by fracturing (heave), and (3) measure change in angular deformation with changes in ground surface movements (i.e. heave or differential tilt) during the injection and history of fracture propagation. Any digital tilt values recorded during injection will be curvefitted to generate the deformation surface using a computer program, and the deformation surface is converted to a contour plot of ground surface heave. Azimuthal self potential (ASP) and azimuthal resistivity. (ARS) measurements will be acquired for fracture characterization using miniature electrodes. Self potential sampling and electrokinetic (EKE) information will be downloaded every 0.5 seconds during injection using a data logger connected to a common electronic network (controlled by laptop). Detailed structural analyses will be conducted by

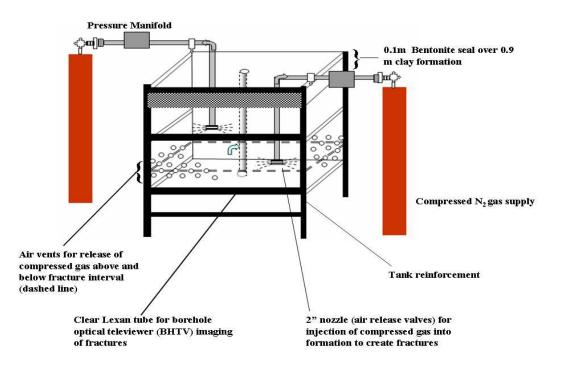


Figure 3. Schematic of experimental tank facility and set up of pneumatic fracturing of the clay formation using the injection of compressed nitrogen gas.

optical imaging (360°) of the pneumatic fractures from a centrally located borehole using a borehole Televiewer (BHV) and a physical density characterization. This final experiment is set to be performed on June 25, 2007 and the results submitted to a peer review journal (Engineering Geophysics) for publication.

Field Investigations

Azimuthal asymmetric arrays of SP measurements were employed to delineate hydraulic (flow) anisotropy at a total of 16 field sites located in the New Jersey Highlands. We examined the potential for geophysical characterization of fractured rock anisotropy by combining asymmetric configurations of azimuthal self potential (ASP) and azimuthal resistivity surveys (ARS), as previously demonstrated in the laboratory, at the field sites in the New Jersey Highlands (NJH) Province. Detailed, site-specific structural analyses were conducted and extrapolated to outcrops exposed on or near the target area at four of the sixteen field sites. A mobile dipole method was used to acquire ASP measurements with two custom-made, nonpolarizable PbCl-PbCl₂ electrodes¹³ kept at a fixed distance from each other and rotated simultaneously at 20° steps through 360° to record electric potential (φ) as a function of azimuth. The radius of the electrode ring used in the site surveys was 21 m. Electrodes were connected to a precision multimeter (input impedance >10 MOhm). Additional processing of ASP measurements involved the transformation of electric potential (SP) signals (φ) with variation in azimuth (a 'time' series) into a frequency domain [the SP signal is a periodic function with a discrete spectrum]. The frequency is the inverse of the signal period defined by the number of degrees of array rotation required to repeat a waveform. The time to frequency conversion of the periodic functions contained in data-transformed peaks of 'odd' and 'even' harmonics were used to derive f(t)-the Discrete Fourier Transform (DFT) of the SP signals using a *Fourier* series representation. The characterization of 'fluid flow' as anisotropic or heterogeneous was quantified by calculating an O/E ratio (odd to even harmonics) or K value for comparison of the magnitudes of the odd and even harmonics of SP spectra for each dataset.

PRINCIPAL FINDINGS AND SIGNIFICANCE

The results of recent laboratory investigations suggest that azimuthal self potential measurements can potentially advance the geoelectrical characterization of hydraulic anisotropy in fractured rocks. Laboratory ASP surveys on a fracture block model show that ASP measurements are capable of distinguishing hydraulically-active fractures from electricallyconductive fractures, and are diagnostic of flow direction and flow rates in fractures (Figure 4a). In contrast, electrical resistivity measurements that are sensitive to the anisotropy in electrical current flow through fractures may not necessarily be equivalent to groundwater flow as previously indicated in earlier authors (Figure 4b). Both ASP and ARS measurements are influenced by anisotropy (due to the strike of major fracture sets) and heterogeneity (due to variable fracture density) of the block model. The existence of the positive polarity of the self potential defines the flow direction and the self potential magnitude within a single fracture set was observed to increase with flow rate. Whereas the ARS anisotropy is primarily controlled by fracture density/connectivity (and hence presumably hydraulic conductivity), ASP anisotropy appears diagnostic of (1) hydraulic gradient driving flow within fracture sets, and (2) fracture density, presumably controlling the strength of the streaming potential coefficient (Figures 1 and 4a).

Preliminary field data from the New Jersey Highlands illustrated that ASP surveys can define hydraulic anisotropy in fractured rock environments. A striking correlation was observed to exist

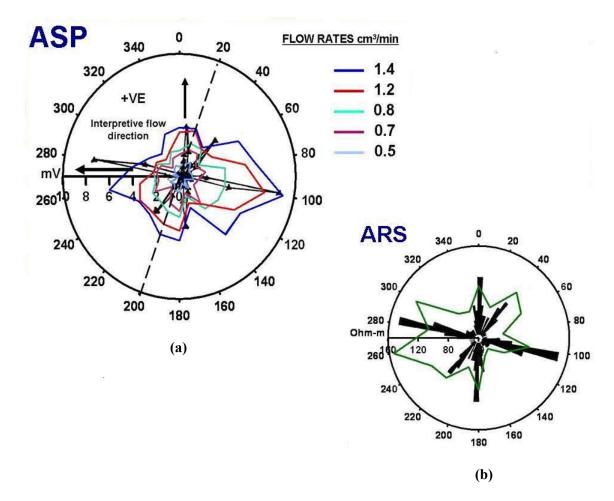


FIGURE 4 (a): Polar plot of the azimuthal self potential superimposed on fracture length rosette of the fracture block in the FAS as a function of flow rate and **(b)** plot of apparent resistivity (ρ_a) anisotropy superimposed on rosette of fracture strike orientation.

between ASP measurements and fracture strike orientations at three of four sites investigated (Figures 5a, 5c, 6a, 6c, and 7). The characteristic anisotropicity at the fourth site is controlled by a master structure; the NE-SW trending Lake Inez Fault Zone (LIFZ) that strikes at N10°E (Figure 6a). The flow directions appear to be conformable with the regional northwest and northeast fracture trend of the NJH (Figures 5a and 5e). ARS (electrical) data suggest three sites are overall heterogeneous and the fourth is anisotropic (Figures 5b, 5d, 6c, 6d, and 8a – 8d).

Quantitative analysis of the magnitude of the energy observed in the odd and even coefficients of the power spectra of self potential (SP) datasets analyzed using a *Fourier* series was useful for characterizing anisotropic or heterogeneous flow in the fracture network. For anisotropic flow, the odd coefficients (harmonics) were close to zero, whereas heterogeneous flow resulted in significant energy in the odd coefficients. The employment of asymmetric geoelectric arrays has allowed this quantitative distinction between anisotropy and heterogeneity in fractured bedrock. Conversely, Figure 9 and Table 1, SP measurements show anisotropic behavior at three of four sites and flow anisotropy corresponds with the occurrence of high fracture density.

