

# **New Jersey Water Resources Research Institute**

## **Annual Technical Report**

### **FY 2005**

## **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. The faculty awards include one study of atmospheric deposition of nitrogen in highly urbanized areas; the project involved detailed monitoring of both soluble and particulate forms of both inorganic and organic N in a wetland site surrounded by high-volume highways, and the collaboration of an atmospheric scientist and an aquatic ecosystem ecologist, and a study of the adsorption-desorption dynamics of PCBs with respect to organic matter chemical structure, work that is expected to enhance the development of TMDLs for PCB-impaired water bodies.

Graduate student grants included projects that 1) addressed the efficacy of BMPs for stormwater pollutant removal and the effects of soil compaction on plant growth and infiltration rates in bioretention swales, 2) nitrogen dynamics and hydrology in urbanized basins, emphasizing denitrification dynamics in stormwater retention basins in developed areas, 3) the use of molecular methods, including DNA and RNA sequencing, to characterize the microbial consortia involved in the biodegradation of MBTE under sulfidogenic conditions, and 4) the development of a low-cost field-applicable chip that can be used to monitor total arsenic concentrations in water, based on supported liquid membrane extraction technology.

As detailed below, our information transfer program was hampered by the lengthy illness of the staff person responsible for managing the program; however, a new assistant has been hired and the information transfer program is being revitalized. However, despite the personnel problems, we were able to collaborate in supporting several meetings, producing two newsletters, redeveloping and expanding the website, and supporting a program of graduate student travel to national meetings to present research results.

## **Research Program**

# Examining Effects of Soil Compaction on Pollutant Removal Efficiency and Lifespan of a NJ Approved Stormwater Best Management Practice

## Basic Information

<b>Title:</b>	Examining Effects of Soil Compaction on Pollutant Removal Efficiency and Lifespan of a NJ Approved Stormwater Best Management Practice
<b>Project Number:</b>	2005NJ82B
<b>Start Date:</b>	3/1/2005
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<b>Congressional District:</b>	6
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<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Michael Mak, Christopher Obropta

## Publication

## The Problem

Probably the greatest detrimental change to water quality is due to urbanization. Urbanization is the change of land use from natural or agricultural, and it occurs in several steps. Urbanization changes the atmospheric composition, the hydrology of the watershed, the receiving streams and other water bodies, and the soil. Waste emissions increase dramatically. The sources of these emissions are industries, transportation, household heating, sewage conveyance and disposal, garbage collection and disposal, litter deposition, fallen leaves on impervious surfaces, and street salting just to name a few (Young *et al.* 1996).

Findings from the Nationwide Urban Runoff Program (NURP) instituted by the United States Environmental Protection Agency (USEPA) confirmed that the most ubiquitous constituents discovered in urban stormwater runoff are metals (USEPA 1983). According to Marsalek *et al.*, 1999, the constituents which predominately produce adverse effects on surrounding bodies of water are lead, copper, and zinc. The source of these metals is ubiquitous, and due to the inability of the surrounding environment to destroy or transform these constituents, urban stormwater runoff is of great concern to our watersheds (FHWA 1998).

Total Maximum Daily Loads (TMDLs) for metals are created in an effort to identify sources of point and non-point pollution in impaired bodies of water. Currently, there are 11,230 waterways impaired by metals within the United States (USEPA 2005). Two hundred eighty one of these impairments are located in the State of New Jersey. It is of importance to note that impairment by metals account for approximately 20% of the state's impairments (NJDEP 2005). It is of greater importance to note that the impairment by metals account for approximately 19% of the total impairments in the nation's waterways. Metals account for the highest number of impairments in the nation (USEPA 2005). For this reason, it is of principal importance to provide treatment alternatives for the mitigation of these impairments. Currently the most accepted form of treatment for polluted stormwater is the development of structural stormwater best management practices (BMPs).

Due to the increasing awareness of the potential hazards of metals in the nation's waterways, legislation and control measures under the National Stormwater Program are in effect or are pending (USEPA 1999). Control measures include the Surface Water Quality Standards created by the New Jersey Department of Environmental Protection (NJDEP) for the regulation of safe levels of water quality throughout the local waterways. Surface water quality criteria for lead, copper, and zinc are designated as 5 µg/L, 5.6 µg/L, and 120 µg/L respectively. These numbers represent the chronic criteria as a four-day average, expressed in maximum concentrations of micrograms per liter (NJDEP 2005).

In addition, soil loss from construction sites can reach magnitudes of over 100 tons per hectare per year. A few percent of the watershed under construction can contribute a major portion of the sediment being carried by the stream, thus affecting the streams themselves, sometimes irreversibly. Straightening and lining with concrete destroys the natural habitat, and the streams can no longer support

fish and other biotic populations. Also, increased imperviousness increases the volume of surface runoff, while at the same time diminishes groundwater recharge.

Furthermore, unsewered communities are typically served by on-site disposal systems such as septic tanks that discharge the wastewater into the soil. Septic tanks provide only minimal treatment by sedimentation and anaerobic decomposition. There are approximately fifty million households in the United States with septic systems, representing the highest total volume of wastewater discharged to the groundwater and the most recorded source of groundwater contamination. When the adsorption capacity of the soil is exhausted, contamination of surface waters by organics and pathogenic microorganisms may occur and be severe (Pitt *et al.* 1996).

In addition, the use of lawn care chemicals in the American suburbs is also a concern. The typical suburban dweller with a lawn uses more chemicals, i.e. fertilizers and pesticides, per lawn area than a farmer would. Therefore, losses of these chemicals into surface and groundwater can be considerable. A steady increase of nitrate contamination of groundwater as well as detection of the chemicals in suburban surface runoff is often exhibited (Novotny 1995).

One of the key water quality stormwater management techniques is bioretention (sometimes referred to as "rain gardens"). Bioretention is a terrestrial-based, water quality, and water quantity control practice using the chemical, biological, and physical properties of plants, microbes, and soils for removal of pollutants from stormwater runoff. Some of the processes that may take place in a bioretention facility include sedimentation, adsorption, filtration, volatilization, ion exchange, decomposition, phytoremediation, bioremediation, and storage capacity.

Bioretention is a fairly new best management practice (BMP), developed in 1987 by Prince George's County, Maryland (PGDER 1993), to be employed by the United States Environmental Protection Agency (USEPA 1999) and the New Jersey Department of Environmental Protection (NJDEP 2000). It can be conceptualized as a modified infiltration trench (Young *et al.* 1996; USEPA 1999). Bioretention areas are originally modeled after the hydrologic and physical characteristics of an upland terrestrial forest or a meadow, as opposed to a wetland community (Coffman and Winogradoff). Typically designed with indigenous trees, shrubs, and grasses known to have high pollutant removal capacities, the bioretention cell can provide both stormwater quantity and quality control (NJDEP 2004). Bioretention areas typically consist of a surrounding grass buffer strip, sand bed infiltration area, ponding area, organic mulch layer, planting soil, and plants. The typical bioretention area consists of five basic features: pretreatment, treatment, conveyance, maintenance reduction, and landscaping (Environmental Protection Handbook).

A well-designed bioretention area consists of: (1) a grass filter strip (or grass channel) between the contributing drainage area and the ponding area, (2) ponding area containing vegetation with a planting soil bed, (3) organic/mulch layer, (4) gravel and perforated pipe underdrain system to collect runoff that has filtered through the soil layers (bioretention areas can optionally be designed to infiltrate into the soil).

Bioretention area design will also include some of the following:

(1) optional sand filter layer to spread flow, filter runoff, and aid in aeration and drainage of the planting soil, (2) a stone diaphragm at the beginning of the grass filter strip to reduce runoff velocities and spread flow into the grass filter, and (3) an inflow diversion or an overflow structure consisting of one of five main methods: (a) a flow diversion structure, (b) an inlet deflector, (c) a slotted curb with the parking lot graded to divert the runoff into the facility, (d) a short deflector weir (maximum height 6 inches) designed to divert the maximum water quality peak flow into the bioretention area, and (e) an in-system overflow consisting of an overflow catch basin inlet and/or a pea gravel curtain drain overflow (PGDER 1993).

During construction of the basin, the planting soil bed may be subject to compaction by construction equipment (Pitt *et al.* 2002). The use of equipment with narrow tracks or narrow tires, rubber tires with large lugs, or high pressure tires will cause excessive compaction resulting in reduced infiltration rates and is unacceptable. Compaction will significantly contribute to design failure (PGDER 1993). Metals are of particular concern because of possible buildup within treatment facilities which raises questions about their long-term fate (Davis *et al.* 2003). Also, metals such as lead, copper, and zinc present a health risk when exceeding the regulated criterion (Pitt *et al.* 1996).

The design of a bioretention system must account for soil compaction within the basin. Compaction can be defined as a process of densification due to the removal of air voids when external stress is applied to the soil (Gray 2002). The effects of soil compaction on soil strength, hydraulic conductivity, and volume stability have been investigated thoroughly (Lambe and Whitman 1969; Seed and Chan 1959). Compaction in soil influences plant growth in multiple dimensions, primarily based on the degree of compaction. High levels of soil compaction result in high soil bulk densities to a degree at which plant roots are hindered from penetrating the soil. Furthermore, due to the high bulk density of compacted soils, filtration rates through the soil media are reduced, causing excessive runoff through the system, and therefore affecting the efficiency of bioretention BMPs. The bioretention media is provided inadequate time to adsorb the metals and the efficiency of the BMP is reduced (Pitt *et al.* 2002).

A bioretention area is an innovative practice for pollutant control. It is a facility that combines the concepts of detention ponds and bioretention in an attempt to provide higher overall pollutant removal. However, little is known about the overall efficiency of bioretention. Typical bioretention facilities consist of a vegetated strip of land that allows stormwater percolation for biological and physical treatment. Bioretention is typically used in an area of 1 acre or less and consists of an excavated bed filled with sand and covered with a layer of permeable soil. Terrestrial vegetation with a high moisture tolerance is suggested for planting in bioretention areas.

Bioretention areas are presumed to be able to remove 80% of the total suspended solids (TSS) load in typical urban post-development runoff when sized, designed, constructed, and maintained in accordance with the recommended specifications. Undersized or poorly designed bioretention areas can reduce TSS

removal performance. The following design pollutant removal rates are conservative average pollutant reduction percentages for design purposes derived from sampling data, modeling, and professional judgment. In a situation where a removal rate is not deemed sufficient, additional controls may be put in place at the given site in a series or “treatment train” approach (Davis *et al.* 2003).

- Total Suspended Solids – 80%
- Total Phosphorus – 60%
- Total Nitrogen – 50%
- Fecal Coliform – insufficient data
- Heavy Metals – 80%

But what happens when the bioretention area is being built, and the planting soil gets compacted? Our investigation will explore five degrees of soil compaction within the bioretention basin. Soil compaction levels will range from light bulk densities (1.07 g/cm<sup>3</sup>) to growth-limiting bulk densities (1.65 g/cm<sup>3</sup>). This will be accomplished through five sets of bench scale bioretention column systems. The metal removal efficiency of the bioretention system for each degree of compaction will be analyzed. Also, an analysis of the metal removal efficiencies will provide a discussion for the optimal degree of soil compaction necessary for the optimization of the bioretention system. This investigation will assist in the mitigation of our nation’s impaired waterways and provide support for further research in this field.

## **Methodology**

For this experiment, fifteen columns were constructed using 8-inch in diameter schedule 40 PVC (poly vinyl chloride) piping (AASHTO M-278). Three of these columns were see through, or clear; the rest were the standard white. Each of these columns had an 8-inch to 6-inch reducing coupling and a 6-inch end cap on one end with the other end open to the atmosphere of the laboratory. Into the end cap of each column, a quarter inch hole was drilled, using a brand new titanium drill bit, to allow the synthetic runoff water to flow through. The end that was open to the atmosphere was covered by placing an autoclave bag over the entire pipe. Between the pipe and the reducer coupling was a single layer of filter fabric, while the reducer coupling below was filled with pea gravel (AASHTO M-43).

All of the columns in this experiment were designed to hold 18 inches of soil, rather than the minimum of 3 feet required by the New Jersey Department of Environmental Protection (NJDEP), and 2 inches of mulch with 6-8 inches to spare, for the ponding of the synthetic runoff water. The soil used was consistent with that of the planting soil of a bioretention area: one-third compost, one-third topsoil, and one-third sand (AASHTO M-6/ASTM C-33). For this experiment, the one foot sand filter at the bottom of the planting soil was not used. These columns were separated into five groups of three, with each group of three holding a different amount of the bioretention area planting soil mix. The first group, which was called Series A, held 35 pounds of soil mix; Series B held 40 lbs. of soil mix; Series C held 45 lbs., Series D held 50 lbs., and Series E held 55 pounds of soil mix. The soil was

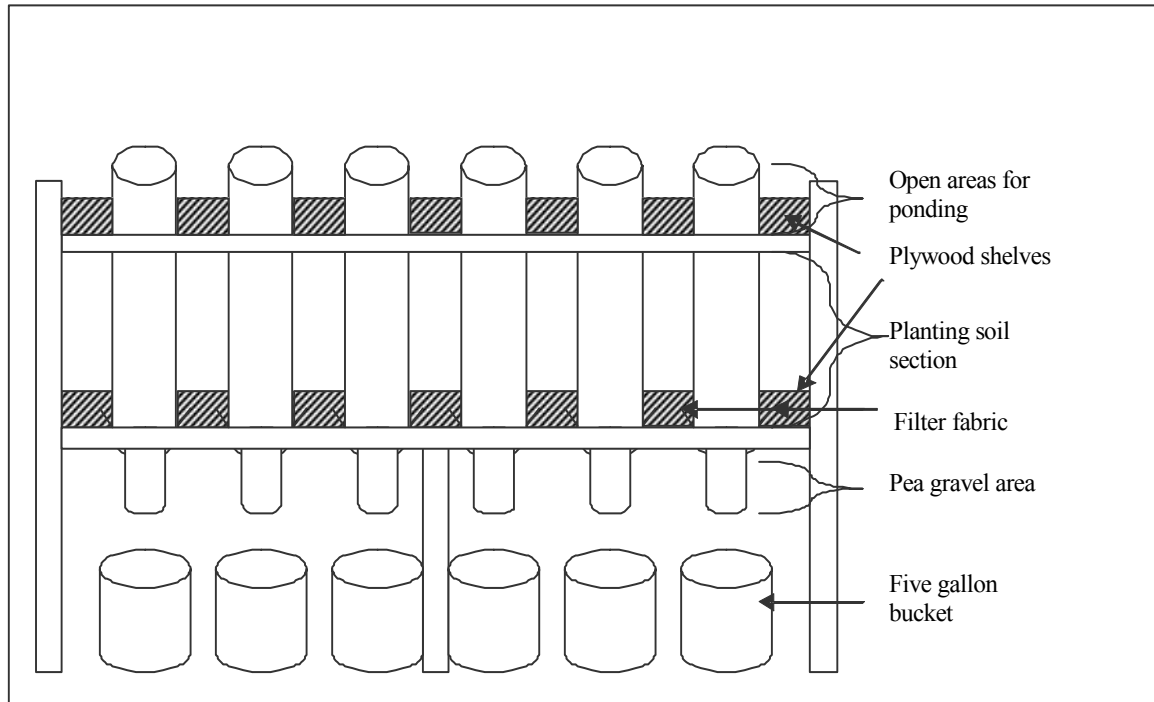


Figure 1: Schematic of bench containing six experimental bioretention area columns.

compacted using a circular piece of plywood, a two-foot section of a 2" by 4", and a small sledgehammer.

Three benches were constructed using heavy-duty plywood, 2" by 4"s, metal brackets, and screws. Each bench was designed to hold six columns, and to hold each column high enough in order to slide a five-gallon pail under the column to facilitate the collection of: whatever synthetic runoff water flowed through the column, and the samples. The last bench held only three columns, even though it was designed to hold six. These benches were approximately 8 feet long, 2 feet wide, and four feet high. They had two shelves with wholes cut in them, for the columns. The 8-inch by 6-inch reducer coupling rested on the lower shelf with the six-inch side of the reducer coupling able to protrude, but not the eight-inch side, see Figure 1 below.

According to the NJDEP's New Jersey Stormwater Best Management Practices Manual (2004) a stormwater quality design storm has a total depth of 1.25 inches and a total duration of 2 hours, or 0.625 in/hr (0.265 mm/min) for 2 hours. This is based on rainfall data collected between 1913 and 1975 in Trenton, New Jersey.

Furthermore, according to the Bioretention Manual (2002), developed by Prince George's County, Maryland, the minimum size for a bioretention area is 7.2% of the drainage area. For this experiment, each experimental bioretention area column was set at 5% of the total drainage area. Then, each column was potentially draining an area approximately 1005.3 square inches (about 7 square feet). Going further, using a stormwater quality design storm and the rational method with a coefficient of 0.8, each bioretention area column would be filtering approximately 8.37 cubic inches per minute (137.21 mL/min).

<b>Business</b>	
Downtown Areas	0.70 – 0.95
Neighborhood Areas	0.50 – 0.70
<b>Residential</b>	
Single-family	0.30 – 0.50
Multi-family detached	0.40 – 0.60
Multi-family attached	0.60 – 0.75
Residential suburban	0.25 – 0.40
Apartments	0.50 – 0.70
Parks, cemeteries	0.10 – 0.25
Playgrounds	0.20 – 0.35
Railroad yards	0.20 – 0.40
Unimproved areas	0.10 – 0.30
Drives and walks	0.75 – 0.85
Roofs	0.75 – 0.95
<b>Streets</b>	
Asphalt	0.70 – 0.95
Concrete	0.80 – 0.95
Brick	0.70 – 0.85

The rational method, first developed in 1889 by Kuichling, is a simple technique for estimating a design discharge from a small watershed. In fact, it was developed for small drainage basins in urban areas. The rational method ( $Q = CIA$ ) is the basis for the design of many small structures. The  $A$  in the equation stands for the area of the drainage basin. The  $I$  stands for the average rainfall intensity, and the  $C$  stands for the runoff coefficient, representing a ratio of runoff to rainfall. The runoff coefficient is the variable of the rational method least susceptible to precise determination and requires judgment and understanding on the part of the designer. Table 1 lists the recommended ranges for the runoff coefficient value classified with respect

to the general land use.

The 137.21 mL/min per each of the 15 column turns out to be a total of 246,978 mL or 65.25 gallons for the two hour design storm. To transport all of this synthetic runoff water, two 20-gallon white plastic drums and two 50-liter carboys were used. To deliver the 137.21 mL/min to each column required the use of pumps (Masterflex model # EW-07553-70 L/S variable speed) and pump heads (Masterflex model # EW-07016-20 standard pump head for L/S 16 tubing) and of course tubing (Masterflex 06404-16 noprrene). To cut down on costs, only three pumps and nine pump heads were purchased for this experiment. Each pump held three pump heads, so only three sets of three columns could be run at a time, rather than running all fifteen columns at the same time.

The synthetic runoff water was modeled after Davis *et al.* (2001) which was based on runoff sampling data obtained by Prince George's County (PGDER 1993). Table 2 specifies the recipe for the synthetic runoff water. However, since this experiment used two of each of the two different sized containers, two different mixtures of chemicals were required. Furthermore, since four containers were used in this experiment, each of the two different mixtures had to be prepared twice. This was done in the concentrated form in a 500-mL container. The two 20-gallon and the two 50-liter containers were filled with qualitative water (Q-water) with a resistance of 17.5 – 17.7 megohm-cm or better. This had to be done for each of the eight different runs of this experiment.

The samples were first collected in 500-mL Nalgene polypropylene containers (02-893C Fisher Scientific, [www.fishersci.com](http://www.fishersci.com)). Then a Target all-plastic 20-mL syringe (03-377-24 Fisher Scientific, [www.fishersci.com](http://www.fishersci.com)) was used to remove the

Table 1: General runoff coefficients for the rational method, adapted from Thompson 2005.



Pollutant	Chemical	Concentration (mg/L)
<i>Nutrients</i>		
Nitrate	NaNO <sub>3</sub>	2 (as N)
Phosphate	Na <sub>2</sub> HPO <sub>4</sub>	0.6 (as P)
<i>Heavy Metals</i>		
Copper	CuSO <sub>4</sub>	0.08 (as Cu)
Lead	PbCl <sub>2</sub>	0.08 (as Pb)
Zinc	ZnCl <sub>2</sub>	0.6 (as Zn)
<i>Dissolved Solids</i>	CaCl <sub>2</sub>	120
<i>pH</i>		7.0

Table 2: Synthetic stormwater recipe modeled after the recipe used by Davis *et al.* 2001 which was based on data obtained by Prince George's County.

sample from the 500-mL container. The next step in acquiring the sample, was to attach an Acrodisc ion chromatography syringe filter (28143-292 VWR International, www.vwr.com) to the syringe and push 10-mL of the sample through the filter into a Corning Brand 15-mL centrifuge tube (05-538-53F Fisher Scientific, www.fishersci.com). Anything that was to come into contact with the sample was first washed with 10% hydrochloric acid (HCl). This was done by filling the items with 10% HCl and then letting them sit in an oven (Fisher Scientific 13-247-

637G, www.fishersci.com) at 60 degrees C overnight. Upon taking the items out in the morning to cool, they were inverted. Once they had cooled, each item was rinsed 5 times with Q-water.