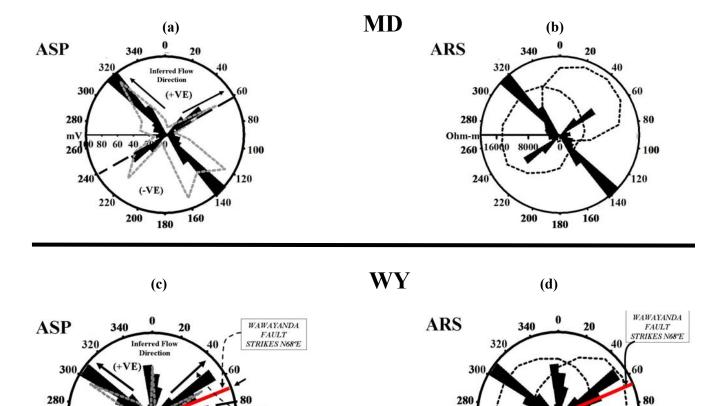


FIGURE 5. Polar plots of self potential anomalies and apparent resistivity (electrical anisotropy) for **(a-b)** MD, Lake Hopatcong, and **(c-d)** WY, Vernon sites in the New Jersey Highlands.

NE FLOW DIRECTION OF WAWAYANDA R. and REGIONAL LAKES

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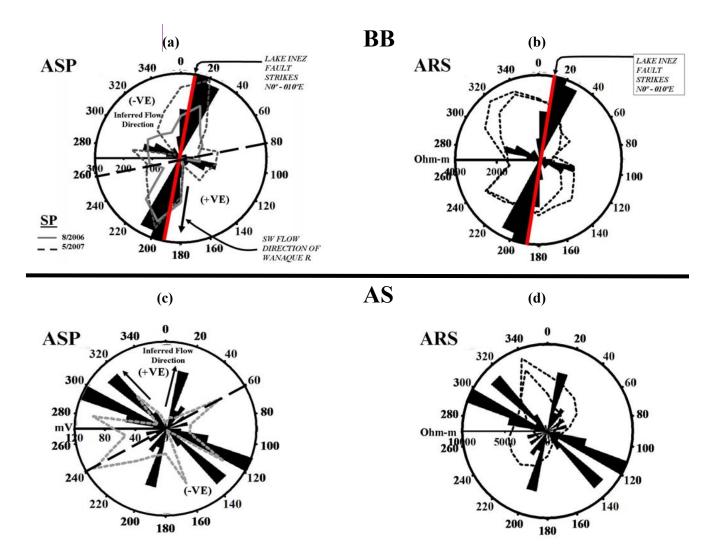


FIGURE 6. Polar plots of self potential anomalies and apparent resistivity (electrical anisotropy) for the **(a-b)** BB, Wanaque and **(c-d)** AS, Wharton sites in the New Jersey Highlands.

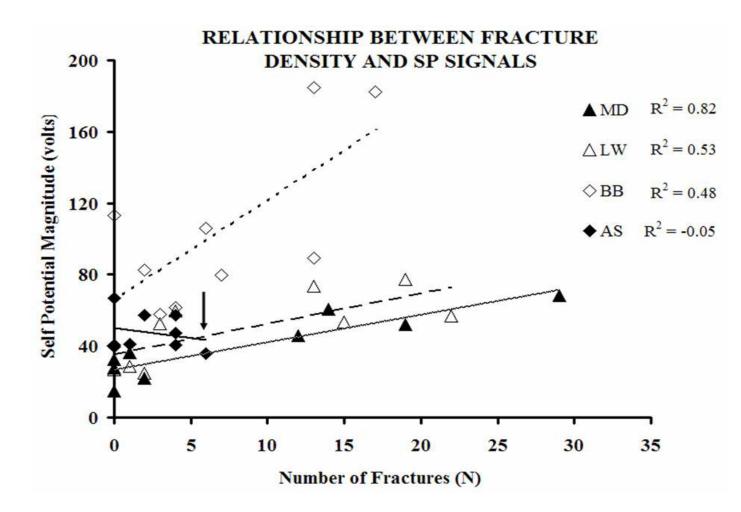


FIGURE 7. Linear relationships between the number of fractures and the intensity and direction of the SP signal at the MD, WY, BB, and AS sites. Higher R^2 values are observed for the sites where fractures outcrops are extended onto or close to the targeted field sites.

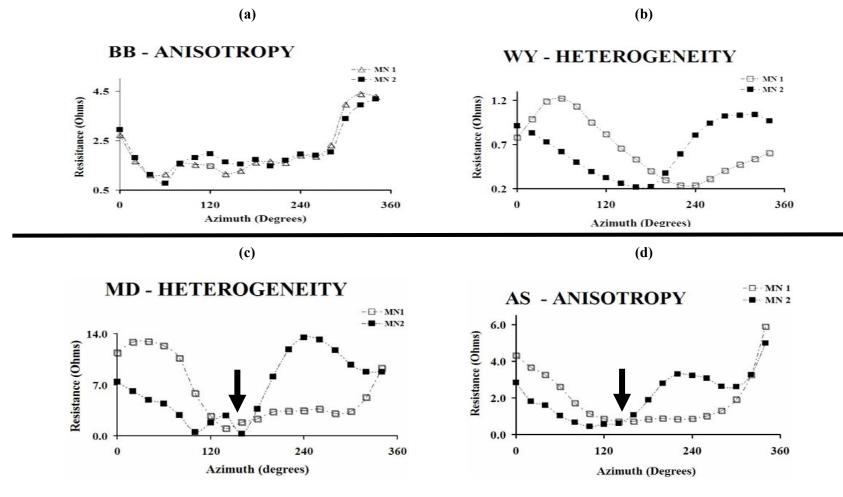
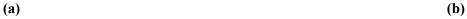


FIGURE 8. Graphs illustrating quantitative distinction of (a) electrical anisotropy at the BB site, and (b-d) electrical heterogeneity at the MD, WY, and AS sites by comparing the values of electrical resistance measured at both MN pairs for each current injection at 20° steps throughout 360° azimuth. [Anisotropy causes similarity in both resistance (MN) curves, whereas disparity in the MN curves signifies heterogeneity].



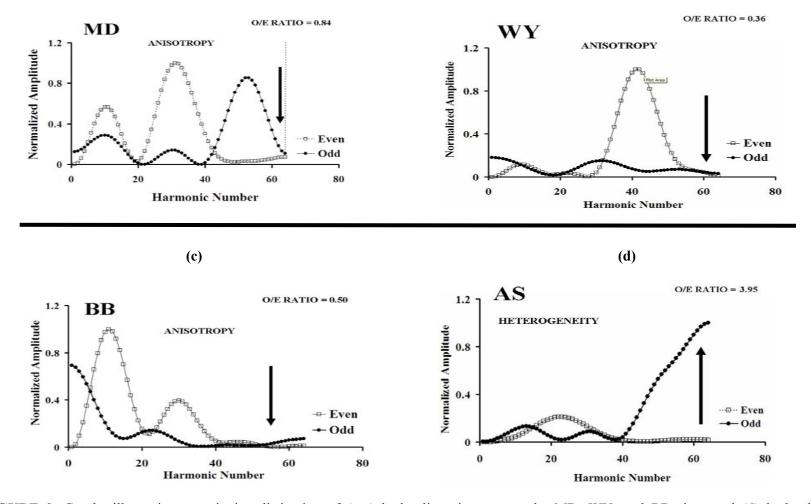


FIGURE 9. Graphs illustrating quantitative distinction of (a-c) hydraulic anisotropy at the MD, WY, and BB sites, and (d) hydraulic heterogeneity at the AS sites from transformation of the SP data using a Fourier series. An O/E ratio < 1.0 indicates anisotropic flow and an O/E ratio > 1.0 indicates heterogeneous flow at the field site. [Upward pointing arrow shows the increase in the energy of the odd harmonics.]

Site	Fracture Orientation (Azimuth)	Fracture Density ² (fractures/meter)	O/E Ratio (K ¹)	Flow ³ Characterization (Hydraulic)	Resistivity ⁴ Characterization (Electrical)
BB	010° - 030° 280° - 290°	6.0	0.50	Anisotropic	Anisotropic
WY	300° - 310° 350° - 010° 050° - 060°	3.0	0.36	Anisotropic	Heterogeneous
MD	310° -320° 050° -060°	12.0	0.84	Anisotropic	Heterogeneous
AS	290° - 300° 310° - 320° 010° - 020°	2.0	3.95	Heterogeneous	Heterogeneous

TABLE 1. Electrical and hydraulic anisotropy characterization of bedrock fractures at four field sites in the New Jersey Highlands
(NJH) Province.

¹ O/E ratio determined from Discrete Fourier Transform (DFT) analysis of the 'odd and even harmonics' of the energy spectra associated with SP data sets.
² Fracture density based on 60 cm counting grid placed over fracture outcrops at field sites.
³ Site hydraulic anisotropy characterization based on the energy spectra for SP data sets.
⁴ Site electrical resistivity anisotropy characterization based on comparison resistance curves measured between potential electrodes MN₁ – MN₂.

Recent laboratory data shows that the polarity of the SP anomaly associated with a fracture set indicates the direction of groundwater flow within the fracture set.²⁴ Limited data obtained from these sites (primarily surface water flow directions) is consistent with this being borne out at these field sites, which is a very exciting result. These data suggest simple field-scale electrical measurements can define not just hydraulic anisotropy, but delineate the direction of groundwater flow. These results show the distinct differences between ARS and ASP surveys and highlight apparent advantages of ASP. ARS is strongly impacted by heterogeneity and it is interesting to note that this may be related to structures that also impart anisotropy (e.g. fault zone at the anisotropic site). Based on observance of a strong correlation between the fracture network and presumed hydraulic anisotropy, ASP appears more intimately connected to hydrogeology than ARS. In conclusion, preliminary field measurements in a fractured rock environment suggest that this work could improve the characterization of fracture systems in bedrock aquifers and promote understanding of regional groundwater resources in fracture-dominated systems required for the design of groundwater remediation strategies.

References Cited

- 1. http://www.highlands.state.nj.us/njhighlands/actmaps/maps/north_zone_map.pdf
- 2. <u>http://www.toxiclegacy.com/</u>
- 3. http://www.vernonweb.com/highlands.htm
- 4. http://www.state.nj.us/dep/highlands
- 5. Bahr, K., 1978. Electrical anisotropy and conductivity distribution functions of fractal networks and of the crust, the scale of connectivity. *Geophys.J.R. Astr.Soc.*, **56**, 477-479.
- Bolshakov, D.K. I.N. Modin, E.V. Pervago, V.A. Shevnin, 1997. Separation of anisotropy and inhomogeneity influence by the spectral analysis of azimuthal resistivity diagrams. Proceedings of the 3rd EEGS-ES Meeting, Aarhus, Denmark, September 1997.
- 7. Borner, F.D., Schopper, J.R., and A. Weller, 1996. Evaluation of transport and storage properties in the soil and groundwater zone from induced polarization. *Geophysical Prospecting*, v.44, 583-601.
- 8. Frohlich, R.K., J.J. Fisher, and E. Summerly, 1996. Electrical-hydraulic conductivity correlation in fractured crystalline rock: Central Landfill Rhode Island, USA. *Journal of Applied Geophysics*, **35**, 249-259.
- 9. LaPointe P.R. and J.A. Hudson, (1985), Characterization and interpretation of rock mass joint Patterns. Geological Society of America Special Paper, *199*, 37 p.
- Montero Santos, F. A., E. Almeida, E. Castro, R. Nolasco, and L. Mendes-Victor, 2003. A hydrogeological investigation using EM34 and SP surveys. *Earth Planets Space*, 54, 655-662.
- 11. Ogilvy A.A. and E.N. Kuzmina, 1972. Hydrogeologic and Engineering–geologic possibilities for employing the method of induced polarization. *Geophysics*, **37**(5), 839-861.
- 12. Olhoeft, G.R., 1985. Low frequency electrical properties. *Geophysics*, **50**(12), 2492-2503.
- 13. Petiau, G., (2000), Second generation of Lead-lead chloride electrodes for geophysical applications. *Pure and Applied Geophysics*. *157*, 357-382.

- 14. Porsani, J.L., V. R. Elis, F. Y. Hiodo, 2005. Geophysical investigations for the characterization of fractured rock aquifers in Itu, SE Brazil, *Journal of Applied Geophysics*, **57**, 119-128.
- 15. Ritzi, R. W. and R. H. Andolsek, 1992. Relation between anisotropic transmissivity and azimuthal resistivity surveys in shallow, fractured, carbonate flow systems. *Ground Water*, **30**, 774-780.
- 16. Sandberg, S.K., L.D. Slater, and R. Versteeg, 2002. An integrated geophysical investigation of the hydrogeology of an anisotropic unconfined aquifer. *Journal of Hydrology*, **267**, 227-243.
- 17. Schon, J.H., 1996. Physical properties of rocks-Fundamentals and principles of petrophysics: Peramon Press.
- Sharma, S.P. and V.C. Baranwal, 2005. Delineation of groundwater-bearing fracture zones in a hard rock area integrating very low frequency electromagnetic and resistivity data. *Journal of Applied Geophysics*, 57, 155-166
- 19. Slater, L.D., and D.P.Lesmes. 2002. Electrical-hydraulic relationships observed for unconsolidated sediments. *Water Resources Research*, **38**(10), 1-13.
- 20. Slater, L.D., S.K. Sandberg, and M. Jankowski, 1998. Survey design procedures and data processing techniques applied to the EM Azimuthal resistivity method. *Journal of Environmental and Engineering Geophysics*, **3**, 167-177.
- 21. Taylor R.W. and A.H. Flemming, 1988. Characterizing jointed systems by azimuthal resistivity surveys. *Ground Water*, **26**, 464-474
- 22. Watson K.A. and R.D. Barker, 1999. Differentiating anisotropy and lateral effects using offset Wenner azimuthal resistivity soundings. *Geophysics*, **64**, 739-745.
- 23. Worthington, P.F. The Influence of formation anisotropy upon resistivity-porosity relationships. *Petrophysics*, **2**(2).
- 24. Wishart, D.N., L.D. Slater, and A.E. Gates, 2006. Self potential improves characterization of hydraulically-active fractures from azimuthal geoelectrical measurements, *Geophysics Research Letters*, *33*, 17314, doi:1029/2006GL027092.