Prior to starting the first run, two gallons of steam distilled water was poured into each column. This was done mainly to wet down the planting soil mix, but it was also used to see whether or not the column would change the pH of the synthetic runoff water. For this run, thirty gallons of distilled water were purchased from local grocery stores, and two gallons were poured slowly into each bioretention area column. The pH was taken prior to the pouring, using a calibrated Accumet Basic pH meter (Fisher Scientific, 13-636-AB15P, www.fishersci.com), by adding a pinch (0.1 g) of salt (NaCl) to 200 mL of the distilled water. The pH was taken after the distilled water had flowed through the column by collecting a sample in a Corning Brand 15-mL centrifuge tube from each column and measuring the pH of each sample.

The second run was conducted two weeks after the columns were wet down and was the first of the eight runs using Q-water. This run was used to collect enough of the samples in order to develop the methods for analysis, i.e. after collecting the sample in the 500-mL container three 10-mL samples were collected instead of one, one for each metal. This was done for each sampling time, or a total of three times. Each sample was then preserved using Optima nitric acid (Fisher Scientific, A467-250, www.fishersci.com). Enough nitric acid was added to lower the pH of the sample to 2 or below, which made each sample about a 0.2% solution of nitric acid.

For the 2<sup>nd</sup> through the 8<sup>th</sup> runs, only one 10-mL sample was collected per column per sampling time. Since the design storm was a 2-hour event, a sample was collected when the synthetic runoff water first started coming out of the

column, another sample was collected 1-hour later, and the final sample was collected from the last of the synthetic runoff water to flow through the columns. Except for the last run during which only the first and last samples were collected, due to the fact that the Corning Brand 15-mL centrifuge tubes were running low.

In addition to analyzing for lead, copper, and zinc; nitrate and phosphate were also analyzed. One 125-mL Nalgene polypropylene container (Fisher Scientific, [www.fishersci.com](http://www.fishersci.com)) was filled from the stormwater runoff flowing through each column for each run for this purpose. One 125-mL sample of the synthetic stormwater runoff from each of the four containers (two 20-gallon and two 50-liter) was collected as well. Lead, copper, and zinc were analyzed by graphite furnace atomic absorption spectrophotometry (Perkin Elmer, 4100ZL, [www.las.perkinelmer.com](http://www.las.perkinelmer.com)). Lead was analyzed using USEPA's method #239.2 with a concentration range of 5-100 µg/L and a detection limit of 1 µg/L. Copper was analyzed using USEPA's method #220.2. The concentration range was 5-100 µg/L, and the detection limit was 1 µg/L. Zinc was analyzed using USEPA's method #289.2 with a concentration range of 0.2-4 µg/L. The method detection limit was 0.05 µg/L. No matrix modifiers were used in any of these methods; however, all three methods required optimization. Only the Zinc method required the dilution of the sample, and in order to calibrate, the background correction had to be turned off for this method as well. Nitrate and phosphate were analyzed by flow injection analysis spectrophotometry (Lachat, QuikChem 8500, [www.lachatinstruments.com](http://www.lachatinstruments.com)). Nitrate was analyzed using Lachat's method #10-107-04-1-A. The concentration range was 0.2-20 mg NO<sub>3</sub>-N/L, and the detection limit was 0.01 mg NO<sub>3</sub>-N/L. Phosphate was analyzed using Lachat's method #10-115-01-1-A with a concentration range of 0.01-2 mg PO<sub>4</sub>-P/L, and a detection limit of 0.002 mg PO<sub>4</sub>-P/L.

### **Principal Findings and Significance**

The lead, copper, and zinc data are included in Tables 3 through 17 which follow, and the nitrate and phosphate data can be found in Tables 18 to 32.

		Column 1											
		Pb				Cu				Zn			
		in		out	in		out	in		out		out	
20-Oct	first run	36.1 ± 1.33	ND	±	69.7 ± 3.05	16.5	±	533.5 ± 0.906	6.45	±	2.34 ± 0.442	1.812	
			ND	±		21.1	±		3.92	±		0.231	
			ND	±		18.6	±		2.12				
					MDL	0.57		MDL	0.66				
3-Nov	second run	8.1 ± 0.74	ND	±	10.2 ± 0.76	13.2	±	217.1 ± 0.708	22.26	±	4.02 ± 0.313	0.873	
			ND	±		10.1	±		11.12	±		0.65	
			ND	±		10.2	±		0.78				
					MDL	0.44		MDL	0.26				
17-Nov	third run	24.6 ± 0.96	ND	±	85.8 ± 13.07	18.9	±	508.2 ± 0.398	11.54	±	8.17 ± 1.166	0.347	
			ND	±		9.7	±		7.88	±		0.782	
			ND	±		9	±		1.26				
					MDL	0.46		MDL	0.76				
1-Dec	fourth run	18.2 ± 0.36	1.8	±	64.8 ± 1.59	10.8	±	524 ± 2.55	21.5	±	3.8 ± 0.43	2.9	
			1.9	±		10.5	±		16.9	±		1.1	
			2	±		11.1	±		0.29				
					MDL	0.33		MDL	0.55				
15-Dec	fifth run	36.6 ± 1.94	0.5	±	68.9 ± 0.48	9.7	±	120 ± 0.01	17.6	±	2.9 ± 0.23	0.04	
			1.2	±		11.2	±		12	±		0.39	
			1.2	±		8.6	±		0.21				
					MDL	0.31		MDL	0.48				
22-Dec	sixth run	29.2 ± 0.1	ND	±	60.6 ± 1.37	9.8	±	226 ± 3.35	8.6	±	5.4 ± 0.67	0.46	
			0.4	±		9.7	±		9.8	±		1.18	
			5.2	±		9.5	±		0.3				
					MDL	0.29		MDL	0.57				
29-Dec	seventh run	9.4 ± 0.08	ND	±	65 ± 3.6	12	±	338 ± 0.56	61.8	±	18.8 ± 0.52	1.21	
			0.3	±		8.6	±		59.9	±		0.52	
			0.5	±		7.6	±		0.25				
					MDL	0.32		MDL	0.63				
13-Feb	eighth run	0	ND	±	0	8.4	±	0	22.1	±	10.2 ± 0.64	1.29	
			0.4	±		6	±		0.13				
					MDL	0.27		MDL	0.43				

Table 3: Metals data for bioretention area column 1

		Column 2											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	36.1	± 1.33	ND	±	69.7	± 3.05	14.1	± 1.84	533.5	± 0.906	12.69	± 3.946
				ND	±			21.9	± 2.37			4.35	± 0.111
				ND	±			17.4	± 1.91			1.6	± 0.085
3-Nov	second run	8.1	± 0.74	ND	±	10.2	± 0.76	15.7	± 0.82	217.1	± 0.708	29.8	± 0.752
				ND	±			12.7	± 0.42			8.03	± 0.154
				ND	±			12.3	± 0.21			5.53	± 0.086
17-Nov	third run	24.6	± 0.96	ND	±	85.8	± 13.07	19.6	± 1.49	508.2	± 0.398	13.18	± 0.203
				ND	±			15.3	± 0.58			9.81	± 0.082
				ND	±			13.7	± 0.92			11.29	± 0.233
1-Dec	fourth run	18.2	± 0.36	5.3	± 0.2	64.8	± 1.59	15.2	± 0.44	524	± 2.55	177	± 6.9
				2	± 0.04			13.9	± 0.45			20.4	± 2.4
				2.3	± 0.81			12.9	± 0.03			5.4	± 0.2
15-Dec	fifth run	36.6	± 1.94	0.5	± 0.16	68.9	± 0.48	11.4	± 0.61	120	± 0.01	25.6	± 0.18
				0.9	± 0.16			10.3	± 0.03			8.4	± 0.26
				0.8	± 0.06			10.3	± 0.12			6.3	± 0.72
22-Dec	sixth run	29.2	± 0.57	0.2	± 0.18	60.6	± 1.37	11.1	± 1.13	226	± 3.35	43.6	± 1.18
				ND	±			11.4	± 0.33			22.4	± 0.49
				1.4	± 0.44			9.4	± 0.38			10.7	± 0.56
29-Dec	seventh run	9.4	± 0.69	ND	±	65	± 3.6	13.2	± 0.51	338	± 0.56	76.3	± 0.35
				ND	±			11.2	± 0.4			66.1	± 0.91
				ND	±			13.4	± 0.19			32	± 0.44
13-Feb	eighth run	0		1.3	± 1.02	0		10	± 0.85	0		46.9	± 0.77
				0.2	± 0.46			8.1	± 1.98			14.1	± 0.42

Table 4: Metals data for bioretention area column 2

		<b>Column 3</b>											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	36.1	± 1.33	ND	±	69.7	± 3.05	25.2	± 0.1	533.5	± 0.906	3.64	± 1.244
				ND	±			28.1	± 0.59			8.61	± 2.832
				ND	±			25	± 1.8			4.31	± 0.028
3-Nov	second run	8.1	± 0.74	ND	±	10.2	± 0.76	13.4	± 0.38	217.1	± 0.708	27	± 0.868
				ND	±			12.2	± 0.15			13.81	± 0.443
				ND	±			8.8	± 1.01			1.73	± 0.071
17-Nov	third run	24.6	± 0.96	ND	±	85.8	± 13.07	15.3	± 1.13	508.2	± 0.398	11.53	± 0.293
				ND	±			12.9	± 0.3			7.69	± 0.191
				ND	±			11.6	± 0.75			6	± 0.131
1-Dec	fourth run	18.2	± 0.36	2.1	± 0.04	64.8	± 1.59	11.3	± 1.03	524	± 2.55	59.6	± 0.43
				2.2	± 0.49			10.8	± 0.1			18.7	± 0.36
				1.8	± 0.13			9.3	± 0.2			2.5	± 0.42
15-Dec	fifth run	36.6	± 1.94	0.2	± 0.23	68.9	± 0.48	8.6	± 0.59	120	± 0.01	19.2	± 0.24
				0.5	± 0.14			7.2	± 0.06			10.2	± 0.03
				0.8	± 0.01			6.9	± 0.16			3.6	± 0.17
22-Dec	sixth run	29.2	± 0.57	0.2	± 0.16	60.6	± 1.37	8.2	± 0.89	226	± 3.35	44.1	± 9.11
				0.1	± 0.14			8.4	± 0.75			4.2	± 0.68
				0.8	± 0.46			11.1	± 0.31			1.3	± 0.37
29-Dec	seventh run	9.4	± 0.69	ND	±	65	± 3.6	9.8	± 0.68	338	± 0.56	81.8	± 1.47
				ND	±			7.7	± 0.16			39.4	± 0.49
				0.4	± 0.13			7.2	± 0.1			18.5	± 0.63
13-Feb	eighth run	0		0.5	± 0.25	0		6.7	± 0.87	0		25.9	± 1.09
				ND	±			6.6	± 1.27			14.9	± 0.41

Table 5: Metals data for bioretention area column 3

		Column 4											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	36.1	± 1.33	ND	±	69.7	± 3.05	21.1	± 0.71	533.5	± 0.906	6.28	± 0.547
				ND	±			18.5	± 1.33			4.34	± 0.157
				ND	±			14.9	± 2.43			3.22	± 0.14
3-Nov	second run	8.1	± 0.74	ND	±	10.2	± 0.76	11.6	± 0.2	217.1	± 0.708	23.73	± 0.265
				ND	±			14.1	± 0.2			9.56	± 0.183
				ND	±			12.4	± 0.61			3.49	± 0.13
17-Nov	third run	24.6	± 0.96	ND	±	85.8	± 13.07	11.7	± 0.04	508.2	± 0.398	16.42	± 0.271
				ND	±			14.7	± 0.43			9.06	± 0.029
				0.5	± 0.49			12.9	± 0.23			7.3	± 0.155
1-Dec	fourth run	18.2	± 0.36	2.7	± 0.13	64.8	± 1.59	9.4	± 0.56	524	± 2.55	28.5	± 1.66
				2.1	± 0.1			9.6	± 0.22			21.3	± 1.13
				2.2	± 0.14			9.3	± 0.26			7.8	± 0.81
15-Dec	fifth run	36.6	± 1.94	0.2	± 0.14	68.9	± 0.48	9.5	± 0.84	120	± 0.01	25.1	± 0.24
				0.3	± 0.09			8.1	± 0.19			10.8	± 0.29
				0.5	± 0.18			7.1	± 0.11			5	± 0.65
22-Dec	sixth run	29.2	± 0.57	ND	±	60.6	± 1.37	11.3	± 0.88	226	± 3.35	26	± 2.32
				ND	±			10.8	± 0.33			6.2	± 2.15
				0.1	± 0.67			8.6	± 1.17			0.9	± 0.5
29-Dec	seventh run	9.4	± 0.69	ND	±	65	± 3.6	7.9	± 0.7	338	± 0.56	57	± 0.5
				ND	±			7.4	± 0.52			32.2	± 0.05
				0.2	± 0.13			5.2	± 1.24			15	± 0.63
13-Feb	eighth run	0		0.4	± 0.45	0		15.4	± 0.4	0		17.1	± 0.51
				ND	±			5.1	± 0.41			10.7	± 0.17

Table 6: Metals data for bioretention area column 4

		Column 5											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	36.1 ± 1.33	ND ±	ND ±	69.7 ± 3.05	20.7 ± 1.41	14.1 ± 1.05	533.5 ± 0.906	3.08 ± 0.261	8.49 ± 0.121	3.18 ± 0.257	ND ±	ND ±
			ND ±	ND ±		13.5 ± 2.61	10.6 ± 0.1		10.4 ± 0.28	23.04 ± 1.369		5.33 ± 0.276	
			ND ±	ND ±		11.1 ± 0.35	11.1 ± 0.35		21.39 ± 0.67				
3-Nov	second run	8.1 ± 0.74	ND ±	ND ±	10.2 ± 0.76	10.6 ± 0.1	10.4 ± 0.28	217.1 ± 0.708	23.04 ± 1.369	5.33 ± 0.276	21.39 ± 0.67	ND ±	ND ±
			ND ±	ND ±		11.1 ± 0.35	11.1 ± 0.35		21.39 ± 0.67				
			ND ±	ND ±		11.1 ± 0.35	11.1 ± 0.35		21.39 ± 0.67				
17-Nov	third run	24.6 ± 0.96	ND ±	ND ±	85.8 ± 13.07	10.6 ± 0.95	15.6 ± 0.49	508.2 ± 0.398	13.22 ± 0.076	9.3 ± 0.212	6.38 ± 0.212	1.1 ± 0.53	15.5 ± 0.47
			1.1 ± 0.53	1.1 ± 0.53		15.5 ± 0.47	15.5 ± 0.47		6.38 ± 0.212				
			1.1 ± 0.53	1.1 ± 0.53		15.5 ± 0.47	15.5 ± 0.47		6.38 ± 0.212				
1-Dec	fourth run	18.2 ± 0.36	2.2 ± 0.69	2.2 ± 0.87	64.8 ± 1.59	8.7 ± 0.48	8.6 ± 0.22	524 ± 2.55	42 ± 0.36	22.4 ± 1.69	9.3 ± 0.65	2.4 ± 0.95	7.4 ± 0.2
			2.2 ± 0.87	2.2 ± 0.87		7.4 ± 0.2	7.4 ± 0.2		22.4 ± 1.69				
			2.4 ± 0.95	2.4 ± 0.95		7.4 ± 0.2	7.4 ± 0.2		22.4 ± 1.69				
15-Dec	fifth run	36.6 ± 1.94	0.3 ± 0.09	0.2 ± 0.08	68.9 ± 0.48	10.8 ± 0.75	6.5 ± 0.25	120 ± 0.01	11.5 ± 0.29	11.8 ± 0.04	4.5 ± 0.51	0.3 ± 0.09	6 ± 0.63
			0.2 ± 0.08	0.2 ± 0.08		6 ± 0.63	6 ± 0.63		11.8 ± 0.04				
			0.3 ± 0.15	0.3 ± 0.15		6 ± 0.63	6 ± 0.63		11.8 ± 0.04				
22-Dec	sixth run	29.2 ± 0.57	ND ±	ND ±	60.6 ± 1.37	12.3 ± 0.25	13.6 ± 0.19	226 ± 3.35	20.8 ± 1.61	9.8 ± 2.44	2.4 ± 0.68	ND ±	ND ±
			ND ±	ND ±		11.3 ± 0.16	11.3 ± 0.16		9.8 ± 2.44				
			ND ±	ND ±		11.3 ± 0.16	11.3 ± 0.16		9.8 ± 2.44				
29-Dec	seventh run	9.4 ± 0.69	ND ±	ND ±	65 ± 3.6	9.8 ± 0.41	8.3 ± 0.4	338 ± 0.56	60.5 ± 0.55	64.6 ± 0.77	18.4 ± 0.53	0.4 ± 0.12	7.2 ± 0.38
			ND ±	ND ±		7.2 ± 0.38	7.2 ± 0.38		64.6 ± 0.77				
			0.4 ± 0.12	0.4 ± 0.12		7.2 ± 0.38	7.2 ± 0.38		64.6 ± 0.77				
13-Feb	eighth run	0	ND ±	ND ±	0	6 ± 0.59		0	30.8 ± 1.21		11.2 ± 0.43	ND ±	ND ±
			ND ±	ND ±		5.5 ± 1.48	5.5 ± 1.48		11.2 ± 0.43				

Table 7: Metals data for bioretention area column 5

		Column 6											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	36.1 ± 1.33	ND ±	ND ±	23.4 ± 1.56	69.7 ± 3.05	17.7 ± 1.37	20.7 ± 4.2	533.5 ± 0.906	3.33 ± 0.582	3.76 ± 0.121	1.24 ± 0.043	
			ND ±		9.4 ± 0.99			21.73 ± 0.712					
			ND ±		12.3 ± 0.15		10.6 ± 0.29	7.33 ± 0.246		6.07 ± 0.058			
3-Nov	second run	8.1 ± 0.74	ND ±	ND ±	9.4 ± 0.99	10.2 ± 0.76	12.3 ± 0.15	10.6 ± 0.29	217.1 ± 0.708	21.73 ± 0.712	7.33 ± 0.246	6.07 ± 0.058	
			ND ±		8.9 ± 0.27			16.3 ± 0.205					
			ND ±		13.9 ± 0.53		15.3 ± 0.44	10.4 ± 0.046		10.71 ± 0.042			
17-Nov	third run	24.6 ± 0.96	0.7 ± 0.59	2.1 ± 0.07	8.9 ± 0.27	85.8 ± 13.07	9.9 ± 0.15	10.4 ± 0.41	508.2 ± 0.398	33.8 ± 0.52	21.8 ± 2.55	4.4 ± 1.03	
			ND ±	2.9 ± 0.49	8.5 ± 0.31			39 ± 0.31					
			ND ±	4.6 ± 1.17	6 ± 0.3		6.3 ± 0.63	12.6 ± 0.51		6.1 ± 0.08			
1-Dec	fourth run	18.2 ± 0.36	0.6 ± 0.09	0.7 ± 0.07	8.5 ± 0.31	64.8 ± 1.59	6 ± 0.3	6.3 ± 0.63	524 ± 2.55	39 ± 0.31	21.8 ± 2.55	4.4 ± 1.03	
			0.5 ± 0.1		6 ± 0.3			12.6 ± 0.51					
					6.3 ± 0.63			6.1 ± 0.08					
15-Dec	fifth run	36.6 ± 1.94	0.6 ± 0.09	0.7 ± 0.07	8.5 ± 0.31	68.9 ± 0.48	6 ± 0.3	6.3 ± 0.63	120 ± 0.01	39 ± 0.31	21.8 ± 2.55	4.4 ± 1.03	
			0.5 ± 0.1		6 ± 0.3			12.6 ± 0.51					
					6.3 ± 0.63			6.1 ± 0.08					
22-Dec	sixth run	29.2 ± 0.57	ND ±	ND ±	12.3 ± 0.83	60.6 ± 1.37	11.6 ± 0.24	10.9 ± 0.52	226 ± 3.35	18.5 ± 1.87	8.1 ± 3.26	5.2 ± 1.45	
			ND ±		7.3 ± 0.32			54.1 ± 0.96					
			ND ±		6.7 ± 0.03		6.2 ± 0.32	39.7 ± 0.61		21.8 ± 1.04			
29-Dec	seventh run	9.4 ± 0.69	0.4 ± 0.05	0.5 ± 0.05	7.3 ± 0.32	65 ± 3.6	6.7 ± 0.03	6.2 ± 0.32	338 ± 0.56	54.1 ± 0.96	39.7 ± 0.61	21.8 ± 1.04	
			0.5 ± 0.05		6.7 ± 0.03			39.7 ± 0.61					
					6.2 ± 0.32			21.8 ± 1.04					
13-Feb	eighth run	0	ND ±	ND ±	5.2 ± 0.75	0	5.6 ± 0.24		0	33.3 ± 0.36			
			ND ±		5.6 ± 0.24			10.1 ± 0.19					

Table 8: Metals data for bioretention area column 6



		<b>Column 7</b>											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	41.9 ± 3.14	ND	±	29.6 ± 0.92	21.5	±	1.35	565.7 ± 2.324	4.58	±	0.424	
			ND	±		21.5	±	1.54		4.33	±	0.226	
			ND	±		21.5	±	1.62		2.26	±	0.07	
3-Nov	second run	10.6 ± 0.83	ND	±	11.1 ± 0.07	8.8	±	0.24	147.5 ± 0.105	11.58	±	0.44	
			ND	±		11.7	±	0.16		7.64	±	0.542	
			ND	±		13.6	±	0.78		5.43	±	0.064	
17-Nov	third run	36.3 ± 1.42	ND	±	105.2 ± 6.15	7.7	±	0.51	547.6 ± 0.201	14.94	±	0.331	
			ND	±		9.8	±	0.54		8.24	±	0.05	
			8.9	±		0.28	12.5	±		1.08	9.99	±	0.602
1-Dec	fourth run	18 ± 1.05	3	±	76.4 ± 2.39	7.8	±	0.5	254 ± 1.66	19.4	±	3.4	
			1.5	±		0.1	7	±		0.42	16.1	±	2.53
			2.4	±		0.1	7.5	±		0.16	11.2	±	2.04
15-Dec	fifth run	35.5 ± 1.02	1.5	±	97.7 ± 1.26	4.8	±	0.12	450 ± 0.43	13.5	±	0.3	
			1.3	±		0.07	5.4	±		0.14	10.4	±	0.06
			0.3	±		0.13	5.2	±		0.32	5.8	±	0.1
22-Dec	sixth run	36.6 ± 3.44	ND	±	59.9 ± 3.23	10.2	±	1.13	208 ± 2.3	18.7	±	1.04	
			ND	±		5.9	±	0.29		16.5	±	2.48	
			4.3	±		0.15	6.6	±		0.34	13.3	±	1.31
29-Dec	seventh run	13.5 ± 0.48	ND	±	59.6 ± 4.78	7.6	±	0.74	316 ± 3.47	36	±	0.82	
			0.2	±		0.11	5.8	±		0.08	31.9	±	0.31
			0.7	±		0.11	6.6	±		0.12	16.3	±	0.75
13-Feb	eighth run	0	ND	±	0	4.1	±	0.63	0	37.7	±	0.3	
			0.9	±		0.91	5.7	±		1.92	27	±	0.33

Table 9: Metals data for bioretention area column 7

		Column 8											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	41.9 ± 3.14	ND ± ND ± ND ±			29.6 ± 0.92	18.4 ± 0.91 13.7 ± 0.86 15.6 ± 1.04			565.7 ± 2.324	4.18 ± 0.358 2.39 ± 0.097 1.31 ± 0.027		
3-Nov	second run	10.6 ± 0.83	ND ± ND ± ND ±			11.1 ± 0.07	8.6 ± 0.53 8.2 ± 0.35 8.3 ± 0.49			147.5 ± 0.105	9.35 ± 1.242 5.87 ± 0.197 2.57 ± 0.41		
17-Nov	third run	36.3 ± 1.42	ND ± ND ± 3.3 ± 0.8			105.2 ± 6.15	6.7 ± 0.42 6.6 ± 0.24 7.3 ± 0.72			547.6 ± 0.201	11.92 ± 0.02 4.68 ± 0.109 5.14 ± 0.233		
1-Dec	fourth run	18 ± 1.05	3.1 ± 0.35 3 ± 0.4 3.1 ± 0.35			76.4 ± 2.39	6.8 ± 0.26 6.8 ± 0.02 6.5 ± 0.01			254 ± 1.66	15.8 ± 3.01 19.4 ± 1.53 14.3 ± 1.03		
15-Dec	fifth run	35.5 ± 1.02	0.8 ± 0.02 1.1 ± 0.09 0.2 ± 0.13			97.7 ± 1.26	6.3 ± 0.2 6.1 ± 0.38 8.5 ± 1.04			450 ± 0.43	14 ± 1.84 9.2 ± 0.77 2.3 ± 0.12		
22-Dec	sixth run	36.6 ± 3.44	ND ± ND ± 3.1 ± 0.04			59.9 ± 3.23	7.6 ± 0.47 6.3 ± 0.3 8.3 ± 0.4			208 ± 2.3	23.7 ± 2.01 17.4 ± 1.24 11.8 ± 0.85		
29-Dec	seventh run	13.5 ± 0.48	ND ± 0.3 ± 0.2 1.5 ± 0.13			59.6 ± 4.78	4.9 ± 0.8 5.3 ± 0.27 6.6 ± 0.22			316 ± 3.47	61.6 ± 0.52 28.5 ± 0.06 16.6 ± 0.66		
13-Feb	eighth run	0	0.8 ± 0.66 0.1 ± 0.46			0	4.7 ± 0.1 4 ± 0.21			0	26.7 ± 0.59 20.6 ± 1.07		

Table 10: Metals data for bioretention area column 8

		Column 9											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	41.9	± 3.14	ND	±	29.6	± 0.92	18.4	± 0.22	565.7	± 2.324	5.5	± 0.73
				ND	±			13.7	± 0.48			3.9	± 0.13
				ND	±			15.6	± 0.56			2.7	± 0.04
3-Nov	second run	10.6	± 0.83	ND	±	11.1	± 0.07	9.1	± 0.94	147.5	± 0.105	9.4	± 0.14
				ND	±			8.2	± 0.35			3.5	± 0.16
				ND	±			8.3	± 0.49			1.8	± 0.09
17-Nov	third run	36.3	± 1.42	ND	±	105.2	± 6.15	6.7	± 0.42	547.6	± 0.201	9.6	± 0.16
				ND	±			6.6	± 0.24			6.7	± 0.06
				1.7	± 0.52			7.3	± 0.72			8.2	± 0.30
1-Dec	fourth run	18	± 1.05	1.7	± 0.1	76.4	± 2.39	6.8	± 0.26	254	± 1.66	15.0	± 1.56
				1.8	± 0.2			6.8	± 0.02			23.9	± 1.42
				1.6	± 0.1			6.5	± 0.01			5.4	± 0.67
15-Dec	fifth run	35.5	± 1.02	0.6	± 0.02	97.7	± 1.26	6.3	± 0.2	450	± 0.43	11.9	± 0.10
				0.7	± 0.07			6.1	± 0.38			16.0	± 2.05
				0.1	± 0.07			8.5	± 1.04			5.1	± 0.12
22-Dec	sixth run	36.6	± 3.44	ND	±	59.9	± 3.23	7.6	± 0.47	208	± 2.3	17.8	± 0.74
				ND	±			6.3	± 0.3			31.3	± 1.06
				2.5	± 0.1			8.3	± 0.4			19.2	± 0.68
29-Dec	seventh run	13.5	± 0.48	ND	±	59.6	± 4.78	4.9	± 0.8	316	± 3.47	33.8	± 0.86
				0.1	± 0.1			5.3	± 0.27			64.9	± 0.28
				0.7	± 0.07			6.6	± 0.22			17.4	± 0.65
13-Feb	eighth run	0		ND	±	0		4.7	± 1.11	0		54.5	± 0.23
				ND	±			4.9	± 1.49			14.0	± 0.64

Table 11: Metals data for bioretention area column 9

		Column 10											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	41.9 ± 3.14	ND	±	29.6 ± 0.92	20.8	±	1.95	565.7 ± 2.324	0.76	±	0.088	
			ND	±		21	±	1.16		6.9	±	0.366	
			ND	±		26.3	±	0.87		1.77	±	0.038	
3-Nov	second run	10.6 ± 0.83	ND	±	11.1 ± 0.07	10	±	0.26	147.5 ± 0.105	35.36	±	0.177	
			ND	±		9.6	±	1.06		10.51	±	0.529	
			ND	±		11.2	±	0.26		2.66	±	0.352	
17-Nov	third run	36.3 ± 1.42	ND	±	105.2 ± 6.15	10.7	±	0.44	547.6 ± 0.201	10.53	±	0.022	
			ND	±		10.4	±	0.62		20.4	±	0.143	
			1.2	±		0.43	8.5	±		0.79	6.2	±	0.17
1-Dec	fourth run	18 ± 1.05	0.8	±	76.4 ± 2.39	11	±	0.37	254 ± 1.66	18.7	±	0.81	
			1.1	±		0.24	8.5	±		0.05	25.7	±	1.09
			1.5	±		0.15	5	±		0.14	48.5	±	1.25
15-Dec	fifth run	35.5 ± 1.02	ND	±	97.7 ± 1.26	4.6	±	0.32	450 ± 0.43	13.6	±	0.29	
			0.2	±		0.02	3.6	±		0.23	13.1	±	0.18
			ND	±		7.2	±	0.14		12.9	±	0.73	
22-Dec	sixth run	36.6 ± 3.44	ND	±	59.9 ± 3.23	13.2	±	1.13	208 ± 2.3	27.6	±	0.54	
			ND	±		5.2	±	1.08		18.3	±	1.08	
			ND	±		4.3	±	0.35		12.4	±	0.76	
29-Dec	seventh run	13.5 ± 0.48	ND	±	59.6 ± 4.78	8.7	±	0.79	316 ± 3.47	30.2	±	0.25	
			ND	±		2.9	±	0.28		33.8	±	1.29	
			ND	±		3.3	±	0.26		27.5	±	1.17	
13-Feb	eighth run	0	ND	±	0	4	±	1.16	0	64.9	±	1.24	
			0.8	±		0.23	5.1	±		1.12	20.5	±	0.32

Table 12: Metals data for bioretention area column 10

		Column 11											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	41.9 ± 3.14	ND ±	ND ±	29.6 ± 0.92	31.7 ± 1.58	37.4 ± 1.26	565.7 ± 2.324	4.3 ± 0.36	3.8 ± 0.16	2.1 ± 0.07	ND ±	ND ±
			ND ±	ND ±		49.1 ± 1.79	11.4 ± 0.22		10.0 ± 0.55				
			ND ±	ND ±		13.9 ± 0.37	2.6 ± 0.51						
3-Nov	second run	10.6 ± 0.83	ND ±	ND ±	11.1 ± 0.07	15.8 ± 0.12	16.2 ± 0.48	147.5 ± 0.105	11.4 ± 0.22	10.0 ± 0.55	2.6 ± 0.51	ND ±	ND ±
			ND ±	ND ±		11.5 ± 0.24	12.0 ± 0.28		11.8 ± 0.09				
			ND ±	ND ±		12.6 ± 0.58	15.9 ± 0.25		11.8 ± 0.09				
17-Nov	third run	36.3 ± 1.42	2.8 ± 0.4	105.2 ± 6.15	11.5 ± 0.24	12.6 ± 0.58	16.8 ± 0.68	547.6 ± 0.201	12.0 ± 0.28	15.9 ± 0.25	11.8 ± 0.09	1.3 ± 0.14	1.8 ± 0.19
			1.3 ± 0.14	1.8 ± 0.19	76.4 ± 2.39	8.1 ± 0.35	8.6 ± 0.26	254 ± 1.66	20.0 ± 1.43	34.1 ± 0.28	21.4 ± 0.51		
			0.7 ± 0.12	11.4 ± 0.56	8.1 ± 0.35	8.6 ± 0.26	11.4 ± 0.56	254 ± 1.66	20.0 ± 1.43	34.1 ± 0.28	21.4 ± 0.51		
1-Dec	fourth run	18 ± 1.05	0.1 ± 0.09	0.6 ± 0.17	97.7 ± 1.26	6.8 ± 0.21	11.3 ± 0.22	450 ± 0.43	17.6 ± 1.01	25.5 ± 0.27	12.5 ± 0.30	0.1 ± 0.09	0.6 ± 0.17
			0.1 ± 0.09	0.6 ± 0.17		11.6 ± 0.74	31.8 ± 0.45		19.3 ± 0.76				
			0.1 ± 0.09	0.6 ± 0.17		9.3 ± 0.56	15.6 ± 1.03		12 ± 1.05				
15-Dec	fifth run	35.5 ± 1.02	ND ±	ND ±	59.9 ± 3.23	11.6 ± 0.74	9.3 ± 0.56	208 ± 2.3	31.8 ± 0.45	19.3 ± 0.76	15.6 ± 1.03	ND ±	ND ±
			ND ±	ND ±		11.6 ± 0.74	31.8 ± 0.45		19.3 ± 0.76				
			ND ±	ND ±		11.6 ± 0.74	31.8 ± 0.45		19.3 ± 0.76				
22-Dec	sixth run	36.6 ± 3.44	0.7 ± 0.09	59.9 ± 3.23	11.6 ± 0.74	9.3 ± 0.56	12 ± 1.05	208 ± 2.3	31.8 ± 0.45	19.3 ± 0.76	15.6 ± 1.03	ND ±	ND ±
			0.7 ± 0.09	59.9 ± 3.23	11.6 ± 0.74	9.3 ± 0.56	12 ± 1.05	208 ± 2.3	31.8 ± 0.45	19.3 ± 0.76	15.6 ± 1.03		
			0.7 ± 0.09	59.9 ± 3.23	11.6 ± 0.74	9.3 ± 0.56	12 ± 1.05	208 ± 2.3	31.8 ± 0.45	19.3 ± 0.76	15.6 ± 1.03		
29-Dec	seventh run	13.5 ± 0.48	ND ±	ND ±	59.6 ± 4.78	8.3 ± 0.67	8 ± 0.19	316 ± 3.47	43.8 ± 0.90	43.0 ± 0.95	15.3 ± 1.16	ND ±	ND ±
			ND ±	ND ±		8.3 ± 0.67	43.8 ± 0.90		43.0 ± 0.95				
			ND ±	ND ±		8 ± 0.19	43.8 ± 0.90		43.0 ± 0.95				
13-Feb	eighth run	0	0.3 ± 0.11	0.5 ± 0.1	0	10.7 ± 0.82	8.8 ± 1.97	0	15.3 ± 1.16	109.0 ± 0.50	32.1 ± 0.21	0.5 ± 0.1	0.6 ± 0.34
			0.3 ± 0.11	0.5 ± 0.1		8.8 ± 1.97	109.0 ± 0.50		0.6 ± 0.34				
			0.3 ± 0.11	0.5 ± 0.1		8.8 ± 1.97	109.0 ± 0.50		0.6 ± 0.34				

Table 13: Metals data for bioretention area column 11

		Column 12											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	41.9 ± 3.14	ND ±	ND ±	27.2 ± 1.36	29.6 ± 0.92	101 ± 2.73	565.7 ± 2.324	7.6 ± 0.89	4.7 ± 0.03	ND ±	ND ±	
			ND ±	39.6 ± 1.58	11.4 ± 0.91		12.7 ± 0.28						
			ND ±		14.1 ± 0.47		8.0 ± 0.13						
3-Nov	second run	10.6 ± 0.83	ND ±	ND ±	11.4 ± 0.91	11.1 ± 0.07	14.1 ± 0.47	147.5 ± 0.105	12.7 ± 0.28	8.0 ± 0.13	ND ±	ND ±	
			ND ±	16.6 ± 0.74	16.6 ± 0.74		5.1 ± 0.23						
			ND ±										
17-Nov	third run	36.3 ± 1.42	ND ±	ND ±	8.1 ± 0.18	105.2 ± 6.15	12.6 ± 0.24	547.6 ± 0.201	14.9 ± 0.07	11.8 ± 0.04	2.8 ± 0.4	13.9 ± 0.24	10.9 ± 0.95
			2.5 ± 0.3	2.3 ± 0.5	7.6 ± 0.54		22.5 ± 6.31						
			1.4 ± 0.1		6.9 ± 0.12		23.2 ± 0.14						
1-Dec	fourth run	18 ± 1.05	2.5 ± 0.3	2.3 ± 0.5	7.6 ± 0.54	76.4 ± 2.39	8.2 ± 0.21	254 ± 1.66	22.5 ± 6.31	15.6 ± 3.13	1.4 ± 0.1		
			0.3 ± 0.05	0.7 ± 0.12	5.5 ± 0.37		15.0 ± 0.96						
			ND ±	ND ±	7 ± 0.32		18.7 ± 0.13						
15-Dec	fifth run	35.5 ± 1.02	0.3 ± 0.05	0.7 ± 0.12	5.5 ± 0.37	97.7 ± 1.26	6.9 ± 0.56	450 ± 0.43	15.0 ± 0.96	7.3 ± 0.54	ND ±	ND ±	
			ND ±	10.8 ± 0.83	10.8 ± 0.83		26.4 ± 0.81						
			ND ±	8.1 ± 0.2	8.1 ± 0.2		31.9 ± 0.57						
22-Dec	sixth run	36.6 ± 3.44	ND ±	ND ±	10.8 ± 0.83	59.9 ± 3.23	9 ± 1.1	208 ± 2.3	26.4 ± 0.81	17.8 ± 0.67	0.5 ± 0.12	9 ± 1.1	17.8 ± 0.67
			ND ±	9.5 ± 0.44	9.5 ± 0.44		37.3 ± 0.83						
			ND ±	6.5 ± 0.63	6.5 ± 0.63		36.6 ± 0.54						
29-Dec	seventh run	13.5 ± 0.48	ND ±	ND ±	9.5 ± 0.44	59.6 ± 4.78	9.6 ± 0.41	316 ± 3.47	37.3 ± 0.83	32.3 ± 0.49	0.6 ± 0.11	9.6 ± 0.41	32.3 ± 0.49
			ND ±	6.5 ± 0.63	6.5 ± 0.63		36.6 ± 0.54						
			0.6 ± 0.11										
13-Feb	eighth run	0	ND ±	ND ±	4.8 ± 1.45	0	4.7 ± 0.55	0	62.8 ± 1.03	22.4 ± 0.37	0.5 ± 0.12	4.7 ± 0.55	22.4 ± 0.37
			0.5 ± 0.12										

Table 14: Metals data for bioretention area column 12

		<b>Column 13</b>																	
		Pb				Cu				Zn									
		in		out		in		out		in		out							
20-Oct	first run	34.5 ± 2.24	ND ± ND ± ND ±	36.6 ± 0.79	30.8 ± 1.36 20.6 ± 1.78 27.8 ± 1.94	609.2 ± 1.729	3.8 ± 0.42 10.1 ± 0.66 6.9 ± 0.45	3.7 ±	ND ±	22.1 ± 1.55	13 ± 0.49 13.5 ± 0.87 15 ± 0.61	109.9 ± 2.45	38.5 ± 0.40 26.2 ± 0.38 12.9 ± 0.31						
														24.9 ± 1.64	ND ± ND ± 2.4 ± 0.77	77.5 ± 12.84	12.6 ± 0.53 9.1 ± 0.55 12.1 ± 0.66	478.8 ± 1.11	20.1 ± 0.34 15.1 ± 0.35 13.7 ± 0.29
15-Dec	fifth run	15.7 ± 0.33	ND ± ND ± ND ±	48.6 ± 0.83	4.6 ± 0.1 3.9 ± 0.16 11.3 ± 0.11	140 ± 0.07	24.0 ± 0.17 20.7 ± 0.24 21.9 ± 0.14	5.2 ± 0.7	ND ± ND ± ND ±	11.7 ± 1.74	8.1 ± 0.92 5.1 ± 0.38 4.5 ± 0.36	284 ± 7.83	42.6 ± 2.11 36.8 ± 1.06 29.3 ± 1.23						
														23.6 ± 0.97	ND ± ND ± ND ±	62.2 ± 6.17	4.9 ± 0.68 3.3 ± 0.22 4.5 ± 0.19	260 ± 2.97	48.6 ± 0.73 53.5 ± 0.06 50.6 ± 1.05
13-Feb	eighth run																		

Table 15: Metals data for bioretention area column 13

		Column 14											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	34.5 ± 2.24	ND ±	ND ±	ND ±	36.6 ± 0.79	45.1 ± 1.55	45.9 ± 1.37	45.3 ± 1.63	609.2 ± 1.729	2.8 ± 0.98	5.0 ± 0.96	8.2 ± 0.36
3-Nov	second run	6.3 ± 0.82	ND ±	ND ±	ND ±	22.1 ± 1.55	20 ± 0.2	21.5 ± 2.86	26.6 ± 1.36	109.9 ± 2.45	11.4 ± 3.25	10.4 ± 3.11	18.4 ± 0.14
17-Nov	third run	24.9 ± 1.64	ND ±	ND ±	ND ±	77.5 ± 12.84	19 ± 0.97	19.8 ± 1.39	25.8 ± 4.74	478.8 ± 1.11	15.7 ± 0.65	13.6 ± 0.32	20.4 ± 0.17
1-Dec	fourth run	8.2 ± 0.95	3.1 ± 0.29	2.5 ± 0.26	3.8 ± 0.51	66.1 ± 3.04	14.4 ± 0.33	15.3 ± 0.35	15.1 ± 0.74	476 ± 6.36	68.9 ± 1.34	30.1 ± 1.48	9.8 ± 0.12
15-Dec	fifth run	15.7 ± 0.33	ND ±	ND ±	ND ±	48.6 ± 0.83	4.2 ± 0.19	11.6 ± 0.28	13.9 ± 1.11	140 ± 0.07	31.0 ± 2.91	12.4 ± 0.32	13.6 ± 0.06
22-Dec	sixth run	5.2 ± 0.7	ND ±	ND ±	ND ±	11.7 ± 1.74	15 ± 1.87	16.8 ± 0.31	16.1 ± 0.17	284 ± 7.83	45.7 ± 0.99	36.5 ± 0.58	22.1 ± 1.07
29-Dec	seventh run	23.6 ± 0.97	ND ±	ND ±	ND ±	62.2 ± 6.17	12.5 ± 0.06	12.4 ± 0.21	11.9 ± 0.2	260 ± 2.97	38.5 ± 0.17	34.0 ± 0.20	60.7 ± 0.17