Enhancing the remediation of Trichloroethene (TCE) using double-walled carbon nanotubes (DWNT)

Basic Information

Title:	Enhancing the remediation of Trichloroethene (TCE) using double-walled carbon nanotubes (DWNT)
Project Number:	2006NJ99B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	6th
Research Category:	Water Quality
Focus Category:	Water Quality, Water Quantity, Groundwater
Descriptors:	None
Principal Investigators:	Sarat Kannepalli, Donna E. Fennell

Publication

Project Summary

Problem and Research Objectives

The chlorinated organic solvent trichloroethene (TCE) is one of the most commonly detected groundwater contaminants (1). Widespread application in vapor degreasing of fabricated metal parts (80% use) and in the production of organic chemicals and pharmaceuticals (5% use), resulted in increased production from 260,000 lbs in 1981 to 320 million lbs in 1991 (2). The Maximum Contaminant Level (MCL) for TCE is 0.005 mg/L. There is some evidence that TCE may cause cancer from lifetime exposure at levels above the MCL (2). The New Jersey Department of Environmental Protection (NJDEP) found that the former General Electric (GE) Company and Atlantic metal products sites in northern NJ are a source of TCE up to 20,000 μ g/L at the GE site and up to 1,600 μ g/L at the Atlantic metal products site. There are many other such sites in New Jersey.

The low viscosity, low interfacial tension with water, high volatility and existence as a non-aqueous-phase liquid make many physical and chemical methods of TCE remediation either ineffective or uneconomical. Furthermore, many hydro-geologic formations make remediation difficult. Reliable, cost effective methods for remediation of TCE contaminated groundwater are still needed.

The proposed research aimed to combine chemical-physical concentration and sequestration using carbon nanotubes and subsequent biodetoxification by dechlorinating bacteria to increase the efficiency of TCE removal from groundwater. The sequestration method involves the sorption of TCE onto carbon nanotubes. Carbon nanotubes are condensed carbon structures with nanoscale dimensions (1-50 nanometers) which have extraordinary mechanical, electronic, and chemical properties (5). They are produced through carbon arc discharge followed by laser removal of carbon or chemical vapor deposition on catalytic particles (6). Carbon nanotubes were superior to activated carbon for sorption and removal of dioxins from air (7). Concentration and sequestration of many environmental contaminants may be possible using carbon nanotubes. Sequestration may result in decreased environmental transport to sensitive receptors such as domestic wells or surface waters. It is currently not known if carbon nanotubesequestered pollutants are bioavailable. If they are, sequestration followed by transformation may be possible — and necessary. Reductive dechlorination of carbon nanotube-sequestered TCE by anaerobic dehalorespiring bacteria could convert TCE to dichloroethene (DC), vinyl chloride (VC) and finally to harmless ethene.

Specific objectives and hypothesis of the study

The specific objectives of this study were two-fold: (1) What is the sorptive capacity of double walled carbon nanotubes (DWNT) for TCE? and (2) Is carbon nanotube-sequestered TCE bioavailable to dehalogenating bacteria? We hypothesized that TCE sorbed on DWNT is bioavailable to bacteria and this sorption/concentration may increase the dechlorinating efficiency of the bacteria. If feasible, a more efficient remediation technology for TCE contaminated groundwater may be developed.

Methodology

The proposed research project was carried out in two main tasks: **Task 1**: Develop an isotherm for TCE sorption to DWNT. **Task 2**: Determine the bioavailability of TCE sorbed on DWNT.

Experimental Methods:

Task 1. Develop an isotherm for TCE sorption to DWNT.

Task 1 used a series of three experiments. First the mass loading of DWNT to be used for sorption isotherm development was determined; the kinetics of TCE sorption to DWNT was examined; and finally a sorption isotherm for TCE to DWNT was developed.

Determination of DWNT mass loading. To carry out experiments with nanotubes and TCE, it was necessary to be able to accurately measure the amount of TCE sorbed onto the nanotubes. Since the TCE mass balance in the bottle (Equation 1) will depend upon headspace analysis of TCE in the gas phase, we must ensure that experiments are carried out under conditions where TCE can be detected in the gas phase. Therefore, a suitable mass loading of DWNT for the TCE concentrations to be used was found. Different loadings of DWNT (1, 5, 15, 30, and 60 mg/bottle) were placed in 60 ml bottles with two different TCE concentrations (0.0015 mM and 0.761 mM) and 40 mL of two different aqueous media: 1) microbial growth media (0.5 g/L NH₄Cl, 0.4 g/L K₂HPO₄, 0.1 g/L MgCl₂•6H₂O, 0.05 g/L CaCl₂•2H₂O, 0.001 g/L resazurin, and 10 mL trace metal solution per liter modified by addition of 0.01 g of NiCl₃•6H₂O per liter) (8); and 2) biologically inactivated synthetic groundwater (0.7351 g/L CaCl₂, 0.1 g/L NaN₃ and 0.005 g/L NaHCO₃) (9). Two media were examined to control for differences in DWNT sorption that may result from the presence of iron sulfide and other precipitates that may be present in living systems. The bottles were incubated in triplicate and agitated at 25°C for three days. After three days of incubation the bottles were analyzed to determine the total TCE adsorbed on to the nanotubes. The DWNT loading at which 30-70% of the TCE mass adsorption is achieved was used for further experimentation as it leaves measurable amounts of TCE in both gaseous and liquid phases to allow accurate determination of the isotherm. The total TCE adsorbed on to the nanotubes was determined from Equation 1.

Total TCE =
$$V_{head space} C_g + V_{aq} C_e + Q_e \cdot M$$
 (Equation 1)
Where:

Total TCE = Mass of TCE added to the bottle (μ mol) $V_{head space}$ = Volume of the gaseous head space (L) C_g = Concentration of TCE in gaseous phase (μ mol/L) V_{aq} = Volume of the aqueous phase (L) C_e = Concentration of TCE in the aqueous phase at equilibrium (μ mol/L) Q_e = TCE sorbed per unit weight of DWNT (μ mol/mg) M = Mass of the adsorbing DWNT (mg).

 $C_{\rm g}$, the gas-phase concentration, was determined from gas chromatography analysis and comparison to known standards as described in the Analytical Methods section. The

liquid-phase equilibrium TCE concentration, C_e was determined using the relationship $C_g = H_c^* C_e$, where H_c is the pseudo-dimensionless Henry's Law Constant (10). Thus, all measurements depended upon the gas-phase analysis of TCE.

<u>Kinetics of TCE sorption to DWNT</u>. In order to develop an isotherm for TCE sorption to DWNT, the kinetics of TCE sorption was first determined to allow selection of an adequate incubation time for the isotherm experiments. To assess kinetics of TCE sorption to DWNT, 60 mL reactors with nanotube mass loading at which 30-70% of the TCE is expected to sorb (as described in the Mass Loading section) were set up with growth media and synthetic groundwater as previously described. Samples will be collected daily and analyzed to determine the rate at which TCE is sorbed, $\frac{dQ_e}{dt}$. Consecutive days when there was no change in TCE adsorption i.e., $\frac{dQ_e}{dt} = 0$, were noted. To be conservative, the equilibrium time to be used in further experiments for isotherm development was assumed to be equal to t = time when $\frac{dQ_e}{dt} = 0$ plus one day.

<u>Development of a sorption isotherm for TCE to DWNT</u>. The feasibility of use of carbon nanotubes as a super sorbent for environmental pollutants will hinge, among other things, on their sorption capacity. A sorption isotherm for DWNT and TCE will be developed to determine the ultimate capacity for TCE uptake by DWNT. To obtain the isotherm, 20 reactors with the optimal experimental DWNT mass loading (as determined in the Mass Loading section) were set up. Ten different concentrations of TCE ranging from 0 to 6.08 mM were added to the reactors. A sorption isotherm was constructed by plotting the concentration of TCE in the aqueous phase at equilibrium (C_e) against TCE sorbed per unit weight of DWNT (q_e). The isotherm was fit with a sorption model (e.g., Freundlich) that will be useful for defining experimental parameters for testing and for calculations related to design aspects for the technology.