Table 16: Metals data for bioretention area column 14



		Column 15											
		Pb				Cu				Zn			
		in		out		in		out		in		out	
20-Oct	first run	34.5 ± 2.24	ND	±	36.6 ± 0.79	30.6 ± 0.64	609.2 ± 1.729	2.9 ± 0.75	ND	±	6.2 ± 2.66	ND	±
			ND	±	28.3 ± 0.73	±		8.2 ± 0.81	ND	±			
			ND	±	27 ± 0.84	±			ND	±			
3-Nov	second run	6.3 ± 0.82	ND	±	22.1 ± 1.55	16.3 ± 0.32	109.9 ± 2.45	20.4 ± 0.59	ND	±	11.9 ± 0.22	ND	±
			ND	±		14.3 ± 0.35		±	23.3 ± 1.16	ND	±		
			ND	±		14.2 ± 0.81		±		ND	±		
17-Nov	third run	24.9 ± 1.64	ND	±	77.5 ± 12.84	11.7 ± 0.32	478.8 ± 1.11	13.7 ± 0.47	ND	±	14.4 ± 0.45	ND	±
			ND	±		11.6 ± 0.6		±	24.8 ± 0.07	ND	±		
			0.6 ± 0.1			13.8 ± 0.5				ND	±		
1-Dec	fourth run	8.2 ± 0.95	1.8 ± 0.48		66.1 ± 3.04	11.9 ± 0.23	476 ± 6.36	27.3 ± 0.49	2.3 ± 0.92		34.3 ± 1.15	2.9 ± 0.87	
			2.9 ± 0.87			10.1 ± 0.15		±	31.8 ± 1.48				
						9.1 ± 0.08		±					
15-Dec	fifth run	36.6 ± 1.94	ND	±	48.6 ± 0.83	12.4 ± 0.3	140 ± 0.07	18.4 ± 0.21	ND	±	17.3 ± 0.23	ND	±
			ND	±		9.1 ± 0.43		±	17.6 ± 0.14	ND	±		
			ND	±		7.7 ± 0.39		±		ND	±		
22-Dec	sixth run	5.2 ± 0.7	ND	±	11.7 ± 1.74	12 ± 0.4	284 ± 7.83	27.7 ± 0.78	ND	±	31.3 ± 0.52	ND	±
			ND	±		14.7 ± 1.2		±	33.8 ± 0.89	ND	±		
			ND	±		11.2 ± 0.56		±		ND	±		
29-Dec	seventh run	23.6 ± 0.97	ND	±	62.2 ± 6.17	8.6 ± 0.23	260 ± 2.97	66.9 ± 0.22	ND	±	72.7 ± 0.08	ND	±
			ND	±		9.7 ± 1.36		±	72.2 ± 0.56	ND	±		
			ND	±		9 ± 0.18		±		ND	±		
13-Feb	eighth run	0	ND	±	0	5.9 ± 1.43	0	74.1 ± 1.19	ND	±		ND	±
			ND	±		5.9 ± 1.05		±	129.0 ± 0.80	ND	±		

Table 17: Metals data for bioretention area column 15

**Column 1**

		NO3				PO4			
		in		out		in		out	
20-Oct	first run	0.67	± 0.0012	13.533	± 0.1527	0.15	± 0.01	0.368	± 0.0028
								MDL	0.012
3-Nov	second run	0.39	± 0.008	1.94	± 0.006	0.087	± 0.0006	0.827	± 0.0017
								MDL	0.009
17-Nov	third run	2.02	± 0.01	9	± 0.025	0.462	± 0.001	1.5	± 0.0058
								MDL	0.01
1-Dec	fourth run	2.08	± 0.015	6.19	± 0.275	1.12	± 0	1.92	± 0
15-Dec	fifth run	1.72	± 0.012	4.31	± 0.02	0.619	± 0.014	2.42	± 0.006
								MDL	0.012
22-Dec	sixth run	1.68	± 0.015	6.09	± 0.057	0.506	± 0.0057	1.51	± 0.0057
								MDL	0.007
29-Dec	seventh run	2.24	± 0.083	4.44	± 0.075	0.515	± 0.002	1.48	± 0.0057
								MDL	0.006
13-Feb	eighth run	0		13.1	± 0.058	0		1.14	± 0.0057
								MDL	0.009

Table 18: Nutrient data for bioretention area column 1

**Column 2**

		NO3				PO4			
		in		out		in		out	
20-Oct	first run	0.67	± 0.0012	7.4133	± 0.0513	0.15	± 0.01	0.441	± 0.0012
3-Nov	second run	0.39	± 0.008	2.48	± 0.012	0.087	± 0.0006	0.335	± 0.0038
17-Nov	third run	2.02	± 0.01	10.3	± 0.058	0.462	± 0.001	0.603	± 0.0015
1-Dec	fourth run	2.08	± 0.015	13	± 0.153	1.12	± 0	0.521	± 0.0021
15-Dec	fifth run	1.72	± 0.012	8.56	± 0.04	0.619	± 0.014	0.467	± 0.0015
22-Dec	sixth run	1.68	± 0.015	6.42	± 0.11	0.506	± 0.0057	0.415	± 0.002
29-Dec	seventh run	2.24	± 0.083	6.29	± 0.015	0.515	± 0.002	0.539	± 0.0133
13-Feb	eighth run	0		23	± 0.208	0		0.378	± 0.01

Table 19: Nutrient data for bioretention area column 2

**Column 3**

		NO3						PO4					
		in			out			in			out		
20-Oct	first run	0.67	±	0.0012	12.47	±	0.1155	0.15	±	0.01	0.46	±	0.0075
3-Nov	second run	0.39	±	0.008	1.26	±	0.006	0.087	±	0.0006	0.907	±	0.001
17-Nov	third run	2.02	±	0.01	7.58	±	0.025	0.462	±	0.001	1.45	±	0.0012
1-Dec	fourth run	2.08	±	0.015	7.58	±	0.057	1.12	±	0	1.67	±	0.0058
15-Dec	fifth run	1.72	±	0.012	7.81	±	0.044	0.619	±	0.014	1.8	±	0.0057
22-Dec	sixth run	1.68	±	0.015	5.46	±	0.06	0.506	±	0.0057	1.13	±	0
29-Dec	seventh run	2.24	±	0.083	5.66	±	0.01	0.515	±	0.002	1.39	±	0
13-Feb	eighth run			0	13.3	±	0			0	1.04	±	0.0057

Table 20: Nutrient data for bioretention area column 3

**Column 4**

		NO3				PO4			
		in		out		in		out	
20-Oct	first run	0.67	± 0.0012	8.81	± 0.0379	0.15	± 0.01	0.342	± 0.0046
3-Nov	second run	0.39	± 0.008	2.57	± 0.006	0.087	± 0.0006	0.802	± 0.0006
17-Nov	third run	2.02	± 0.01	8.56	± 0.023	0.462	± 0.001	1.65	± 0
1-Dec	fourth run	2.08	± 0.015	6.39	± 0.062	1.12	± 0	1.95	± 0.0057
15-Dec	fifth run	1.72	± 0.012	1.89	± 0.023	0.619	± 0.014	2.07	± 0.0153
22-Dec	sixth run	1.68	± 0.015	4.76	± 0.015	0.506	± 0.0057	1.18	± 0
29-Dec	seventh run	2.24	± 0.083	7.29	± 0.059	0.515	± 0.002	1.46	± 0
13-Feb	eighth run	0		9.96	± 0.046	0		1.23	± 0.0057

Table 21: Nutrient data for bioretention area column 4

**Column 5**

		NO3						PO4					
		in			out			in			out		
20-Oct	first run	0.67	±	0.0012	9.04	±	0.0153	0.15	±	0.01	0.303	±	0.0228
3-Nov	second run	0.39	±	0.008	2.23	±	0	0.087	±	0.0006	1	±	0
17-Nov	third run	2.02	±	0.01	7.57	±	0.012	0.462	±	0.001	1.67	±	0
1-Dec	fourth run	2.08	±	0.015	13.1	±	0.058	1.12	±	0	2.44	±	0
15-Dec	fifth run	1.72	±	0.012	3.73	±	0.006	0.619	±	0.014	2.45	±	0.0057
22-Dec	sixth run	1.68	±	0.015	6.98	±	0.055	0.506	±	0.0057	1.2	±	0.0057
29-Dec	seventh run	2.24	±	0.083	4.87	±	0.012	0.515	±	0.002	1.83	±	0
13-Feb	eighth run			0	21	±	0.115			0	0.705	±	0.012

Table 22: Nutrient data for bioretention area column 5

**Column 6**

		NO3					PO4				
		in		out			in		out		
20-Oct	first run	0.67	± 0.0012	11.33	± 0.0577	0.15	± 0.01	0.268	± 0.0006		
3-Nov	second run	0.39	± 0.008	2.3	± 0.006	0.087	± 0.0006	0.614	± 0.0026		
17-Nov	third run	2.02	± 0.01	4.94	± 0.015	0.462	± 0.001	1.53	± 0		
1-Dec	fourth run	2.08	± 0.015	9.32	± 0.06	1.12	± 0	2.2	± 0.0057		
15-Dec	fifth run	1.72	± 0.012	7.92	± 0.035	0.619	± 0.014	2.22	± 0		
22-Dec	sixth run	1.68	± 0.015	5.18	± 0	0.506	± 0.0057	1.47	± 0.021		
29-Dec	seventh run	2.24	± 0.083	7.68	± 0.012	0.515	± 0.002	1.78	± 0		
13-Feb	eighth run	0		21.6	± 0.115	0		1.2	± 0.026		

Table 23: Nutrient data for bioretention area column 6

**Column 7**

		NO3						PO4					
		in			out			in			out		
20-Oct	first run	0.38	±	0.0207	0.84	±	0.0006	0.07	±	0.005	0.511	±	0.0052
3-Nov	second run	0.369	±	0.0006	0.625	±	0.002	0.085	±	0.0004	1.07	±	0
17-Nov	third run	2.36	±	0.006	3.81	±	0.006	0.564	±	0.0021	1.75	±	0.0058
1-Dec	fourth run	2.03	±	0.01	5.8	±	0.042	0.482	±	0.0014	1.61	±	0
15-Dec	fifth run	2.34	±	0.022	0.944	±	0.022	0.739	±	0.0026	2.19	±	0.0057
22-Dec	sixth run	1.71	±	0.021	0.703	±	0.276	0.516	±	0.0035	2.32	±	0.0057
29-Dec	seventh run	1.9	±	0.029	1.77	±	0.104	0.456	±	0.0015	1.87	±	0
13-Feb	eighth run	0			11.3	±	0.1	0			0.635	±	0.004

Table 24: Nutrient data for bioretention area column 7



**Column 8**

		NO3					PO4				
		in		out			in		out		
20-Oct	first run	0.38	± 0.0207	2.23	± 0.0404	0.07	± 0.005	0.273	± 0.0032		
3-Nov	second run	0.369	± 0.0006	1.45	± 0.006	0.085	± 0.0004	1.31	± 0		
17-Nov	third run	2.36	± 0.006	4.13	± 0.006	0.564	± 0.0021	2.36	± 0.0058		
1-Dec	fourth run	2.03	± 0.01	5.43	± 0.067	0.482	± 0.0014	2.57	± 0.0057		
15-Dec	fifth run	2.34	± 0.022	5.65	± 0	0.739	± 0.0026	2.26	± 0		
22-Dec	sixth run	1.71	± 0.021	1.15	± 0.01	0.516	± 0.0035	2.47	± 0.0115		
29-Dec	seventh run	1.9	± 0.029	8.24	± 0.015	0.456	± 0.0015	1.48	± 0.0057		
13-Feb	eighth run	0		7.48	± 0.042	0		0.689	± 0.031		

Table 25: Nutrient data for bioretention area column 8

**Column 9**

		NO3						PO4					
		in			out			in			out		
20-Oct	first run	0.38	±	0.0207	1.86	±	0.0231	0.07	±	0.005	0.398	±	0.017
3-Nov	second run	0.369	±	0.0006	0.57	±	0	0.085	±	0.0004	0.362	±	0.001
17-Nov	third run	2.36	±	0.006	2.68	±	0.006	0.564	±	0.0021	0.871	±	0.0137
1-Dec	fourth run	2.03	±	0.01	9.67	±	0.049	0.482	±	0.0014	0.704	±	0.002
15-Dec	fifth run	2.34	±	0.022	1.65	±	0.012	0.739	±	0.0026	1.47	±	0
22-Dec	sixth run	1.71	±	0.021	0.87	±	0.001	0.516	±	0.0035	1.01	±	0
29-Dec	seventh run	1.9	±	0.029	1.07	±	0.006	0.456	±	0.0015	0.914	±	0.0023
13-Feb	eighth run	0			22.8	±	0.058	0			0.81	±	0.017

Table 26: Nutrient data for bioretention area column 9

**Column 10**

		NO3						PO4					
		in			out			in			out		
20-Oct	first run	0.38	±	0.0207	1.07	±	0.0058	0.07	±	0.005	0.733	±	0.0078
3-Nov	second run	0.369	±	0.0006	1.41	±	0.006	0.085	±	0.0004	1.16	±	0
17-Nov	third run	2.36	±	0.006	1.09	±	0.006	0.564	±	0.0021	1.43	±	0
1-Dec	fourth run	2.03	±	0.01	9.59	±	0.09	0.482	±	0.0014	1.26	±	0.0057
15-Dec	fifth run	2.34	±	0.022	0.876	±	0.008	0.739	±	0.0026	1.65	±	0
22-Dec	sixth run	1.71	±	0.021	0.78	±	0.0006	0.516	±	0.0035	1.27	±	0
29-Dec	seventh run	1.9	±	0.029	0.857	±	0.002	0.456	±	0.0015	1.2	±	0
13-Feb	eighth run	0			39.4	±	0.503	0			0.129	±	0.014

Table 27: Nutrient data for bioretention area column 10

**Column 11**

		NO3					PO4				
		in		out			in		out		
20-Oct	first run	0.38	± 0.0207	1.78	± 0.0231	0.07	± 0.005	0.96	± 0.0035		
3-Nov	second run	0.369	± 0.0006	1.22	± 0	0.085	± 0.0004	0.393	± 0.0096		
17-Nov	third run	2.36	± 0.006	5.25	± 0.01	0.564	± 0.0021	0.562	± 0		
1-Dec	fourth run	2.03	± 0.01	21.8	± 0.153	0.482	± 0.0014	0.425	± 0.0032		
15-Dec	fifth run	2.34	± 0.022	3.49	± 0.035	0.739	± 0.0026	0.588	± 0.013		
22-Dec	sixth run	1.71	± 0.021	1.56	± 0.025	0.516	± 0.0035	0.419	± 0.0318		
29-Dec	seventh run	1.9	± 0.029	1.64	± 0	0.456	± 0.0015	0.452	± 0.001		
13-Feb	eighth run	0		47.2	± 1.8	0		0.317	± 0.012		

Table 28: Nutrient data for bioretention area column 11

**Column 12**

		NO3						PO4					
		in			out			in			out		
20-Oct	first run	0.38	±	0.0207	1.41	±	0	0.07	±	0.005	0.348	±	0.0156
3-Nov	second run	0.369	±	0.0006	0.59	±	0.002	0.085	±	0.0004	0.478	±	0.0021
17-Nov	third run	2.36	±	0.006	4.4	±	0.012	0.564	±	0.0021	1.48	±	0
1-Dec	fourth run	2.03	±	0.01	14.3	±	0.321	0.482	±	0.0014	0.875	±	0.0006
15-Dec	fifth run	2.34	±	0.022	0.596	±	0.012	0.739	±	0.0026	2.47	±	0
22-Dec	sixth run	1.71	±	0.021	0.545	±	0.01	0.516	±	0.0035	2.42	±	0
29-Dec	seventh run	1.9	±	0.029	0.597	±	0.004	0.456	±	0.0015	2.29	±	0
13-Feb	eighth run	0			47	±	2.3	0			0.292	±	0.003

Table 29: Nutrient data for bioretention area column 12

**Column 13**

		NO3						PO4					
		in			out			in			out		
20-Oct	first run	0.54	±	0.0077	0.88	±	0.0031	0.1	±	0.027	0.593	±	0.0031
3-Nov	second run	0.415	±	0.001	0.72	±	0.002	0.089	±	0.0003	0.716	±	0.0012
17-Nov	third run	1.74	±	0.006	1.02	±	0.006	0.486	±	0.0017	1.05	±	0.0058
1-Dec	fourth run	1.96	±	0.017	0.607	±	0.008	0.524	±	0.001	1.41	±	0
15-Dec	fifth run	1.68	±	0.023	0.845	±	0.004	0.668	±	0.0015	1.75	±	0
22-Dec	sixth run	1.12	±	0.006	0.307	±	0.008	0.897	±	0.0015	1.39	±	0.0057
29-Dec	seventh run	2.14	±	0.035	0.34	±	0.017	0.625	±	0.0006	1.71	±	0.0057
13-Feb	eighth run	0			6.18	±	0.021	0			0.45	±	0.009

Table 30: Nutrient data for bioretention area column 13

**Column 14**

		NO3					PO4				
		in		out			in		out		
20-Oct	first run	0.54	± 0.0077	2.53	± 0.0153	0.1	± 0.027	0.312	± 0.002		
3-Nov	second run	0.415	± 0.001	3.52	± 0.055	0.089	± 0.0003	0.229	± 0.0006		
17-Nov	third run	1.74	± 0.006	2.21	± 0.01	0.486	± 0.0017	0.268	± 0.001		
1-Dec	fourth run	1.96	± 0.017	1.59	± 0.01	0.524	± 0.001	0.332	± 0		
15-Dec	fifth run	1.68	± 0.023	1.3	± 0.006	0.668	± 0.0015	0.299	± 0.0156		
22-Dec	sixth run	1.12	± 0.006	1.96	± 0	0.897	± 0.0015	0.214	± 0.0006		
29-Dec	seventh run	2.14	± 0.035	0.98	± 0.006	0.625	± 0.0006	0.259	± 0.0006		

Table 31: nutrient data for bioretention area column 14

**Column 15**

		NO3				PO4			
		in		out		in		out	
20-Oct	first run	0.54	± 0.0077	1.07	± 0.0208	0.1	± 0.027	0.446	± 0.0055
3-Nov	second run	0.415	± 0.001	2.49	± 0.006	0.089	± 0.0003	0.517	± 0.001
17-Nov	third run	1.74	± 0.006	2.47	± 0.015	0.486	± 0.0017	0.484	± 0.0017
1-Dec	fourth run	1.96	± 0.017	1.41	± 0.006	0.524	± 0.001	0.663	± 0.002
15-Dec	fifth run	1.68	± 0.023	0.882	± 0.004	0.668	± 0.0015	0.627	± 0.002
22-Dec	sixth run	1.12	± 0.006	0.523	± 0.003	0.897	± 0.0015	1.16	± 0
29-Dec	seventh run	2.14	± 0.035	0.57	± 0.006	0.625	± 0.0006	0.581	± 0.001
13-Feb	eighth run	0		1.35	± 0.058	0		0.762	± 0.019

Table 32: Nutrient data for bioretention area column 15



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# The Influence of Urbanization on Watershed Nitrogen Cycling Watersheds

## Basic Information

<b>Title:</b>	The Influence of Urbanization on Watershed Nitrogen Cycling Watersheds
<b>Project Number:</b>	2005NJ84B
<b>Start Date:</b>	3/1/2005
<b>End Date:</b>	2/28/2006
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	6th
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Water Quality, Hydrology, Geochemical Processes
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Bernice Rosenzweig, Peter Jaffe

## Publication

1. Rosenzweig, B. and P. Jaffe. December, 2005. Stormwater Detention Ponds and Nitrogen Cycling in Urban Watersheds. In Poster Presentation at the American Geophysical Union Fall Meeting.
2. Rosenzweig, B. and P. Jaffe. May, 2006. The Significance of High Discharge Events to Nitrogen Transport in Urban Watersheds. In Poster Presentation at the AGU Joint Assembly Meeting.

## Problems

As the amount of land devoted to urban and suburban use increases, understanding the impact of this type of development on ecosystem processes will become increasingly important. This issue is one of particular urgency in the state of New Jersey, where 27% of the total land area was categorized as urban at the end of the 20<sup>th</sup> century and approximately 16,600 acres of land are converted to urban development each year (Hasse and Lathrop, 2001). In spite of its importance, the study of nutrient cycling in urban watersheds is still in its infancy. Our research investigates the coupled hydrologic and nitrogen cycles in an urban watershed and how they are modified by urban land use.

Understanding the dynamics of nitrogen is particularly important because, when transported in excess to coastal ecosystems, this nutrient can lead to harmful coastal eutrophication. Well-publicized examples of this phenomenon include the 'dead zone' in the Gulf of Mexico and the anoxia problem in the Chesapeake Bay (Mitsch et al. 2001). Previous research (Groffman et al., 2002) has shown that riparian zones can serve as important control points in determining the amount of nitrogen that will enter surface waters and eventually be transported to coastal systems. The hydrologic changes induced by urbanization can significantly modify the ability of riparian systems to process nitrogen.