Task 2. Determine the bioavailability of TCE sorbed on DWNT.

The second overall objective of the study was to determine whether once sorbed to DWNT, if TCE is readily bioavailable. If nanotubes are to be used as super-sorbing sequestration agents for remediation, then the concentrated contaminants must then be non-bioavailable and difficult to desorb or they must be amenable to destructive reactions in their concentrated forms. The bioavailability of sorbed TCE to dechlorinating bacteria was examined. This will allow us to determine the extent of irreversible sequestration of the pollutants and to test our hypothesis that concentration and subsequent biotransformation could be a new effective technology for TCE remediation. Reactors filled with anaerobic growth medium and DWNT-sequestered TCE were inoculated with a dehalogenating bacterium, Dehalococcoides ethenogenes, known to grow on TCE and dechlorinate it to ethene (11). The bioavailability of TCE to the bacteria was determined by analyzing the end products of TCE degradation – i.e., DCE, VC and ethene over a 135 day incubation period at 25°C. We utilized DWNT-TCE equilibrated reactors filled with anaerobic media as described in the section on Sorption Isotherm Development as the starting reactors for this experiment. An inoculum of a mixed culture containing Dehalococcoides ethenogenes (12) was added to achieve approximately 10⁻⁶ cells/mL.

Control reactors that contained no nanotubes were run to check the viability of the culture transfer and to obtain rates of dechlorination to which to compare to DWNT rates. The mass of TCE desorbed and transformed by the bacteria was determined through headspace analysis for dechlorination daughter products.

Analytical methods and chemicals:

<u>TCE</u> and dechlorination daughter product analysis. Gas samples were removed from bottle headspaces and analyzed for TCE, DCE, VC and ethene concentrations using a gas chromatograph (GC) coupled to flame ionization detection. A five- point standard curve was developed for each compound of interest. Double walled nanotubes were selected instead of single walled nanotubes as they have more surface area, are less expensive and commercial access to them is less problematic. The DWNT selected for this study have a wall thickness of 1-2 nm, length 0.5- 2 μ m and a density of 2.1 Sigma-Aldrich, St. Louis, MO.

Principal Findings and Significance Progress Report

Our major results at this time are related to the use of an anaerobic growth medium to examine bioavailability of TCE sorbed to DWNTs and its subsequent use by dechlorinating bacteria as outlined in Task 2. We examined biotransformation of TCE in the presence of different amounts of DWNTs as outlined in the methodology section above. Table 1 shows the experimental matrix for this task. Triplicate bottles were prepared for each treatment.

Table 1. Experimental protocol for examination of TCE bioavailability when added with carbon nanotubes.

Medium	TCE Conc. (mM)	Nanotube Loading (mg/bottle)					
Anaerobic	0.0015	0	1	5	15	30	60
Anaerobic	0.761	0	1	5	15	30	60

We developed methods to distribute the DWNTs to serum bottles—a somewhat difficult task. After several attempts to do this, the bottles were ultimately loaded with DWNTs using a DWNT stock solution that was prepared by sonicating a solution of anaerobic medium (600 mL) and DWNT (900 mg) for 24 hours. The appropriate amount of the resulting suspension was transferred to the 60 mL bottles using a glass syringe purged with sterile, anoxic gas in order to accomplish the desired DWNT loading as shown in Table 1. After the medium-DWNT suspension was added, anaerobic medium without DWNT was also added to achieve a final volume of 36 mL. The bottles were then amended with TCE from a methanol-TCE stock solution. After preparation, the bottles were incubated on a shaker at 25°C and analyzed for TCE after 4 days and then again after 8 days.

On day 14, the bottles were inoculated with 4 mL of a mixed culture containing *Dehalococcoides*. The bottles were analyzed again on day 28, 45 and 135. Our findings

suggest that TCE could be dechlorinated to DCE, VC and ethene by *Dehalococcoides* in the presence of the DWNT. Further analyses of these data are on-going and will be reported at a future date.

References

- (1) National Research Council. 1994. Alternatives for Groundwater Cleanup. National Academy Press, Washington, D.C.
- (2) United States Environmental Protection Agency. Last update Monday, February 14th, 2005.Technical Fact sheet on Trichloroethene. http://www.epa.gov/OGWDW/dwh/t-VOC/trichlor.html
- (3) New Jersey Department of Environmental Protection. Last update August 31, 2005. News releases. "DEP Directs General Electric And Atlantic Metals to Conduct Cleanup along Rahway River". <u>http://www.state.nj.us/dep/newsrel/2005/05_0109.htm</u>
- (4) Masciangioli, M.; Zhang, W.-X. March 1, 2003. Environmental Technologies at the Nanoscale. *Environmental Science & Technology*. p. 102A-108A.
- (5) Hood, E. September 2004. Nanotechnology: Looking As We Leap. *Environmental Health Perspectives*. Vol.112, Number 13. p. A741-A747.
- (6) Baughman, R.H.; Zakhidov, A.A. 2002. Carbon Nanotubes- the Route Toward Applications. *Science*. 297, p. 787-792.
- (7) Long, R.Q.; Yang, R.T. 2001. Carbon Nanotubes as Superior Sorbent for Dioxin Removal. *Journal of American Chemical Society*. Vol.123. p. 2058.
- (8) Fennell, D.E. 1998. Composition of Alternative Hydrogen Donors For Anaerobic Reductive Dechlorination of Tetrachloroethene. Ph.D. Dissertation. Cornell University.
- Huang, W.; Schlautman, M.A.; Weber JR, W. 1996. A distributed Reactivity Model for Sorption by Soils and Sediments. 5. The Influence of Near-Surface Characteristics in Mineral Domains. *Environmental Science and Technology*. 30. p. 2993-3000.
- (10) Gossett, J.M. 1987. Measurement of Henry's Law Constants for C₁ and C₂ Chlorinated Hydrocarbons. *Environmental Science & Technology*. 21:202-208.
- Maymo- Gatell, X.; Anguish, T.; Zinder, S.H. July 1999. Reductive Dechlorination of Chlorinated Ethenes and 1,2 Dichloroethane by "Dehalococcoides ethenogenes" 195. Applied and Environmental Microbiology. Vol. 65, No. 7. p. 3108-3113.
- (12) Fennell DE, Nijenhuis I, Wilson SF, Zinder SH, Häggblom MM. 2004. Dehalococcoides ethenogenes strain 195 reductively dechlorinates diverse chlorinated aromatic pollutants. Environmental Science & Technology. 38:2075-2081.

Information Transfer Program

The information transfer program has emphasized development of the website and e-based communications with stakeholder groups and the production of substantive newsletters addressing individual issues as effective methods of communication of water resource information to the public.

Three issues of the newsletter were produced. One issue reviewed notable water research in New Jersey, including some of the research funded by NJWRRI in FY 2005. A second issue highlighted material presented in the Second Passaic River Symposium, and a third issue addressed the topic of beneficial reuse of wastewater in New Jersey. A fourth issue, currently in production, is reporting the proceedings of a conference on the Meadowlands that was held in May 2007. Each issue was eight pages, and was primarily distributed via our e-mail lists to approximately 2,000 people throughout the state, and as hard copies to all members of our state legislature and the Congress.