We would like to determine how hydrologic changes resulting from urban land use influence the occurrence of these locations and periods of biogeochemical importance (McClain, 2000). Our work tests the following hypotheses:

- Urban land development leads to modifications in the mechanisms of runoff production and modifications to stream channel morphology
- As a result of these physical and hydrologic changes, urban stream channels have reduced capacity for nitrogen retention and can no longer function as watershed-scale hotspots of nitrogen removal and retention. Urban development also creates additional sources of nitrogen that can be transported by streams.
- As a result of these physical and hydrologic changes, there are enhanced cycles of subsurface wetting and drying which can result in 'hot moments of nitrogen export from urban watersheds
- Stormwater detention ponds function as hot spots of nitrogen retention in urban watersheds

## Methodology

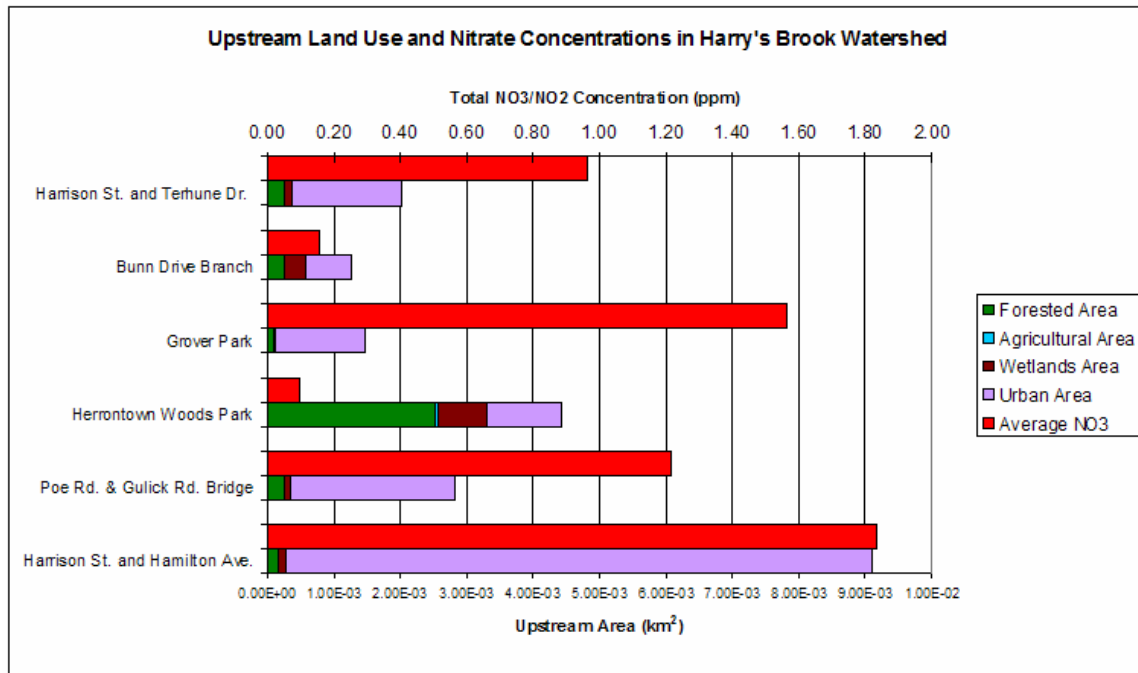
Our research to date has focused on characterizing spatial and temporal variation in stream nitrogen loads in the Harry's Brook watershed in Princeton, NJ. This 6.7 km<sup>2</sup> watershed contains a great deal of diversity in its development history. It consists of a branch that remains undeveloped as a forest preserve, branches of pre-Clean Water Act development where no structural best management practices (eg. detention ponds) are in place and branches where detention ponds are used for stormwater control.

In order to investigate spatial and seasonal variation in instream nitrate concentrations, grab samples were collected regularly during low flow conditions at 26 sampling sites throughout the watershed. Stream gages were located at 6 of these sites and record a continuous time series of stage at 1-minute intervals. The stream nitrogen response to storm events was also assessed by obtaining time series of water quality samples during storm events. Storm event samples were collected using ISCO 6712 Automated Samplers at intervals from 15 minutes to 1 hour. The storm event results provided in this report were obtained at the Terhune Rd. site, where a rating curve has been developed to relate stream stage to discharge.

Water quality samples were filtered using 0.2µm nylon filters and analyzed for Total  $\text{NO}_3^- + \text{NO}_2^-$ ,  $\text{NH}_3$ , and Total Dissolved Nitrogen using a Lachat Quik-Chem 8500 Flow Injection Analyzer. Samples were also analyzed (without filtration) for TOC using a Shimadzu TOC-500 Combustion Analyzer. For this study, we were most interested in  $\text{NO}_3^-$ , which is usually present in dissolved form and easily transported to surface waters. ( $\text{NO}_2^-$  in Harry's Brook surface waters can be assumed to be negligible. Future work will also focus more on other forms of nitrogen, in which a significant fraction is sorbed to particles as well as in dissolved form. The procedures developed for storm event sampling and analysis will be modified for future use in University campus detention ponds this summer.

## Principal Findings and Significance

Our results from this work show that there is significant spatial variation in instream nitrogen loads and that this variation can be correlated to land use. The figures below summarize results from 6 representative sites throughout the watershed with varying upstream catchment area and land use. Upstream Land Use was assessed using the New Jersey Department of Environmental Protection's 1995-1997 Land Use/Land Cover Dataset and 10m Digital Elevation Models.

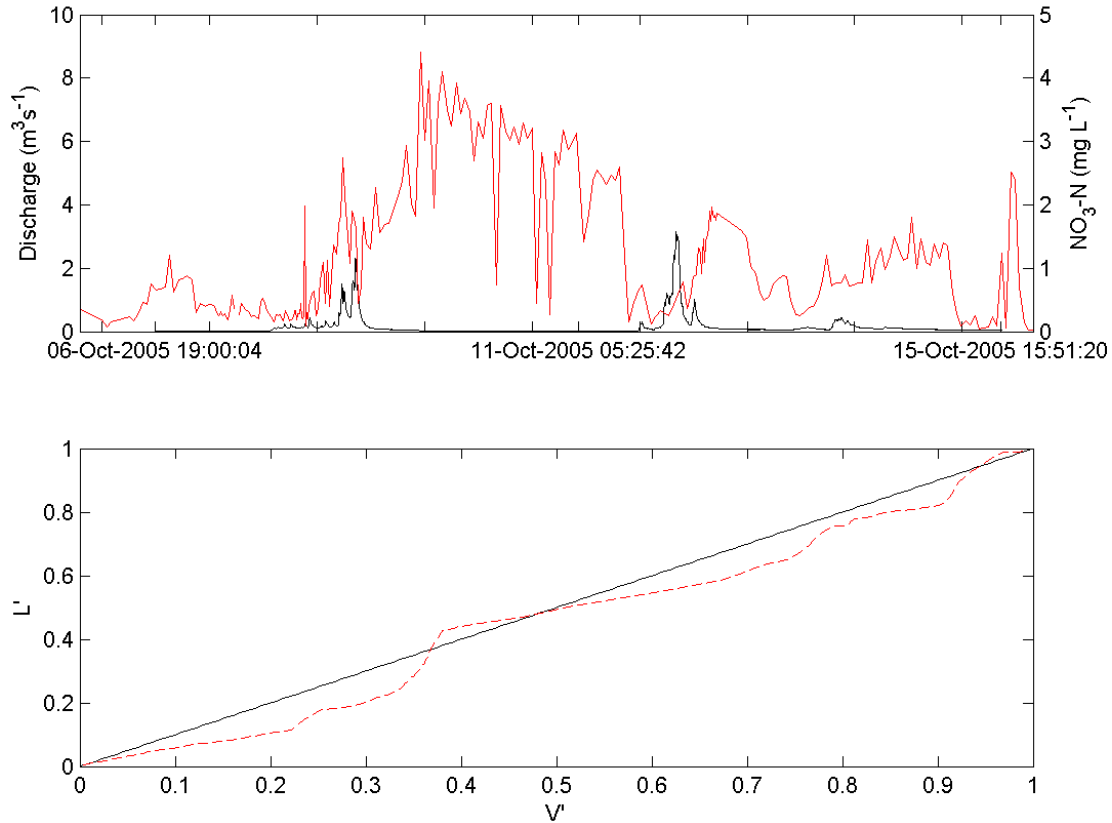


The total  $\text{NO}_3^-$  concentrations shown in the chart above are the average from 12 sampling events. Sites with highly urbanized upstream catchments, such as the Grover Park site that drains the commercial area of the Princeton Shopping Center and the Hamilton Ave site downstream of the downtown Princeton storm drain outfall, tend to have higher instream  $\text{NO}_3^-$  concentrations than less developed sites such as the Herrontown Woods Forest Preserve site. Upstream Land Use seems to be a more important control on instream nitrate concentrations than catchment area- for example the Grover Park site is much smaller in area than the Hamilton Ave Site, but both have comparably high average  $\text{NO}_3^-$  concentrations.

Our most significant storm event sampling took place during a 9-day period in October, 2005 in which the Harry's Brook Watershed received ~300 mm of rainfall. This was an extreme rainfall event in this region- the average rainfall for the entire month of October in the Princeton

area is only 86mm. In spite of the significant rainfall, this was not a high discharge even since it followed an extremely dry summer. The rainfall was distributed with two periods of peak intensity on October 8th and 12th (with 166 and 77 mm of rainfall reported, respectively) with intermittent periods of light rain in between.

The figure below shows time series of discharge and NO<sub>3</sub><sup>-</sup> as well as a dimensionless L'V' Curve:



Average baseflow in 24 hours preceding event:	n/a*
Total Baseflow in 24 hours preceding event:	n/a*
Days since previous rainfall event (>0.1cm of rain):	8 days
Event Total Flow Volume (24 hours):	105067 m <sup>3</sup>
Event Total NO <sub>3</sub> Load:	60 kg
Event Avg. Conc:	1.2 ppm

\*The stream gage at this site was offline until the morning of 10/6/2006

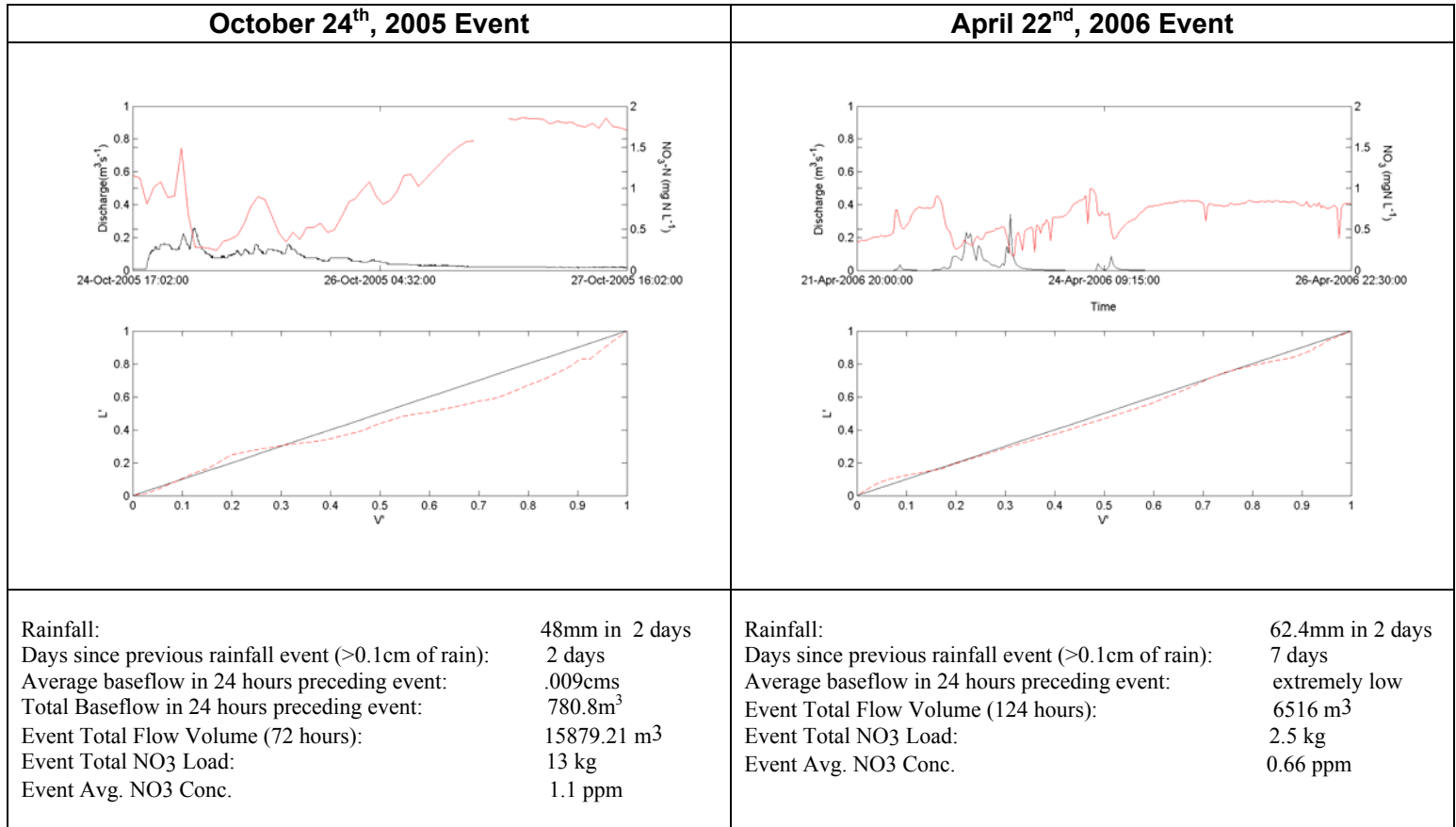
L'V' curves compare the timing of the total analyte load that has been transported to the site (normalized cumulative load, L') to the fraction of the total runoff volume (normalized cumulative discharge, V') that has passed through the site from their source within the watershed. The 'first flush' phenomena (Deletic, 1998) commonly described in the literature would appear when >75% of the total analyte load has passed through the site when only 25% of the runoff volume has.

We did not observe a first flush for nitrate during this event. Instead, the nitrate response lags behind the runoff hydrograph until the receding limb of the first discharge peak. This may indicate that the analyte is being transported by slower pathways (e.g. shallow subsurface flow), while the bulk of the stormwater runoff takes more rapid routes (eg. rapid runoff over impervious surface and through storm drain networks). Extremely high nitrate concentrations (with a maximum of 4.5ppm, which is greater than that observed in all of our sampling efforts at Harry's Brook) were observed approximately 12 hours after the most intense period of rainfall. These data suggest that the period during the receding limb of an extreme storm hydrograph may constitute a hot moment of nitrogen export. This is significant since many stormwater BMPs are now being designed to capture the first flush of stormwater for water quality improvement and would, as a result, not reduce the bulk of the nitrate load being exported at this site. Further work is necessary to determine the significance of this event to annual nitrogen loads in Harry's Brook.

For comparison, the results from four more typical storm events are shown below. These figures show time series of discharge (black line) and NO<sub>3</sub> concentration (red line) and the corresponding L'V' curves at the Terhune Rd. site.

<b>August 31<sup>st</sup>, 2005 Event</b>		<b>September 26<sup>th</sup>, 2005</b>	
Rainfall:	6.1mm in 2 hrs	Rainfall:	14.5 mm in 3 hrs
Days since previous rainfall event (>0.1cm of rain):	16 days	Days since previous rainfall event (>0.1cm of rain):	11 days
Average Baseflow in 24 hours preceding event:	extremely low	Average baseflow in 24 hours preceding event:	0.002cms
Event Total Runoff Volume (24 hours):	3728.5m <sup>3</sup>	Total Baseflow in 24 hours preceding event:	158.08m <sup>3</sup>
Event Total NO <sub>3</sub> Load:	2.1 kg	Event Total Flow Volume (24 hours):	1834.9 m <sup>3</sup>
Event Avg. NO <sub>3</sub> Conc.	0.57ppm	Event Total NO <sub>3</sub> Load:	1.4 kg
		Event Avg. Conc:	0.78ppm





Our results show that there is considerable variation in both the total NO<sub>3</sub>-N load that will be exported with any given event and the timing of the nitrate response. The intensity and duration of precipitation, time of year and, most importantly, antecedent conditions appear to play a role in determining the nitrate response. For example, the October 24<sup>th</sup>, 2005 and April 22<sup>nd</sup>, 2006 storms were comparable in magnitude and duration but produced very different N loads at this site. This was probably resulted from high instream N concentrations before the October 24<sup>th</sup> storm as a result of the extreme event a few weeks earlier.

Further work is required to better understand the controls on nitrogen transport to streams by stormwater. The results will be used to better understand the potential large-scale role of detention ponds in watershed nitrogen cycling. Future work will also be conducted within detention ponds to determine whether they are sources or sinks of nitrogen and the key N cycling processes within them. Our ultimate goal is to optimize the design of stormwater detention ponds to act as 'sinks' of nitrogen in urban watersheds.

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# Microbial degradation of MTBE in anaerobic environments

## Basic Information

<b>Title:</b>	Microbial degradation of MTBE in anaerobic environments
<b>Project Number:</b>	2005NJ86B
<b>Start Date:</b>	3/1/2005
<b>End Date:</b>	2/28/2006
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	6
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Toxic Substances, Treatment
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Laura K. G. Youngster, Max Haggblom

## Publication

1. Youngster, L., P. Somsamak, L. Kerkhoff, and MM Haggblom. 2006. Characterization of anaerobic MTBE-degrading bacterial communities. Abstract Q-081. American Society for Microbiology 106th General Meeting, Orlando, FL, May 20-25, 2006.
2. Youngster, L., P. Somsamak, L. Kerkhoff, and MM Haggblom. 2006. Characterization of anaerobic MTBE-degrading bacterial communities. International Symposium on Environmental Biotechnology, Leipzig, Germany, July 9-13, 2006.

## **Problem and Research Objectives**

Methyl *tert*-butyl ether is a synthetic chemical, primarily used as a fuel additive to reduce emissions (NJDEP, 2001). It is also a common environmental contaminant, introduced into water by spills and leaks during production, transportation, and storage. MTBE has a strong turpentine-like taste and smell and can only be tolerated in drinking water at low levels. MTBE is also a skin and respiratory irritant and can be carcinogenic in rats and mice (Werner, 2001). The USEPA issued a 1996 recommended limit of 20-35 ppb in drinking water (NJDEP, 2001). Many states have adopted lower thresholds of 13-14 ppb (Stefan, 2000, Ayotte, 2005). Municipal water supplies have been closed due to MTBE contamination and a USGS survey found MTBE to be the second most common aquifer contaminant in urban United States areas (Squillace, 1996).

Aquifer contamination with MTBE is widespread and travels quickly. For most contaminated groundwater, the most financially realistic treatment option is natural attenuation (Bradley, 2001). Physical and chemical properties of MTBE make environmental contamination a challenging problem. Most treatment plans for handling gasoline spills are optimized for removing BTEX components (benzene, toluene, ethylbenzene, or *o*-, *m*-, *p*-xylene) and are not very effective for MTBE removal (USEPA, 2004). Relative to other gasoline components, MTBE has a higher vapor pressure, higher solubility, and low Henry's constant (USEPA, 2004). Together these properties mean that when MTBE is spilled it is likely to dissolve in water and migrate quickly throughout the water system without being hindered by volatilization or adherence to soil. MTBE is also less prone to biodegradation. The tertiary carbon structure and stable, unreactive ether bond increase its resistance (Stocking, 2000). MTBE was initially thought to be entirely unsusceptible to microbial attack. Now there have been several reports of MTBE biodegradation by both aerobic and anaerobic cultures (Bradley, 2001, Pruden, 2001, Hristova, 2003, Somsamak, 2001). The aerobic cultures have been investigated and several organisms have been identified as able to biodegrade MTBE however, there is little information about anaerobic MTBE-biodegradation.

If we want to rely on natural attenuation for most MTBE removal, it is important that we know whether or not biodegradation is occurring in contaminated aquifers. We need to be able to measure the natural attenuation rate in the environment and to determine which metabolites are being formed. Since many fuel-contaminated aquifers have large anoxic zones (Mormile, 1996), it is important that we find out more about anaerobic MTBE biodegradation. In the Häggblom lab, anaerobic MTBE-degrading microcosms have been established using inocula from various sites (Somsamak, 2001, Youngster, 2004). Enrichments were initially established in 1996 with polluted estuarine sediment and since then, these cultures have been successfully transferred into fresh medium with enrichment of MTBE-degrading populations. They have retained MTBE degradation activity when tested with fresh sediments from different sites, different microbial populations, and different terminal electron accepting processes (Somsamak, 2005). These are the first, and very likely the only stable MTBE-utilizing anaerobic enrichment cultures available for more detailed microbial analysis. For my thesis research, I intend to identify the microbes in these communities, to develop methods for determining the rate of biodegradation in anaerobic environments, and to find out how to optimize conditions for such biodegradation to occur.

## **Methodology**

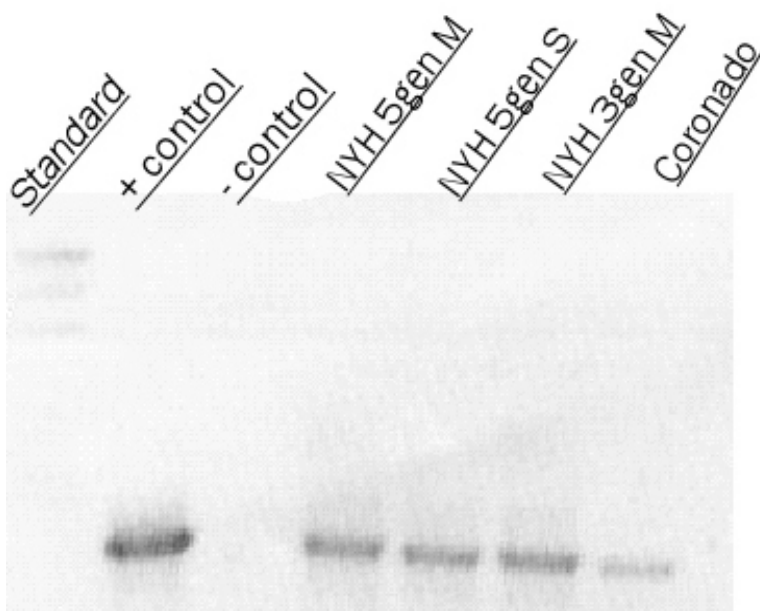
Funded by the NJWRRI fellowship, complementary molecular tools are now being used to identify organisms in the MTBE-degrading cultures. Metagenomic techniques are valuable for analyzing the physiology and genetics of uncultured organisms from environmental samples. Comparative community analysis has been started by terminally labeled restriction fragment length polymorphism (T-RFLP) analysis. From several consortiums, 16S rRNA genes have been amplified and fluorescently labeled using PCR with a 5' labeled 6-FAM 27F primer and an unlabeled 1525R primer (Figure 2). The amplified DNA was digested with restriction enzymes and the fragments were separated on an ABI sequence analyzer. Chromatograms are produced indicating the fragment sizes their relative abundance.