In the first issue, we illustrated the importance of research in addressing key water resources, and showcased the diversity of research that is occurring statewide. In addition to projects funded by NJWRRI, research conducted by the New Jersey Department of Environmental Protection (NJDEP) was also featured. Topics included: an assessment of the Delaware River Basin, coal and charcoal particles in Hudson River sediments and their roles in binding PAHs and PCBs, and forecasting algal blooms at a surface water system with artificial neural networks.

The Second Passaic River Symposium was held at Montclair State University in October 2006, and focused on the environmental challenges facing the Passaic River basin and the progress made in addressing problems since the first symposium. The event drew over 300 people interested and involved in the basin, including federal and state environmental officials, environmental advocates and scientists. In addition to an overview of the event, the newsletter featured reports from a breadth of symposium topics, including the environmental history of the Lower Passaic River, municipal stormwater regulations, phosphorus TMDL development, and benefits of natural flood storage areas.

With a recent history of drought and an ever-decreasing supply of fresh water, the issue of wastewater reuse in New Jersey is gaining more attention from the spectrum of water resources professionals. In an effort to foster discussion, the Spring 2007 issue of our newsletter focused on this important subject. We published articles from a range of viewpoints, from a member of the NJDEP Reclaimed Water for Beneficial Reuse Task Force, to a scientist from a non-profit environmental group, to an environmental consultant for a development group. As a result of the positive response from this issue, we are in the planning stages of a conference or workshop on wastewater reuse.

We also began the New Jersey Water Blog in March 2007 (http://njwrri.blogspot.com/). It was created to address a significant communication gap within the New Jersey water resource community. While the state has a wealth of water expertise, water-related organizations, and water resources, there was no effective way for people to communicate with each other outside of very specific meetings. There was an unmet need for people across the range of water resource topics and various agencies and organizations to be able to communicate with one another. The blog is a place where people interested and involved with water can exchange ideas, questions, knowledge, and concerns with each other. NJWRRI functions as administrator of the blog, and posts topics of discussion for the water community. We regularly review water-related issues of concern, and post comments on the blog with the aim of stimulating general discussion. Utilization of the blog has been positive, but depends on the prominence of water issues in the

news and new developments in regulations and management to maintain interest.

Our website (http://njwrri.rutgers.edu/) has been continually updated with information on water resource events and information in New Jersey, the U.S. and around the world. We have created pages for new book releases, recent articles on water issues, and water courses at Rutgers University, and an area on our main page for New & Noteworthy information. This year also saw a reorganization of the Research section of the site to distinguish faculty, graduate student, and undergraduate research projects, and current and past projects. The website is our primary means of information transfer to the water community and the public, and we will continue to update and improve its functionality with new pages and greater content.

Another important and new component of our information transfer program is the development of targeted, group-specific e-mail lists. The lists are continuously updated and expanded, and are used to keep these groups informed of events, conferences, publications, and funding opportunities. These lists enable us to initiate and maintain frequent contact with stakeholder groups (rather than passively waiting for individuals to contact us). We believe these lists are an excellent method of keeping the water-related public aware of the WRRI as well as informed about water-related news and information.

We continue to participate in the New Jersey Water Monitoring Council, a statewide body representing both governmental and non-governmental organizations involved in water quality monitoring. As a result of our involvement in the council, we expect to be a co-sponsor of the National Water Quality Monitoring Council's Sixth National Monitoring Conference to be held in Atlantic City, NJ in May 2008.

Student Support

Student Support							
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total		
Undergraduate	2	0	0	0	2		
Masters	1	0	0	0	1		
Ph.D.	8	0	0	0	8		
Post-Doc.	0	0	0	0	0		
Total	11	0	0	0	11		

Notable Awards and Achievements

The data collected during the project Nitrate removal in urban wetlands: examining the roles of vegetations, soils, and hydrology in the creation of 'hot spots' and 'hot moments' of denitrification, is being used in the restoration and management design of Teaneck Creek Conservancy (TCC). The major goals for the managers of this site are stormwater control, plant community restoration, and improved nitrogen (N) retention and removal. The findings suggest that hydrology and soil texture may be most instrumental in determining where N removal and retention is highest, and further imply that the hydrologic modifications currently proposed by the restoration plan (i.e. increased areas of flooding and ponding within the site for stormwater control) may not be ideal for N removal; flooded soils must also have sufficient time to dry out (allowing for the buildup of nitrate).

Because the study found good correlations between N dynamics and soil textural and chemical qualities, it has also elicited interest among TCC managers in constructing a soil map for the entire TCC area, outlining the soil textural and chemical properties in areas not covered by the initial study. To construct this map, Monica Marie Palta has received a grant of \$1000 from the Rutgers University Graduate Program in Ecology and Evolution Academic Excellence Fund. Using the data collected and models subsequently constructed last year with WRRI funding, a soil map can be used to determine what N dynamics might be in areas ranging across TCC, and design further studies in these areas to field test the robustness of the N removal models.

This project has also allowed her to design a long-term, larger-scale project incorporating both the field site used in this study and other field sites around New Jersey. Since receiving funding from WRRI, she has been awarded three years of stipend and research funding through an EPA STAR fellowship, and several small (\$1000-\$5000) grants from various funding agencies supporting her dissertation work.

Several awards resulted from the project, Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution (2004NJ73B). 1. American Society of Microbiology's Corporate Activities Program Student Travel Grant award for attending the 107th General meeting held in Toronto (2007); 2. Annual Robert S. and Eileen A. Robison Scholarship Award for Excellence in Graduate Studies, Department of Biochemistry and Microbiology, Rutgers University (2007); 3. Outstanding

student poster presentation award at the 8th International Conference on Mercury as a Global Pollutant. Madison, WI (2006); 4. Cook College/NJAES Scientific Communication Award, Rutgers University (2006)

Publications from Prior Projects

- 1. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") Articles in Refereed Scientific Journals Hernandez, A.D., J.F. Bunnell, and M.V.K. Sukhdeo. 2007. Composition and diversity patterns in metazoan parasite communities and anthropogenic disturbance in stream ecosystems. Parasitology. In press.
- 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") Book Chapters -Sukhdeo, M.V.K. and A.D. Hernandez. 2005. Food web patterns and the parasites perspective, in: F. Thomas, J.F. Guegan, and F. Renaud (eds), Parasitism and Ecosystems. New York: Oxford University Press. 54-67.
- 2000NJ07 ("Role of Peat in the Development of River Morphology") Conference Proceedings -Claude M. Epstein. 2007. Stream restoration under "natural" conditions: the Oswego River at Martha Furnace. In: Proceedings of the Seventh International Conference on Hydroscience and Engineering. Philadelphia, PA. September 10-13, 2006. Proceedings available online at Drexel E-repository and Archives: http://hdl.handle.net/1860/732.
- 2000NJ07 ("Role of Peat in the Development of River Morphology") Articles in Refereed Scientific Journals - Claude M. Epstein. 2002. Application of Rosgen Analysis to the New Jersey Pine Barrens. Journal of the American Water Resources Association. 38(1): 69-78.
- 2002NJ8B ("Salt Marsh Macrophyte Rhizosphere Effects on Sediment Microbial Community Catabolic Response Profiles") - Articles in Refereed Scientific Journals - Ravit, B., J.G. Ehrenfeld, and M. M. Haggblom. 2006. Effects of vegetation on root-associated microbial communities: A comparison of disturbed versus undisturbed estuarine sediments. Soil Biology & Biochemistry. 38: 2359-2371.
- 2002NJ8B ("Salt Marsh Macrophyte Rhizosphere Effects on Sediment Microbial Community Catabolic Response Profiles") - Conference Proceedings - Ravit, B. 2007. Rhizosphere Sediment Microbial Communities: Does the Plant Matter? Meadowlands Symposium II, Lyndhurst, NJ. May 15-17, 2007. (Oral presentation)
- 2004NJ74B ("HIgh resolution geophysical imaging as a novel method for noninvasive characterization of contaminated wetlands: application to Kearny Marsh ") - Articles in Refereed Scientific Journals - Mansoor, N. and L. Slater. 2007. Marine electrical resistivity imaging of shallow-water wetlands. Geophysics. In Press.
- 2004NJ74B ("HIgh resolution geophysical imaging as a novel method for noninvasive characterization of contaminated wetlands: application to Kearny Marsh ") - Articles in Refereed Scientific Journals - Mansoor, N. and L. Slater. 2007. On the relationship between iron concentration and induced polarization in marsh soils. Geophysics. 72(1): A1-A5.
- 9. 2004NJ74B ("HIgh resolution geophysical imaging as a novel method for noninvasive characterization of contaminated wetlands: application to Kearny Marsh ") Articles in Refereed Scientific Journals Mansoor, N., L. Slater, and F. Artigas. 2006. Case history: High-resolution geophysical characterization of shallow-water wetlands. Geophysics. 71(4): B101-B109.
- 10. 2004NJ74B ("HIgh resolution geophysical imaging as a novel method for noninvasive characterization of contaminated wetlands: application to Kearny Marsh ") Dissertations Mansoor,