A 16S rRNA clonal library is being constructed. To do this, DNA has been extracted from the samples. 16S rRNA genes have been amplified by PCR using standard eubacterial primers 27F and 1525R. DNA fragments are currently being cloned into a plasmid vector. The ligated vector/insert plasmids will be transformed into high transforming efficiency *Escherichia coli* DH5, then plated onto a selective media plate. Colonies will be screened by plasmid extraction and digestion with restriction enzyme to identify unique clones.

I am also studying carbon isotope fractionation patterns in our MTBE degrading cultures. Natural attenuation rates of MTBE cannot be determined based on concentration measurements. MTBE's high solubility in water means that a decrease in concentration could be due to dispersal throughout the water system rather than degradation. If contamination occurs from multiple, sometimes unknown sources, concentration may be remaining stable or actually increasing despite the occurrence of degradation. Stable carbon isotope fractionation has been used to monitor in situ degradation of several environmental contaminants. Due to the greater stability of bonds involving  $^{13}\text{C}$  versus  $^{12}\text{C}$ , MTBE containing the lighter isotope is degraded preferentially, leading to an increased  $^{13}\text{C}:^{12}\text{C}$  ratio in the remaining MTBE.

### Principal Findings and Significance

So far, DNA has been extracted from several different enrichment consortia (Figure 1) and community analysis by T-RFLP has been conducted using this DNA (Figure 2).



**Figure 1.** 16S rRNA gene PCR product

PCR amplification of 16S rRNA genes from community DNA extracts with 27 Forward fluorescent and 1525 Reverse primers

This initial analysis of the dilute cultures gives us several useful pieces of information. The T-RFLP fingerprints show reduced diversity in the communities as a result of the enrichment process. Therefore, identification of these organisms will provide information about how MTBE-degradation occurs.

The profiles obtained from sediments from New York Harbor, Coronado Cay, and Cheesequake Park are all strikingly different in composition and diversity. Further analysis of these cultures and identification of the microbes may reveal multiple organisms that are capable of anaerobic MTBE-biodegradation. Even within the 3rd generation samples which are both from New York Harbor there are differences between communities. The two 5th generation New York Harbor samples, however, are less diverse and extremely similar to each other, indicating that methanogenic and sulfidogenic conditions are selecting for the same population from this sediment.

This project is ongoing. T-RFLP analysis of additional enrichment cultures is in progress. This data will be compared to current data to determine the effects of substrate variation and cultural conditions on the community. As mentioned above, a clonal library is in the process of being constructed. Unique clones will then be sequenced. At this point a computer program will be used to align the sequences from unique clones and construct phylogenetic trees. Gene databases will be searched for the closest matches to the sequences obtained from clones. The genes identified may elucidate the community physiology and phylogeny. T-RFLP analysis of clonal libraries will also be done to compare the representation seen in the T-RFLP fingerprint to the clones that are obtained

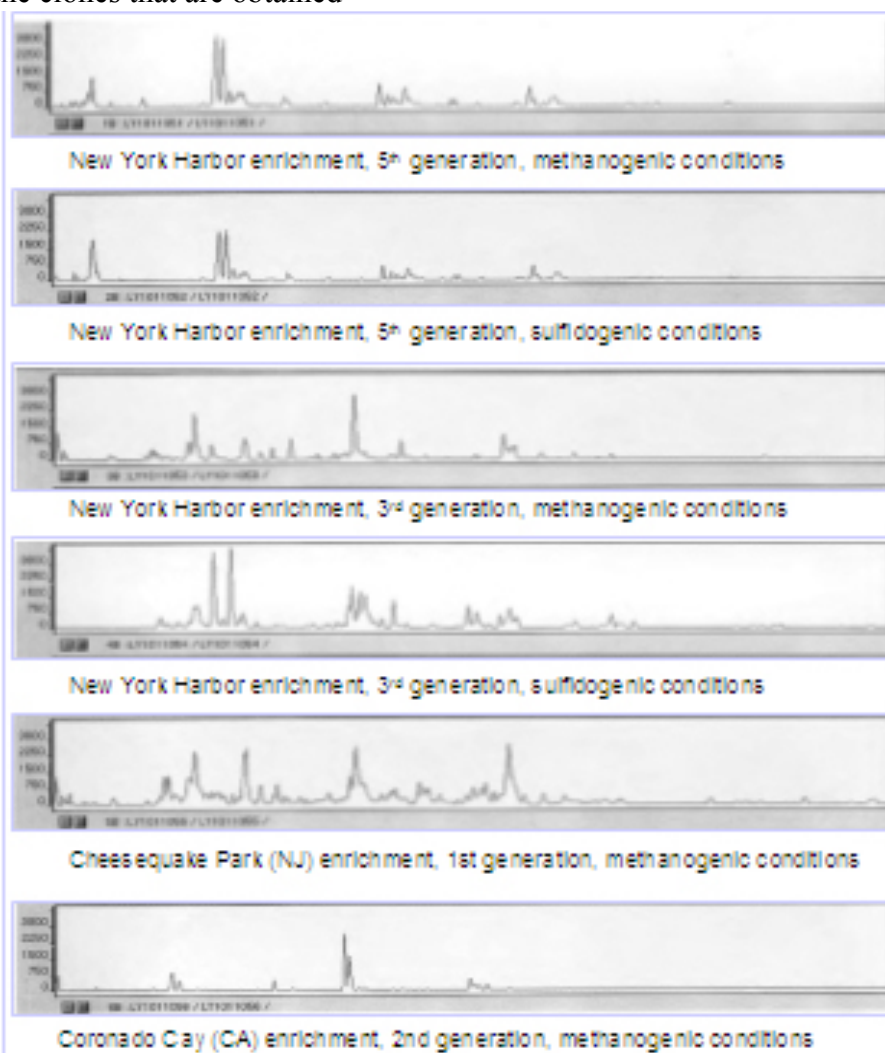


Figure 2.

**Terminal  
Restriction  
Fragment Length  
Polymorphism  
analysis of various  
enrichment  
communities**

Other plans include RNA extraction from enrichment cultures and subsequent analysis to determine which members of the population are actively growing, cultural isolation experiments, and eventually constructing anaerobic MTBE-degrading microcosms consisting of identified organisms

Characterization of MTBE-degrading anaerobic communities will be an important step toward assessing how to enhance MTBE biodegradation in the environment and to encourage complete mineralization of MTBE. It will also be useful for developing methods to monitor *in situ* biodegradation and thus determine whether or not remediation of polluted environments by natural attenuation is a viable option.

Studies done by Piyapawn Somsamak have demonstrated that the carbon isotopic fractionation during anaerobic biodegradation of MTBE is greater than that observed in aerobic culture (Somsamak, 2005). In July of 2006 I am going to be using Gas Chromatography-Isotope Ratio Mass Spectrometry to analyze the stable carbon isotope fractionation that occurs in sulfidogenic and methanogenic MTBE-degrading microcosms. Variations of culture conditions are currently being tested, including cultures grown in the presence of substrates which are likely to be present in fuel contaminated aquifers, such as ethanol and benzene. Other conditions that are being tested are amendments with syringate, a methoxylated aromatic carbon which may enhance the rate of MTBE degradation by enhancing acetogen growth. The effects of additional chemicals on the isotope fractionation that occurs during MTBE-degradation will help develop this assay as a tool for monitoring contaminated areas. We have also acquired an aerobic strain of MTBE-degrading bacteria from Finland. This strain is being tested for the effects of temperature on the growth rate, for degradation of tert amyl methyl ether (TAME), and the carbon and hydrogen isotope fractionation rates will be studied for all of these conditions.

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Youngster, L., P. Somsamak, L. Kerkhoff, and MM Haggblom. 2006. Characterization of anaerobic MTBE-degrading bacterial communities. Abstract Q-081. American Society for Microbiology 106<sup>th</sup> General Meeting, Orlando, FL, May 20-25, 2006.



# Lab-on-a-chip device for monitoring trace level arsenic

## Basic Information

<b>Title:</b>	Lab-on-a-chip device for monitoring trace level arsenic
<b>Project Number:</b>	2005NJ87B
<b>Start Date:</b>	3/1/2005
<b>End Date:</b>	2/28/2006
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	10
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Methods, Toxic Substances
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Kamilah Hylton, Somenath Mitra

## Publication

1. Wang, Xiaoyan, Somenath Mitra. 2006, Enhancing micro-scale membrane extraction by implementing a barrier film, Journal of Chromatography A (Article in Press)
2. Wang, Xiaoyan, Dawen Kou, Somenath Mitra, 2005, Continuous, on-line monitoring of haloacetic acids via membrane extraction, Journal of Chromatography A, 1089, 39-44
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4. Wang, Xiaoyan, Somenath Mitra, Development of a total analytical system by interfacing membrane extraction, pervaporation and high-performance liquid chromatography, Journal of Chromatography A, 1068, 237-242
5. Wang, Xiaoyan, Somenath Mitra, 2005, Microfluidic supported liquid membrane extraction, Annual Meeting of the American Chemical Society, San Diego, CA
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### Problem and Research Objectives

Manufacturing (e.g. semiconductors and ceramics), agriculture, veterinary medicine and food preservation are some areas in which arsenic (both organic and inorganic) are used. All these lead to the release of the metal into the environment and consequently human contact. Exposure to inorganic arsenic may result in stomach and intestine irritation, skin lesions, nerve injury and increased risk of cancer (skin, bladder, kidney and lung). A recent review by Hung et. al (1) summarizes analytical methods for As monitoring. It reports atomic spectroscopy (e.g. graphite furnace atomic absorption, hydride generation-atomic fluorescence and inductively coupled plasma mass spectroscopy), neutron activation analysis and electrochemical techniques as the most commonly used methods for As monitoring.

Even though these techniques offer low detection limits (below 10ppb), they are expensive, time consuming and do not lend themselves to field or on-line monitoring. The currently available portable field sensors are not necessarily accurate and do not have high accuracy and precision (1). This coupled with the acknowledgement that arsenic's permanence in the environment necessitates long-term routine analysis (2) points to the urgent need for portable devices that allow for fast and reliable measurements. The majority of field instruments depend upon what is known as the Gutzeit method (3) in which a reducing agent is used to produce arsenic trihydride (which is a toxic gas). The lowest detection limits reported by these field instruments is around  $2\text{mgL}^{-1}$  or 2ppm (1).

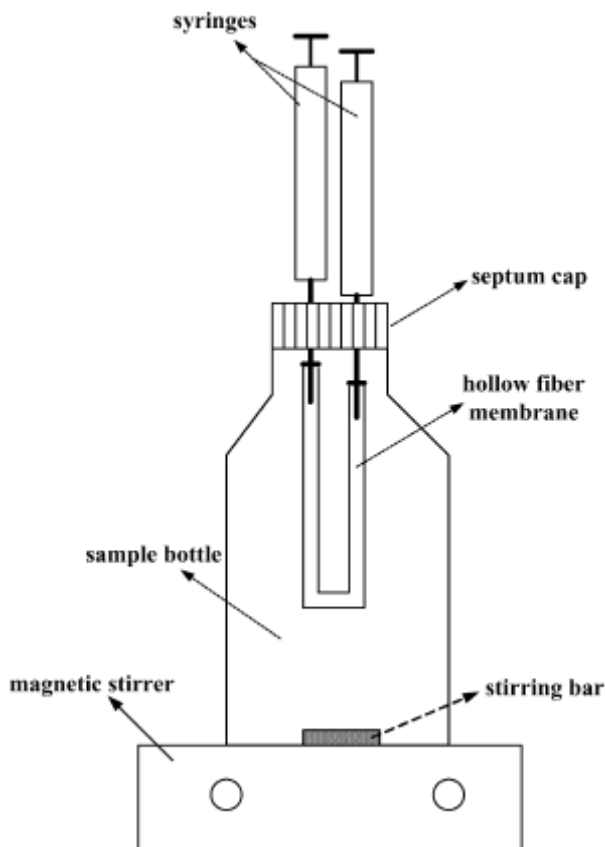
The study aims at the development of a low cost, lab-on-a-chip field instrument that is capable of determining the total inorganic arsenic concentration in water samples in a rapid, continuous, reproducible and accurate manner. The approach also precludes the tedious hydride generation methods used in conventional methodologies. By using a chelating agent and Supported Liquid Membrane Extraction (SLME) on a micro-scale platform, we propose to extract and concentrate As from aqueous samples, thus allowing for faster analysis and lower detection limits. The problem with trace analysis however lies in being able to effectively separate the analyte from complex matrices and achieving low detection limits. If the extraction process is lengthy or if the agitation of the sample (to enhance mass transfer) is forceful, then there may be significant loss of the extractant and consequently the analyte. It is therefore necessary to design the hollow fiber extraction in a manner that minimizes analyte loss and therefore results in good reproducibility and high enrichment.

### Methodology

The first part of the project therefore consisted of the improvement of the hollow fiber membrane extraction process. This was done by coating the membrane with a barrier film. This film was made by soaking the membrane in an organic solvent for a few seconds before extraction. Dihexyl ether, n-undecane, 1-octanol and n-decane were investigated as the barrier solvents. The membrane was held in place by two 50  $\mu\text{l}$  syringes (Hamilton, Reno, NV, USA), one of which was used to inject the acceptor into the lumen and the other for withdrawal of the extract. The PAHs anthracene, naphthalene, fluorene, phenanthrene, pyrene and acenaphthene were used as the analytes. The coated

membrane, filled with acceptor, was placed in a solution of the analytes and stirred (Cimarec 3, Barnstead/Thermolyne, Dubuque, Iowa, USA) for a given time period. At the end of this time, the extract was withdrawn and analyzed using HPLC-UV.

The diagram below illustrates the set-up.



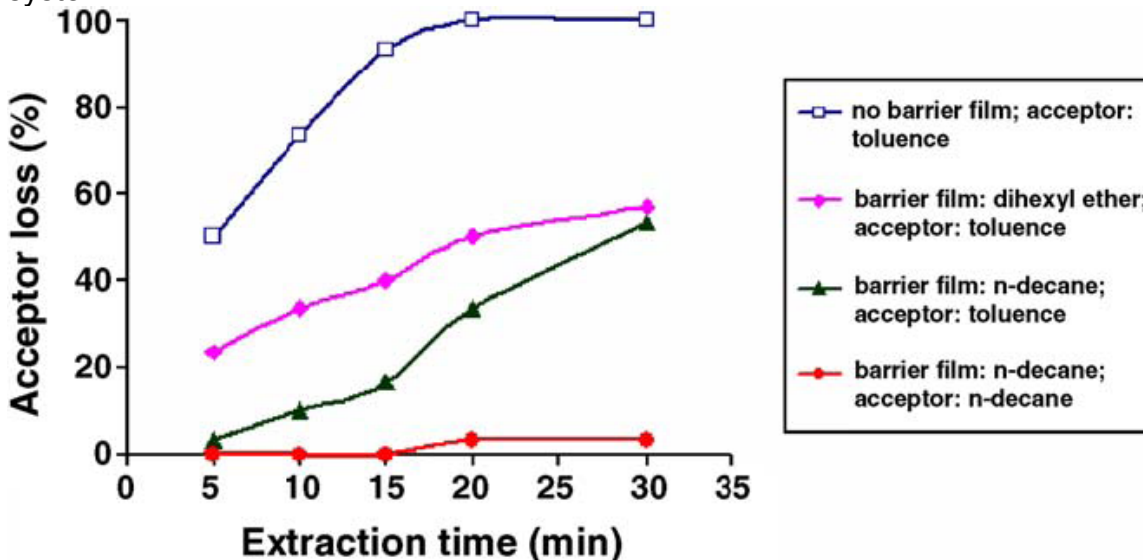
**Figure 1** Schematic diagram of the hollow fiber microextraction assembly.

Using the MiniTech program by Minitex Machinery Corporation, the extraction module (3.5 cm x 4.8 cm) was made by machining channels with a 3-axis (x,y,z) TechDesign Labvolt Milling Machine. 18 cm of a polypropylene hollow fiber membrane with an internal diameter of 0.6 mm and an average pore size of 0.2 microns (Accurel Q 3/2, Membrana GmbH, Wuppertal, Germany) was then placed in the channels and using syringe pumps, the sample solutions and extractants were pumped through the device for 10 to 30 minutes. Since this is the development stage the optimal flow rate, extraction time and extractant concentrations have not yet been determined. The extract was then collected and concentrations determined using absorption spectroscopy.

#### Principal Findings and Significance

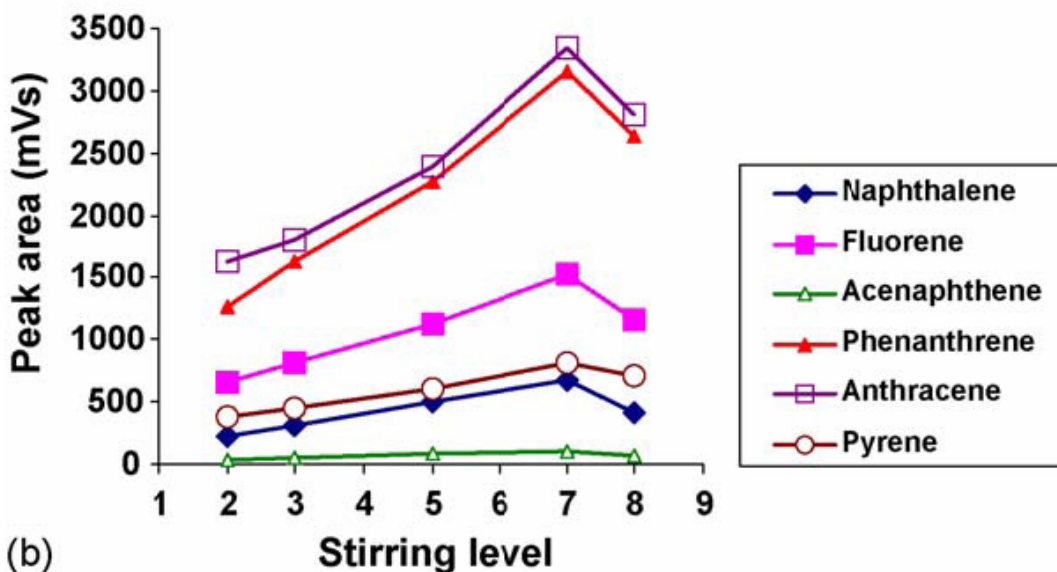
When n-decane was used as the acceptor as well as the barrier film, acceptor loss was minimal and hence enrichment was greatest. This is illustrated in the graph below. For a 20 minute extraction without the barrier film, all the

acceptor was lost compared to the small loss with the n-decane/n-decane system.



**Figure 2** shows acceptor loss as a function of time

Once a suitable acceptor/barrier film combination was chosen, stirring level was investigated to determine its effect on analyte enrichment. Stirring level was varied between 2 and 8 arbitrary units. It was discovered that up to level 7, enrichment was enhanced and so level 7 was chosen as the optimal stirring speed. This is illustrated in the graph below



**Figure 3** illustrates the effect of stirring speed on peak area

The barrier film allowed for stabilization of the acceptor and so longer extraction times could be used which translates into greater enrichment. It also allowed for greater reproducibility and lower detection limits.

**Table1** shows effect of barrier film on acceptor loss and enrichment factor.

Barrier film	Water solubility (20 °C)	Boiling point (°C)	Enrichment factor						Acceptor loss (%)
			Naphthalene	Fluorene	Acenaphthene	Phenanthrene	Anthracene	Pyrene	
Without barrier film	0.515 g/L <sup>a</sup>	110.6 <sup>b</sup>	nd <sup>c</sup>	67.5	nd	68.0	54.6	76.6	73.3
Dihexyl ether	Insoluble	226.6	nd	164.1	nd	150.3	129.3	175.4	33.3
1-Octanol	Insoluble	194.5	nd	117.9	nd	117.9	77.3	117.6	26.7
<i>n</i> -Undecane	Insoluble	196.0	248.7	120.6	95.6	121.2	87.2	125.9	10
<i>n</i> -Decane	0.009 ppm	174.0	485.6	146.2	185.7	144.0	94.6	158.2	10

<sup>a</sup> Toluene's water solubility.

<sup>b</sup> Toluene's boiling point.