Nasser. 2007. High-Resolution Geophysical Imaging of Shallow-Water, Contaminated Wetlands: A Novel Application to Kearny Freshwater Marsh, New Jersey Meadowlands. Ph.D. Dissertation. Department of Earth & Environmental Sciences, Rutgers-Newark, Newark, NJ. 146 pages.

- 2004NJ74B ("HIgh resolution geophysical imaging as a novel method for noninvasive characterization of contaminated wetlands: application to Kearny Marsh ") - Conference Proceedings -Mansoor, N. and L. Slater. 2007. Marine electrical resistivity imaging of shallow-water wetlands. Meadowlands Symposium II. Lyndhurst, NJ. May 15-17, 2007. (Oral presentation)
- 12. 2004NJ74B ("HIgh resolution geophysical imaging as a novel method for noninvasive characterization of contaminated wetlands: application to Kearny Marsh ") Conference Proceedings Slater, L. and N. Mansoor. 2007. Aquatic electrical resistivity imaging of rainfall-driven solute transport in contaminated wetlands, Eos Trans. AGU. Jt. Assem. Suppl. Abstract H42B-01.
- 2004NJ74B ("HIgh resolution geophysical imaging as a novel method for noninvasive characterization of contaminated wetlands: application to Kearny Marsh ") - Conference Proceedings -Slater, L. and N. Mansoor. 2006. The dependence of induced polarization on natural iron concentration in wetland soils, Eos Trans. AGU, 87(52), Fall Meet. Suppl., Abstract NS31A-1568.
- 2005NJ87B ("Lab-on-a-chip device for monitoring trace level arsenic") Articles in Refereed Scientific Journals - Hylton, K. and S. Mitra. 2007. Barrier film protected, and mixed solvent optimized micro-scale membrane extraction of methyl carbamate pesticides. Journal of Chromatography A. 1154: 6065.
- 2005NJ87B ("Lab-on-a-chip device for monitoring trace level arsenic") Conference Proceedings -Hylton, K., X. Wang, and S. Mitra. 2007. Trace Monitoring of New and "Emerging" Pollutants via Microscale Membrane Extraction. Meadowlands Symposium II, Lyndhurst, NJ. May 15-17, 2007. (Oral presentation)
- 2005NJ87B ("Lab-on-a-chip device for monitoring trace level arsenic") Conference Proceedings -Hylton, K. and S. Mitra. 2007. Trace Monitoring of Antibiotics Using Microscale Membrane Extraction. Annual ISPE poster competition. Stevens Institute of Technology. Hoboken, NJ. April 26, 2007. (Poster presentation)
- 2005NJ87B ("Lab-on-a-chip device for monitoring trace level arsenic") Conference Proceedings -Hylton, K. and S. Mitra. 2007. Monitoring of Pesticides and Antibiotics in America's Water. Third Annual Provosts Student Research Showcase. New Jersey Institute of Technology. Newark, NJ. April 11, 2007. (Poster presentation)
- 2005NJ87B ("Lab-on-a-chip device for monitoring trace level arsenic") Articles in Refereed Scientific Journals - Hylton, K. and S. Mitra. 2007. Automated, On-line Membrane extraction. Journal of Chromatography A. 1152: 199214.
- 19. 2005NJ87B ("Lab-on-a-chip device for monitoring trace level arsenic") Articles in Refereed Scientific Journals Hylton, K. and S. Mitra. 2007. Membrane Extraction as a Versatile Sample Preparation Technique. GIT Laboratory Journal (Europe). 3/4: 2-4.
- 2003NJ42B ("Microbial respiration of arsenic and selenium") Articles in Refereed Scientific Journals - Narasingarao, P. and M.M. Häggblom. 2006. Sedimenticola selenatireducens, gen. nov., sp. nov., an anaerobic selenate-respiring bacterium isolated from estuarine sediment. Systematic and Applied Microbiology. 29: 382-388.
- 2003NJ42B ("Microbial respiration of arsenic and selenium") Articles in Refereed Scientific Journals - Narasingarao, P. and M.M. Häggblom. 2007. Identification of anaerobic selenate-respiring bacteria from aquatic sediments. Applied and Environmental Microbiology. 73: 3519-3527.
- 22. 2003NJ42B ("Microbial respiration of arsenic and selenium") Articles in Refereed Scientific Journals Narasingarao, P. and M.M. Häggblom. 2007. Pelobacter seleniigenes sp. nov., a

selenate-respiring bacterium and reclassification of Malonomonas rubra as Pelobacter ruber comb. nov. International Journal of Systematic and Evolutionary Microbiology. In press.