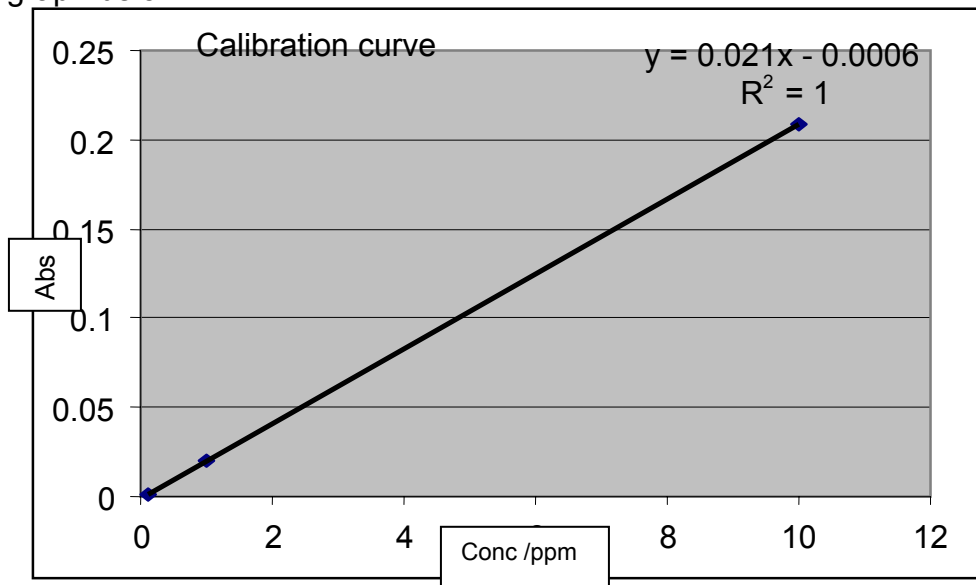
<sup>c</sup> Not detected.

Initial findings indicated that the microfluidic channels are capable of absorbing significant amounts of metals. To verify this, the membrane was removed from the channels and an aqueous sample containing known amounts of a metal was allowed to flow through the channels and the absorbance of the exiting solution measured. The initial concentration of the sample solution was 1ppm.

**Table 2** below illustrates absorption by the microfluidic device by comparing initial and final concentrations.

Initial Conc/ppm	Final concentration/ ppm	Sample Flow Rate /mlmin <sup>-1</sup>	Extractant Flow Rate /mlmin <sup>-1</sup>
1.00	0.22	0.41	0.08
1.00	0.46	0.20	0.05
1.00	0.70	0.43	0.05

The final concentrations were calculated using the calibration equation. See graph below:



The results also indicate that increasing the flow rate of the sample solution leads to an even greater absorption by the polycarbonate device. This could be explained by the fact that the surfaces come in contact with a larger amount of sample in a given time.

In light of these findings, it was decided that an acrylic material coated with silica would be investigated as an alternative. Jack Rundel under the direction of his advisor (Vincent Remcho) at Oregon State University is in the process of coating the microfluidic channels. The material is first cleaned by sonicating it in methanol. It is then blow dried with nitrogen and then a RF sputtering system is used to deposit a thin silica film with a thickness of about 500nm. Once this is in place, we will then focus on optimizing the method to extract, concentrate and detect arsenic. Sodium m-arsenite and sodium arsenate dibasic heptahydrate will be used to make standard As(III) and As(V) solutions. Dibutylphosphonate(DBP) and tributylphosphate(TBP) will be investigated as possibilities for the supported liquid membrane. To allow for valid comparisons with our detection module we will first use GFAAS to quantify the arsenic. When it is determined that significant extraction and enrichment is being achieved, the detection module will then be coupled to the extraction module to determine its effectiveness.

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# A Study to Link Atmospheric N Deposition with Surface and Ground Water N and Denitrification Capabilities in an Urban New Jersey Wetland

## Basic Information

<b>Title:</b>	A Study to Link Atmospheric N Deposition with Surface and Ground Water N and Denitrification Capabilities in an Urban New Jersey Wetland
<b>Project Number:</b>	2005NJ88B
<b>Start Date:</b>	3/1/2005
<b>End Date:</b>	2/28/2006
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Nitrate Contamination, Wetlands, Water Quality
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Barbara Turpin, B. W. Ravit

## Publication

1. Ravit, Beth, 2006, Presentations to 200 Middle School Students on Wetlands Ecology using Teaneck Creek research results to provide a site-specific example; 1200 Student-hours (200 students/day x 5 days), Curriculum Enrichment, Teaneck Middle School, Teaneck, NJ.
2. Ravit, Beth, Mary Arnold, 2006, What in the World Science, Teacher handbook (5 modules) on Wetlands Ecology using Teaneck Creek as a Site-Specific Example, Designed for the Teaneck Middle School, Teaneck, NJ.

## **Project Summary**

### ***Objectives:***

Atmospheric deposition is a major source of nitrogen in northeastern U.S. ecosystems. Local sources related to urbanization and regional transport from power plants are both likely to be substantial contributors to atmospheric nitrogen deposition in urban areas. However, atmospheric nitrogen deposition measurements have mostly been made in more remote locations. There have been few measurements of atmospheric nitrogen fluxes to urban ecosystems.

The Teaneck Creek Conservancy, a private non-profit organization, has been granted a long-term license to manage a 46 acre site within the Bergen County Parks system. Scientists at Rutgers University and elsewhere are participating in their effort to characterize, restore and enhance 20 acres of urban wetlands within the public park. A baseline monitoring study is underway to characterize the fluxes of nitrogen species through this system and determine the denitrification capabilities of the system prior to restoration. Inorganic and organic atmospheric wet and dry deposition inputs are being provided through this funding mechanism.

The specific objective of this project is to characterize the amounts and the chemical composition of total N-species, inorganic and organic, present in the atmospheric wet and dry N deposition within the Teaneck Creek site as annual fluxes. This was accomplished through monitoring over all four seasons.

### ***Methodology:***

Rainwater was collected using a wet-dry deposition collector (Aerochem Metrics Model 301, Bushnell, FL), fitted with a stainless steel bucket that opened only during storm events. A clean bucket was deployed before each sampling event. The collector was positioned on the roof of the Thomas Jefferson School, adjacent to the Teaneck Creek site. Water was retrieved from the collectors within ~12 hours to minimize microbial degradation of dissolved organic matter and consumption of inorganic nutrients. Sample temperature and pH were measured immediately after collection and samples were filtered through pre-combusted glass fiber filters (Whatman, GFF; baked for four hours at 500 °C; then rinsed with deionized water). Rainwater was frozen in polypropylene screw-capped tubes for storage until analysis. A total of 19 rain events were sampled from spring 2005 through spring 2006 (6 in spring, 6 in fall, 3 in summer, 4 in winter).

The water-soluble component of dry particle deposition was collected using the method of Lindberg and Lovett (1985). Briefly, dry deposition was collected on polycarbonate plates (Fisherbrand, #08-757-12, 100x15mm, sterile polystyrene) exposed to the atmosphere during rain-free periods. Plates were positioned horizontally, 1.6–1.8 m above the ground, on an arm extending laterally from a vertical pole. Measurements were made concurrently about 3 m, 25 m, 47 m, 69 m and 91 m from Degraw Avenue where the Avenue passes through the Teaneck Creek site (Figure 1). Measurements were also made in two locations on the roof of the Thomas Jefferson School, adjacent to the Teaneck Creek site. Duplicate samples were collected at 47 m. Plates were exposed from 1-5 days. Plates were extracted in the laboratory with 20 ml of DI water using an acid washed stir bar, by spinning on a stir plate for 30 min. Each extract was filtered through a 25 mm pre-combusted glass fiber filter (Whatman, GFF; baked for four hours



at 500 °C; then rinsed with deionized water). Extracts were frozen in polypropylene screw-capped tubes for storage until analysis. Early in the experiment plates were acid washed and reused, but we rapidly became aware that these reused plates yielded unacceptably high blank levels. Thus, all reported data were collected with new plates.

Samples were collected April 8-13, 2005, August 17-19 and 23-27, 2005, October 17-21 and 26-31, 2005, January 25-29, 2006, and February 6-10, 2006. During August and October, 2005 an experiment was conducted to examine the assumption that samples obtained really provide a measure of particle deposition fluxes and do not reflect gaseous dry deposition fluxes. Initially this method was used by the deposition community to provide estimates of total dry deposition. However, recently researchers have become increasingly convinced that this method provides, instead, an estimate of particle dry deposition. Gases are expected to deposit until adsorbed phase – gas phase equilibrium is achieved. After that point, no further net deposition is expected. Particles, on the other hand, will continue to deposit at a rate dependent on their size, concentration in the atmosphere, wind speed and surface roughness. Thus, if the fluxes measured were dominated by gaseous deposition, composites of short duration measurements would yield larger fluxes than longer duration measurements collected concurrently. If measured fluxes really provide a measure of particle deposition, as the deposition community is now concluding, calculated fluxes would be independent of sample duration.



Figure 1. Location of dry deposition sampling locations at Teaneck.

Dry Deposition Plate #	Site ID	Post Height
1	Degraw1	5'10"
2	Degraw2	5'3"
3	Degraw3	5'6"
4	Degraw4	5'6"
5	Degraw5	5'6"
6	Degraw6	5'9"

Bulk nutrients ( $\text{NO}_3^- + \text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ) in each rain sample and dry deposition extract were measured with an automated nutrient analyzer and standard colorimetric methods (Lachat, Inc; QuickChem methods,  $\text{NH}_4^+$ : 31-107-06-1-A;  $\text{NO}_3^- + \text{NO}_2^-$ : 31-107-04-1-A;  $\text{PO}_4^{3-}$ : 31-107-04-1-A). Dissolved organic nitrogen (DON) was determined as the difference between total dissolved N measured with an Antek 7000 TN Analyzer (Seitzinger and Sanders, 1999) and the dissolved inorganic nitrogen ( $\text{NO}_3^- + \text{NO}_2^-$ , and  $\text{NH}_4^+$ ). DOC was measured with a Shimadzu 5000A TOC analyzer (Sharp et al. 1993).

The depositional flux of nutrients in each rainwater event sampled was calculated by multiplying the nutrient concentration by the volume of rainwater and normalizing to a  $\text{m}^2$  area ( $\mu\text{moles}/\text{m}^2\text{-event}$ ), taking into account the surface area of the rainwater collector ( $0.0642 \text{ m}^2$ ). Dry particle deposition for each sample ( $\mu\text{moles}/\text{m}^2\text{-day}$ ) was calculated by multiplying the measured concentration ( $\mu\text{M}$ ) by the volume of DI water used for extraction (20 mL) and dividing by the area of the deposition plate ( $5.67 \times 10^{-3} \text{ m}^2$ ) and the time (days) the plate was deployed.

### ***Principal Findings and Significance:***

Concentrations of nitrate plus nitrite (2-72  $\mu\text{M}$ ), ammonium (2-51  $\mu\text{M}$ ), DON (0-27  $\mu\text{M}$ ), DOC (16-311  $\mu\text{M}$ ) and phosphate (0.1-1.0  $\mu\text{M}$ ) in wet deposition showed considerable variation among rain events during the study period (Table A1; Figure 2). In general, higher concentrations were measured during relatively small rain events and lower concentrations during high volume rain events for all constituents (Figure 2). The range of nutrient concentrations in rainwater collected at Teaneck Creek was similar to the range in concentrations measured in rainwater collected at other locations in New Jersey, including New Brunswick, Camden and the Pinelands during the past 5 years (Seitzinger et al. 2005).

The total amount of rainwater sampled at Teaneck Creek during the study period (March 2005-February 2006) was 323 mm. Rainwater volume at a nearby location, Pascack, NJ, is measured by the USGS (unpublished data). The most recent data, however, for that site are only available through 2005. During 2005 a total of 1324 mm of rain fell at Pascack. Therefore, until more recent data is available, we assumed that the total rainfall during our annual study period was similar to that during the 2005 calendar year. Based on that assumption, we measured the nutrient concentrations in approximately 25% of the total annual rainfall. We estimated the total annual amount of inorganic and organic nitrogen deposited in wet deposition at Teaneck Creek by multiplying the total measured nutrient flux in all events sampled during the March 2005-February 2006 period (Table 1) by a factor of 4, to account for deposition during events that we did not sample. The annual wet deposition was estimated to be:  $\text{NO}_3^- + \text{NO}_2^-$ :  $15,560 \mu\text{mol}/\text{m}^2\text{-year}$  (2.18 kg N/ha-year);  $\text{NH}_4^+$   $11,600 \mu\text{mol}/\text{m}^2\text{-year}$  (1.62 kg N/ha-year); DON  $6,850 \mu\text{mol}/\text{m}^2\text{-year}$  (0.96 kg N/ha-year). These rates are slightly lower than reported by NADP for the Hudson/Raritan watershed (3.9 and 1.9 kg N/ha-year for  $\text{NO}_3^- + \text{NO}_2^-$  and  $\text{NH}_4^+$ , respectively; Meyers et al. 2001). However, given the relatively small number of sampling dates in the current study relative to that from the multi-year NADP measurements, no firm conclusions should be drawn about differences at this time. Overall, the rates we measured at Teaneck are within the range of rates reported for inorganic N deposition to thirty watersheds along the East and Gulf coasts of the US from

Maine to Texas (1.2-4.4 and 1.1-2.8 kg N/ha-year for  $\text{NO}_3^- + \text{NO}_2^-$  and  $\text{NH}_4^+$ , respectively; Meyers et al. 2001).

Annual dry deposition fluxes were estimated from Degraw Avenue sample fluxes by multiplying the average of seasonal measurements by the number of days in calendar year 2005 with no rain (242 days; USGS Pascack). The annual particle dry deposition of  $\text{NO}_3^- + \text{NO}_2^-$  and  $\text{NH}_4^+$  were more than one order of magnitude lower than the wet deposition. Particle dry deposition of dissolved organic nitrogen (DON) is only a factor of two smaller. DON fluxes were highly variable from sample to sample, and thus the uncertainties in the annual flux of DON are reasonably large.

Lovett et al. (2000) measured particulate  $\text{NO}_3^-$  deposition within and north of New York City in June – September, 1997 and found deposition fluxes of 16, 7, and 3  $\mu\text{mol NO}_3^-/\text{m}^2\text{-day}$  a distance 11, 45, and 128 km from Central Park. The particulate  $\text{NO}_3^-$  deposition fluxes from this study are within this range, and more similar to the suburban measurements of Lovett than the NYC measurements (1 - 11  $\mu\text{mol NO}_3^-/\text{m}^2\text{-day}$ ).

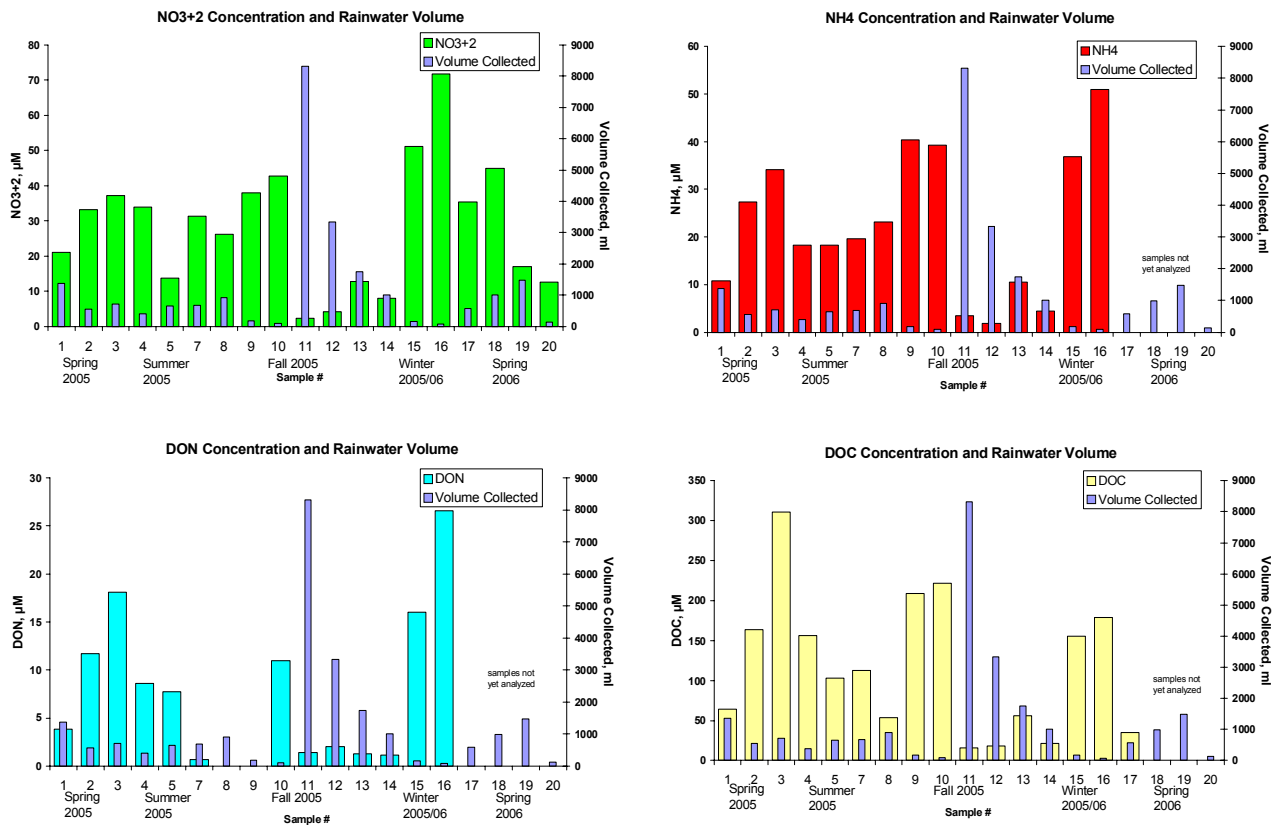


Figure 2. Nutrient concentrations and rainwater volume collected during rainwater events sampled during 2005-2006 at Teaneck Creek, NJ.

**Table 1. Dry deposition fluxes calculated from deposition plate measurements.** Seasonal fluxes have units of ( $\mu\text{mol}/\text{m}^2\text{-day}$ ) and annual average fluxes are in units of ( $\mu\text{mol}/\text{m}^2\text{-year}$ ). Shown are mean  $\pm$  1 standard deviation of seasonal measurements made at all 5 Degraw Ave locations (Figure 1). \*\*indicates samples not yet analyzed;  $\text{NO}_3$  represents  $\text{NO}_3^- + \text{NO}_2^-$ . DOC is dissolved organic carbon. TDN is total dissolved nitrogen. DON is dissolved organic nitrogen.  $\text{DON} = \text{TDN} - \text{NO}_3 - \text{NH}_4$ .

Flux ( $\mu\text{mol}/\text{m}^2\text{-day}$ )	$\text{NO}_3$	$\text{NH}_4$	$\text{PO}_4$	DOC	TDN	DON
<b>Spring</b> (Apr 8-13, 2005)	$4.8 \pm 0.7$	$2.8 \pm 0.7$	$3.1 \pm 1.5$	$378 \pm 194$	$43 \pm 20$	$36 \pm 20$
<b>Summer</b> (Aug 17-19; 23-27)	$4.9 \pm 3.5$	$2.1 \pm 1.0$	$0.5 \pm 0.2$	$139 \pm 52$	$12.3 \pm 4.8$	$4.8 \pm 3.2$
<b>Fall</b> (Oct 17-21; 26-30)	$4.2 \pm 3.6$	$2.0 \pm 2.1$	$0.4 \pm 0.2$	$55 \pm 26$	$10.4 \pm 6.7$	$5.1 \pm 2.6$
<b>Winter</b> (Jan 25-29; Feb 6-10)	$4.9 \pm 1.6$	**	$0.3 \pm 0.6$	**	**	**
<b>Annual Avg Flux</b> ( $\mu\text{mol}/\text{m}^2\text{-year}$ )	<b>1,140</b>	<b>557</b>	<b>260</b>	<b>129,600</b>	<b>14,200</b>	<b>3,700</b>
<b>Annual Avg Flux</b> (kg N, P or C/ha-year)	<b>0.16</b>	<b>0.08</b>	<b>0.08</b>	<b>15.6</b>	<b>2.0</b>	<b>0.52</b>

Detection limits for dry deposition samples, expressed as three times the standard deviation of the plate blank, were  $\text{NO}_3^- + \text{NO}_2^-$ :  $1.8 \mu\text{M}$  ( $1.3 \mu\text{mol}/\text{m}^2\text{-day}$ );  $\text{NH}_4^+$   $0.3 \mu\text{M}$  ( $0.2 \mu\text{mol}/\text{m}^2\text{-day}$ );  $\text{PO}_4$ :  $0.1 \mu\text{M}$  ( $0.08 \mu\text{mol}/\text{m}^2\text{-day}$ ); and DOC  $2.6 \mu\text{M}$  ( $1.9 \mu\text{mol}/\text{m}^2\text{-day}$ ). (Detection limits in parentheses are fluxes and assume a 5-day sample). Detection limit calculations for TDN and DON are awaiting analysis of a final set of samples. A total of 80% of  $\text{NO}_3^- + \text{NO}_2^-$ , 100% of  $\text{NH}_4^+$ , 56% of  $\text{PO}_4$  and 100% of DOC samples were above detection limits. Samples were not blank corrected.

Dry deposition fluxes calculated from composites of short duration samples (1-2 days) were not significantly different from those calculated from concurrently-collected long duration samples (2-4 days) according to a paired t-test with 95% confidence values. (Calculations were performed for  $\text{NO}_3$  and  $\text{NH}_4$  only, with  $N=6$  and  $N=4$ , respectively.) The fact that these differences are not significant agrees with the growing body of evidence from the broader dry deposition research community (G. Lovett, personal communication) that dry deposition plates predominantly collect particle dry deposition and do not reflect gaseous dry deposition.

Although the differences were not significant, it must be noted that composites of short duration samples yielded fluxes that were 20% and 16% higher (for  $\text{NO}_3$  and  $\text{NH}_4$ , respectively), on average, than long duration samples. A composite of two short duration particle deposition samples would have twice the gas adsorption artifact of a single concurrently-collected long duration sample. Thus, there is some evidence of a gas adsorption artifact, suggesting that particle dry deposition fluxes reported here are upper limit estimates.