- 2003NJ42B ("Microbial respiration of arsenic and selenium") Dissertations Narasingarao, Priya.
 2006. Anaerobic bacterial respiration of selenium oxyanions. Ph.D. Dissertation. Graduate Program in Environmental Sciences, Rutgers University, New Brunswick, NJ. 164 pages.
- 2003NJ42B ("Microbial respiration of arsenic and selenium") Conference Proceedings -Narasingarao, P. and M.M. Häggblom. 2006. Anaerobic bacterial respiration of selenium oxyanions. The First Annual International Conference of Metagenomics, La Jolla, CA. October 3-5, 2006.
- 25. 2002NJ4B ("CONTINUOUS, ON-LINE MONITORING OF HALOACETIC ACIDS IN WATER USING ANALYTICAL MEMBRANE EXTRACTION") - Book Chapters - Kou, Dawen and Somenath Mitra. 2003. Extraction of Semi-volatile Organic Compounds from Solid Matrices, in S. Mitra (ed), Sample Preparation Techniques in Analytical Chemistry. New York: John Wiley & Sons, pages 139-182.
- 26. 2002NJ4B ("CONTINUOUS, ON-LINE MONITORING OF HALOACETIC ACIDS IN WATER USING ANALYTICAL MEMBRANE EXTRACTION") - Book Chapters - Slack, Gregory, Nicholas Snow, and Dawen Kou. 2003. Extraction of Volatile Organic Compounds from Solids and Liquids, in S. Mitra (ed) Sample Preparation Techniques in Analytical Chemistry. New York: John Wiley & Sons, pages 183-226.
- 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") Book Chapters - Häggblom, M.M., L.K.G. Youngster, P. Somsamak, and H.H. Richnow. 2007. Anaerobic biodegradation of methyl tert-butyl ether (MTBE) and related fuel oxygenates, in: A. Laskin, S. Sariaslani, and G Gadd (Eds.), Advances in Applied Microbiology. Amsterdam: Elsevier. In press.
- 2004NJ68B ("Dechlorination of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans by Dehalorespiring Bacterial Cultures ") - Conference Proceedings - Liu, Fang and Donna E. Fennell. 2005. Microbial dechlorination of 1,2,3,4,7,8-hexachlorodibenzofuran by a Dehalococcoides-containing culture. The 21th Annual International Conference on Soils, Sediments and Water, Amherst, MA. October 2005. (Poster presentation)
- 2004NJ68B ("Dechlorination of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans by Dehalorespiring Bacterial Cultures ") - Conference Proceedings - Liu, Fang and Donna E. Fennell. 2005. Dechlorination of polychlorinated dioxins and furans in a Dehalococcoides-containing culture. The Eighth International Symposium on In Situ and On-Site Bioremediation, Baltimore, MD. June 6-9, 2005. (Platform presentation)
- 30. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") Articles in Refereed Scientific Journals Kritee, K., Joel D. Blum, Marcus W. Johnson, Bridget A. Bergquist, and Tamar Barkay. 2007. Mercury stable isotope fractionation during reduction of Hg(II) to Hg(0) by mercury resistant microorganisms. Environmental Science and Technology. 41:1889-1895.
- 31. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") Conference Proceedings Kritee, K., J. D. Blum, M. W. Johnson, B. A. Bergquist, and T. Barkay. 2007. Variation in the extent of mercury(Hg) stable isotope fractionation during reduction of Hg(II) to Hg(0) by different microbial strains. American Society of Microbiologys 107th General Meeting, Toronto, Canada. May 21 -25, 2007. (Poster presentation)
- 32. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") - Conference Proceedings - Kritee, K., J. D. Blum, M. W. Johnson, B. A. Bergquist, and T. Barkay. 2007. Stable isotope fractionation of mercury during its microbial reduction. Joint Molecular Biosciences Student Symposium, Rutgers University, New Brunswick, NJ. Feb 23, 2007. (Oral presentation)

- 33. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") Conference Proceedings Kritee, K., J. D. Blum, M. W. Johnson, B. A. Bergquist, and T. Barkay. 2007. Mercury stable isotope fractionation during microbial reduction of Hg(II) to Hg(0). Microbiology at Rutgers University: A mini symposium. Jan 25-26, 2007 (Poster presentation)
- 34. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") - Conference Proceedings - Kritee, K., J. D. Blum, M. W. Johnson, B. A. Bergquist, and T. Barkay. 2006. Microbial Mercury isotopic fractionation during the reduction of Hg(II) to Hg(0). North Eastern Microbiologists: Physiology, Ecology and Taxonomy Annual Meeting, Blue Mountain Lake, NY. June 23-26, 2006. (Oral presentation)
- 35. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") Conference Proceedings Kritee, K., J. D. Blum, M. W. Johnson, B. A. Bergquist, and T. Barkay. 2006. Measurement of mercury stable isotope fractionation during bacterial reduction. Theobald Smith Societys Annual Meeting, New Brunswick, NJ. June 2006. (Poster presentation)
- 36. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") Conference Proceedings Kritee, K., J. D. Blum, M. Johnson, B. A. Bergquist, and T. Barkay. 2006. The measurement of microbial mercury stable isotope fractionation and its potential utility for distinguishing between Hg sources. The 8th International Conference on Mercury as a Global Pollutant. Madison, WI. Aug. 1116, 2006. (Poster presentation)
- 37. 2003NJ43B ("Development of Supported Liquid Membrane Micro-Extraction (SLMME) followed by Ion-Pair Chromatography (IPC) for analysis of halo-acetic acids (HAAs) and chlorinated acid herbicides (CAHs) in water") - Articles in Refereed Scientific Journals - Wang, Xiaoyan and Somenath Mitra. 2006. Enhancing micro-scale membrane extraction by implementing a barrier film. Journal of Chromatography A. 1122: 1-6.
- 2003NJ43B ("Development of Supported Liquid Membrane Micro-Extraction (SLMME) followed by Ion-Pair Chromatography (IPC) for analysis of halo-acetic acids (HAAs) and chlorinated acid herbicides (CAHs) in water") - Conference Proceedings - Wang, Xiaoyan and Somenath Mitra. 2006. Enhancing micro-scale membrane extraction by implementing a barrier film. 45th Eastern Analytical Symposium, Somerset, NJ. Nov. 13-16, 2006. (Poster presentation)
- 2003NJ43B ("Development of Supported Liquid Membrane Micro-Extraction (SLMME) followed by Ion-Pair Chromatography (IPC) for analysis of halo-acetic acids (HAAs) and chlorinated acid herbicides (CAHs) in water") - Conference Proceedings - Mitra, Somenath, Xiaoyan Wang, Dawen Kou, and Ed Bishop. 2006. Total analytical systems for on-line, real-time water monitoring. Abstract SRM06-025. 58th Southeast Regional Meeting of the American Chemical Society, Augusta, GA. Nov. 1-4, 2006. (Oral presentation)
- 2003NJ43B ("Development of Supported Liquid Membrane Micro-Extraction (SLMME) followed by Ion-Pair Chromatography (IPC) for analysis of halo-acetic acids (HAAs) and chlorinated acid herbicides (CAHs) in water") - Conference Proceedings - Wang, Xiaoyan. 2005. Development of micro-scale and automated membrane extraction. New Jersey Institute of Technology, Newark, NJ. Oct. 5, 2005. (Invited seminar)
- 2004NJ75B ("Fate of Brominated Flame Retardants in New Jersey Wastewater Treatment Facilities")

 Conference Proceedings Fennell, D.E., F. Liu, E.-K. Son, A. Zarnadze, U. Krogmann, and L.A. Totten.
 2006. Fate of Brominated Flame Retardants in New Jersey Wastewater Treatment Facilities. USDA NECC 1010 Meeting, Ithaca, NY. October 18-19, 2006.
- 42. 2004NJ75B ("Fate of Brominated Flame Retardants in New Jersey Wastewater Treatment Facilities")
 Conference Proceedings Krogmann, U., D.E. Fennell, and L.A. Totten. 2006. Fate of Pharmaceuticals and Personal Care Products (PPCPs) and Brominated Flame Retardants (PBDEs) in Wastewater and

Biosolids. 91th Annual NJWEA Conference, Atlantic City, NJ. May 3, 2006.

43. 2004NJ75B ("Fate of Brominated Flame Retardants in New Jersey Wastewater Treatment Facilities")
- Conference Proceedings - Fennell, D.E., F. Liu, E.-K. Son, A. Zarnadze, U. Krogmann, and L.A. Totten.
2005. Fate of Brominated Flame Retardants in New Jersey Wastewater Treatment Facilities. USDA NE
1001 Meeting, Ithaca, NY. July 7-8, 2005.