Figure 3 shows  $\text{NO}_3$  particulate dry deposition flux ( $\mu\text{mol}/\text{m}^2\text{-day}$ ) with distance from Degraw Avenue. A decreased flux with distance is clearly evident within 100 m of the roadway. Inorganic  $\text{NO}_3$  in ambient atmospheric particles is found primarily in the form of  $\text{NH}_4\text{NO}_3$  in continental areas, and is predominantly formed in the atmosphere (secondary) from nitric acid and ammonia. Because nitric acid is also predominantly

formed in the atmosphere (i.e., from oxides of nitrogen), its concentrations are fairly homogeneous over large areas. A decreased flux with distance from the roadway suggests that, in close proximity to this busy roadway (within 50-100 m), roadway emissions are contributing to particle dry deposition. The enhancement is on the order of 20-50% greater than the values at 100 m. This could be a result of either primary nitric acid emissions and/or primary ammonia emissions converting ambient nitric acid (gaseous) to particulate ammonium nitrate.

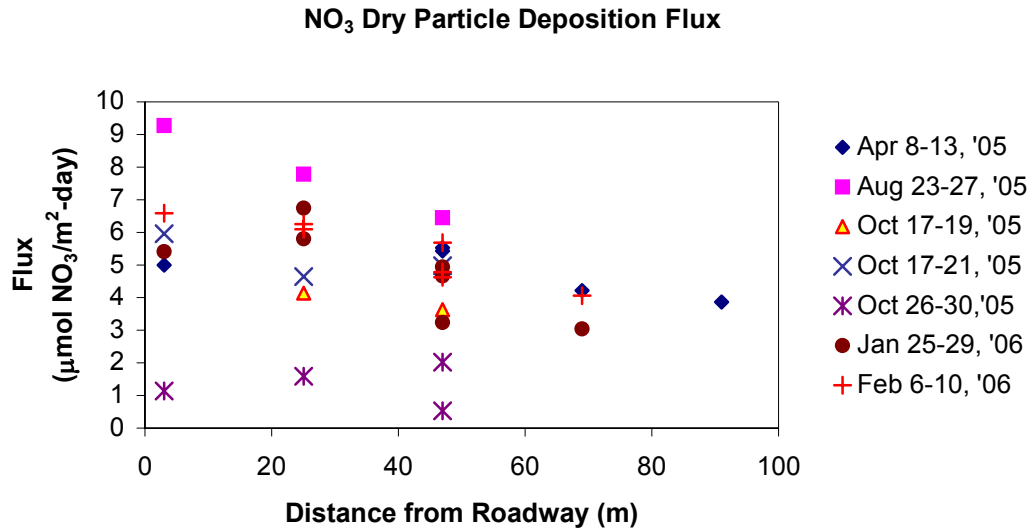


Figure 3. NO<sub>3</sub> Particle Dry Deposition Flux (µmol/m<sup>2</sup>-day) and distance from Degraw Avenue.

**Ongoing Activity:**

Analyses of wet and dry (particle) deposition are being completed for a few samples collected after the end date of the award. In addition, a sampler to measure dry gaseous deposition of N is being tested and samples will be collected at Teaneck for selected dates in the upcoming months.

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## APPENDIX

**Table A1.** Nutrient concentrations and rainfall amount for wet deposition at Teaneck Creek, NJ. Blank cells indicate samples not yet analyzed.

Collection Date	Sample #	Volume collected (ml)	Deposition Amount (mm)	pH	NO <sub>3</sub> (μM)	NH <sub>4</sub> (μM)	DON (μM)	DOC (μM)	PO <sub>4</sub> (μM)	μmol N/m <sup>2</sup> /event		
										NO <sub>3,2</sub>	NH <sub>4</sub>	DON
4/8/2005	1	1365	21.3	4.1	21.0	10.8	3.8	64	0.9	446	230	59
4/28/2005	2	555	8.6	4.2	33.1	27.4	11.7	164	0.3	286	237	182
5/23/2005	3	710	11.1		37.2	34.1	18.1	311	0.8	411	377	282
6/7/2005	4	395	6.2	4.4	33.9	18.2	8.6	156	0.2	209	112	134
6/28/2005	5	645	10.0	4.2	13.8	18.3	7.7	103	0.2	138	184	120
7/5/2005	7	675	10.5	4.0	31.3	19.6	0.7	112	0.1	329	206	11
9/16/2005	8	910	14.2	4.7	26.2	23.1	0.0	54	0.1	371	327	0
9/27/2005	9	170	2.6	4.7	37.9	40.4	0.0	209	0.1	100	107	0
9/30/2005	10	99	1.5	4.1	42.7	39.3	11.0	222	0.3	66	61	171
10/10/2005	11	8320	129.6	3.9	2.4	3.5	1.4	16	0.1	311	454	22
10/26/2005	12	3330	51.9	5.0	4.1	1.8	2.0	18	0.1	213	93	31
11/18/2005	13	1745	27.2	n/a	12.8	10.5	1.3	56	0.1	348	285	20
12/12/2005	14	1000	15.6	5.0	7.9	4.4	1.1	22	0.1	123	69	17
1/31/2006	15	165	2.6	4.2	51.1	36.8	16.0	156	0.1	131	95	249
2/7/2006	16	82	1.3	4.0	71.8	51.0	26.6	179	0.5	91	65	414
2/14/2006	17	573	8.9	4.7	35.3			35	1.0	315		
4/6/2006	18	994	15.5	4.3	44.9				0.1	695		
4/10/2006	19	1476	23.0	4.7	17.1				0.2	392		
5/4/2006	20	127	2.0	4.7	12.5				0.2	25		

# Impacts of Organic Matter Heterogeneity on Desorption and Availability of Sediment-bound PCBs

## Basic Information

<b>Title:</b>	Impacts of Organic Matter Heterogeneity on Desorption and Availability of Sediment-bound PCBs
<b>Project Number:</b>	2005NJ89B
<b>Start Date:</b>	3/1/2005
<b>End Date:</b>	2/28/2006
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	6
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Hydrogeochemistry, Toxic Substances, Sediments
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Weilin Huang, Lisa Totten

## Publication

1. Ma, Yingjun; Song, Jianzhong; Xiao, Baohua; Totten, Lisa A.; Huang, Weilin (2006) Carbonaceous materials in sediments and their role in the equilibrium sorption of phenanthrene by sediments. (in preparation)
2. Ma, Yingjun; Xiao, Baohua; Totten, Lisa A.; Huang, Weilin (2006) Quantification of exchangeable phenanthrene bound on soils and sediments with isotope-labeled compounds. (in preparation)

## ***Problem and Research Objectives***

Anthropogenic organic chemicals typically bind to suspended particulate matter and colloids, facilitating their transport via surface runoff or advective flow and allowing them to accumulate in estuarine sediments. These sediment-bound contaminants can later be released to the water column via resuspension and desorption, becoming available to living organisms and posing serious risks to the ecosystem. Although some severely contaminated coastal and estuary sites may be partially restored by dredging, containment or other remediation schemes, PAH/PCB residues in many estuaries remain uncontrolled due to high cost of clean-up procedures, becoming potential long-term threats for exposure. A detailed scientific understanding of mobility, reactivity and availability of these contaminants is critical to predicting fate of contaminants and their effects on organisms and ecosystems and to assessing related environmental risks in uncontrolled coastal and estuary environments. This scenario is occurring in the Hudson River/New York-New Jersey Harbor Estuary. PCBs released into the Upper Hudson River and stored in the riverine sediments are being transported into the New York-New Jersey Harbor Estuary, where they have the potential to accumulate in the estuarine sediments and/or to desorb from the particulate matter, rendering them bioavailable to the estuarine food chain. The Upper Hudson contributes about half of the entire PCB load to the New York-New Jersey Harbor Estuary (TAMS Consultants et al., 1997; Farley et al., 1999; Totten, 2004). Thus desorption of PCBs from Upper Hudson sediments has the potential to be the single most important mechanism for releasing PCBs in to the food chain of the estuary. Alternatively, Yan (2003) demonstrated that phytoplankton in Raritan Bay display PCB congener patterns similar to those found in the atmosphere, and argue, based on kinetic modeling of air-water exchange and uptake by phytoplankton, that the atmosphere is the single most important source of bioavailable PCBs in the system. This research will determine whether desorption of PCBs from contaminated sediments is fast enough to compete with air-water exchange as an important process controlling the bioavailability of PCBs in the estuary. The answer to this question has important implications in the management of PCB contamination in the Estuary.

We proposed this study to characterize and quantify Humic Acid (HA), Black Carbon (BC) and kerogen in sediments and to investigate the role of each of the three Sediment Organic Matter (SOM) fractions in the sorption, desorption and bioavailability of PAHs/PCBs bound on sediments. Our major hypotheses were that the sediments in the Hudson River Estuary and NJ/NY Harbor contain both coaly material and black carbon and that particulate organic matter such as BC and coaly materials dominate the sorption, desorption and environmental availability of bound PAHs and PCBs. The specific objectives of this study were to:

- 1) fractionate, quantify, and characterize major SOM fractions for Hudson River sediments;
- 2) characterize the role of particulate organic matter in the sorption of PAHs and PCBs on Hudson River sediments;



3) quantify desorption of PAHs/PCBs from the sediments;

4) estimate the availability of sediment-bound PAHs/PCBs to environmental acceptors.

## ***Methodology***

### *Fractionation and characterization of SOM*

We obtained seven Hudson River sediment samples from the Institute of Marine and Coastal Sciences at Rutgers. For comparison, we selected three additional sediments collected from the Delaware River, Baltimore Harbor, and the Anacostia River of Washington DC. These samples were characterized in terms of their contents of HA, BC, and kerogen following a procedure of Song et al. (2002). Briefly, each sediment sample was extracted with NaOH following a standard base extraction procedure (Hayes, 1985) to obtain humic acid (HA). The HA was recovered from the extract and the solid residue was demineralized using an HCl (6 M) + HF (22 M) acid mixture at 60°C for 20 hrs. After digestion, the content was centrifuged, the residue was rinsed with 2 M HCl and milli Q water and dried at 60°C. The solid residue contained both kerogen and BC, and was designated as KBC (kerogen + black carbon). The latter (BC) was isolated by treating the solid with a hot dichromate/sulfuric acid in which kerogen was oxidized while BC remains mostly unchanged.

The isolated HA, KBC, and BC were freeze-dried, weighted, and stored in glass bottles for use in characterization. The total organic carbon (TOC) contents of the SOM fractions were analyzed with a high temperature combustion method. The ash contents were determined independently by complete oxidation of each SOM fraction under 950°C in a furnace. The organic facies and the shapes, sizes, and degree of maturation of the BC and KBC fractions were examined under an optical microscopy in transmitted and reflected mode.

### *Sorption experiments*

All ten sediment samples were used in this study as the sorbents. To examine the role of BC and kerogen in the sorption of PAHs and PCBs, the 10 samples were Soxhlet extracted with dichloromethane to remove any existing PAH/PCB residues, and the extracted sediments were used as sorbents for sorption studies.

Phenanthrene and two PCB congeners (3,4,6'-trichlorobiphenyl (IUPAC #35) as a planar congener and 2,2',6,6'-tetrachlorobiphenyl (IUPAC #54) as a non-planar congener) were chosen as the Hydrophobic Organic Chemical (HOC) probes in this study. The aqueous solution used in the sorption equilibrium experiments contained 0.005 M CaCl<sub>2</sub> to simulate the electrolytes present in natural water and 100 mg/L of NaN<sub>3</sub> as a microbial inhibitor. The pH of the solution was adjusted and maintained at 7.0 ± 0.2 with NaHCO<sub>3</sub>. A primary solute stock solution was prepared by dissolving an appropriate amount of

each chemical in HPLC-grade methanol. Methanol stock solutions of various solute concentrations were obtained by sequential dilution from the primary solution. Initial aqueous solutions with different solute concentrations were prepared by mixing desired volumes of the appropriate stock solution with the aqueous solution and were used for sorption experiments. All aqueous solutions used for sorption experiments contained < 0.2% of methanol.

Sorption equilibrium experiments were conducted at 22 °C using flame-sealed glass ampules (10 mL, Kimble) as batch reactor systems. The experimental procedures detailed in Huang et al. (1998) and Xiao et al. (2004) were exactly followed. Preliminary tests were run to determine an appropriate solid-to-solution ratio for each sorbent-sorbate system to achieve 40-60% reduction of the initial aqueous phase concentrations. Sorption rate tests were performed, and the results showed that a solid-solution contact time of 21 d was sufficient for attainment of apparent sorption equilibrium for all sorbent-solute systems.

The final tests were conducted with the same procedure as the preliminary tests for collecting the sorption data reported here. In each test, ampules containing a predetermined amount of sorbent and an appropriate amount of aqueous solution, with a headspace of about 0.8 mL, were flame-sealed in a natural gas flame. After being checked for leakage and shaken by hand for initial mixing of the contents, the sealed ampules were placed on a shaker set a speed of 125 rpm for mixing. After shaking for 21 d, the ampules were set upright for 2 d to allow solids to settle, then were flame opened. Immediately an aliquot of ~3 mL of the clear supernatant was carefully withdrawn from each reactor without disturbing the settled solid phase, and mixed with ~2 mL of HPLC grade methanol in a pre-prepared 5-mL glass vial. The amounts of methanol and supernatant were weighed on a balance, and a dilution factor was calculated based on mass ratio and the density data of the mixture. The supernatant-methanol mixtures were used for analysis of solute concentrations in the equilibrated solution phase with an HPLC method described below.

Control experiments were conducted using reactors containing no sorbent for assessing loss of solutes to reactor components during sorption tests. Results showed that average system losses were consistently less than 4% of initial concentrations of sorbate; hence, no correction was made during reduction of sorption data.

Solute concentrations in the initial and the equilibrated supernatants were measured with a reverse-phase HPLC (ODS, 5  $\mu$ m, 2.1  $\times$  250 mm column on a Hewlett-Packard model 1100) with both diode array UV detector at a detection wavelength of 250 nm and fluorescence detector (model HP 1046A, UC excitation/emission wavelengths at 250/332 nm for phenanthrene). External standards in methanol of each solute were used to establish linear calibration curves for both detectors. Each aqueous-phase solute concentration was calculated from the solute concentration in its respective aqueous methanol mixture determined from HPLC and the dilution factor. The solid-phase sorbate concentrations ( $q_e$ ) at equilibrium condition were computed on the basis of mass balance between the two phases.

### *Desorption Equilibrium*

We have developed an exchange method for measuring desorption of organic pollutants bound on sediments. Briefly, the equilibrium sorption of non-labeled phenanthrene was attained for reactor systems described above. The ampules were flame-opened and an aliquot of supernatant was transferred out for analysis of phenanthrene distribution between the water and the sediment phase. The reactor was then spiked with  $^{14}\text{C}$ -labelled phenanthrene. The reactor was then flame-sealed and equilibrated for 21 d. After requilibration, the reactor was opened for analysis of both  $^{14}\text{C}$ -labelled phenanthrene and the total phenanthrene concentrations in the supernatant. Through accurate mass balance calculation, the exchangeable fraction of sediment-bound non-labeled phenanthrene can be quantified at different concentrations of the phenanthrene. Similarly, an array of reactors with  $^{14}\text{C}$ -labelled phenanthrene as the starting solute were initiated, and the non-labeled phenanthrene was introduced as the solute for displacing  $^{14}\text{C}$ -labeled phenanthrene that had been bound on sediments. In addition to these two sets of experiments, two types of control reactors with non-labeled phenanthrene were run for 21 days and 42 days, respectively, to trace the effect of slow sorption rate on the observed difference in the measured sorption equilibria with respect to exchangeable versus non-exchangeable fraction of phenanthrene bound on the sediments.

The data collected using this method are still being processed. It is expected that the exchangeable fraction of the phenanthrene bound on sediments could be bioavailable whereas the non-exchangeable fraction could be less bioavailable or could not be accessed at all by microorganisms in the aquatic environment.

### ***Principal Findings and Significance***

#### *Black Carbon in Hudson River Sediments*

The major finding of this study with respect to the characterization of sediment organic matter is that kerogen and BC particles are the major organic components in the river sediments. The quantitative results are summarized in Table 1, which indicates that HA is less than 25% of the total organic carbon, and BC is about 25%. Other organic matter such as coaly particles constitute approximately half of the organic matter.

KB particles were identified based on the characteristics observed under the petrographic microscope in transmitting and reflecting modes. Major representative organic facies are shown in the Figures 1 and 2. Generally, kerogen and BC of SOM have a spectrum of features under the microscope, depending upon their origins, types of macerals, and maturation. Under the reflecting microscope (Figure 1), more matured and condensed BC (fusinite and semifusinite) particles are brighter and hence have higher reflectance. Kerogen (i.e., vitrinite), a major maceral of coal materials derived diagenetically from plant or humus materials, is identified in the KB fractions with characteristics of gray color, relatively low reflectance indices, and smooth and

homogeneous surfaces (Figure 1 (a)-(d)). Fusinite and semifusinite, having unique burning and charring properties, are identified in KB and BC fraction. Compared to vitrinite, fusinite was characterized by its brightness, irregular dark-colored pores, spherical structures (Figure 1 (a), (e), (h)) and irregular shapes (Figure 1 (c), (d), (f), and (h)). Semifusinite was found in smaller quantities having yellow color and smooth surfaces (Figure 1 (f)). Under the transmitting microscope (Figure 2), the transparency of an SOM particle is inversely related to its maturation or condensation. Less matured kerogen is semitransparent, whereas highly matured BC particles are opaque with spherical (Figure 2-(e)), elongate (Figure 2-(f)) and irregular shapes.

### *Sorption isotherms*

All sets of equilibrium sorption data collected in this study were fitted to one of the Freundlich equations shown below.

$$q_e = K_F C_e^n \quad (1)$$

$$\log q_e = \log K_F + n \log C_e \quad (2)$$

where  $q_e$  and  $C_e$  are the equilibrium solid-phase and aqueous-phase solute concentrations expressed as  $\mu\text{g}/\text{kg}$  and  $\mu\text{g}/\text{L}$ , respectively;  $K_F$  ( $(\mu\text{g}/\text{kg})/(\mu\text{g}/\text{L})^n$ ) and  $n$  are the Freundlich model capacity parameter and the isotherm nonlinearity index, respectively. A linear regression procedure with SigmaPlot software (Version 9.0) was used for fitting Eq. 1 to the logarithmically transformed sorption data collected for each sorbent-sorbate system. The resulting model parameters, along with standard errors in the estimation of the parameters, and the  $R^2$  values, are listed in Table 2. The  $K_{oc}$  ( $= (q_e/C_e)/f_{oc}$ ) values of phenanthrene were calculated at four different  $C_e$  levels ( $C_e/S_w = 0.001, 0.01, 0.1,$  and  $C_e = 10 \text{ ng}/\text{L}$ ) from their respective Freundlich model parameters. The results are also presented in Table 2. The sorption isotherms are shown in Figures 3 and 4.

The sorption data for the two PCB congeners have not been analyzed yet, which will be available within 3 months.

### *Isotherm nonlinearity and sorption capacity*

The data presented in Table 2 and Figures 3 and 4 show that the sorption isotherms of the original Hudson River sediments for phenanthrene are nonlinear, with the  $n$  values ranging from 0.840 to 0.962. Comparatively, the sorption isotherms of the other three rivers are generally more linear than those of the Hudson River, ranging from 0.934 to 0.991. The sediments Soxhlet-extracted with DCM exhibited much more nonlinear sorption equilibria than do the original sediments, with the  $n$  values ranging from 0.667 to 0.792 for the Hudson River sediments and from 0.728 to 0.814 for other river sediments. A possible explanation for this change is that the original sediments may contain simple organic chemicals such as fatty acids and organic pollutants such as chlorinated pesticides, PCBs and PAHs (Tabak et al., 2003). The preloaded organic molecules may have preferentially occupied the high energy “sites” that exhibit more nonlinear sorption. The unoccupied “sites” may exhibit relatively more linear sorption so

that the overall sorption isotherms measured for the target sorbates are more linear due to the competitive effect (Xiao et al., 2004).

These preexisting simple chemicals in the original sediments may have also decreased the sorption capacity for the target solutes. Removal of the chemicals by Soxhlet extraction could increase both the capacity and nonlinearity of the sorption isotherms for phenanthrene. This competitive effect is more prominent when total  $q_e$  is far less than the saturation limit, or  $C_e$  is in low concentration ranges. The data in Table 2 indicate that, due to variations in TOC contents and  $n$  values, the  $\log K_F$  values vary from 2.997 to 3.375. Compared to their respective original sediments, Soxhlet extracted sediments exhibit  $\log K_F$  values approximately twice as high as their original samples. As mentioned above, this is likely due to the preoccupation of the high energy “sites” by the preexisting organic molecules.

The calculated  $K_{OC}$  values exhibit much less variation since the effect of TOC content was eliminated (Table 2). From the calculated results of single-point  $\log K_{OC}$  (Table 2), we can find that (i) the  $K_{OC}$  value decreases as a function of  $C_e$ , indicating the effect of isotherm nonlinearity; (ii) at lower  $C_e$  levels, the original sediments exhibit much lower sorption capacities than their respective Soxhlet extracted samples; (iii) at  $C_e = 10$  ng/L, which is approximately the concentration of phenanthrene in natural waters, the  $K_{OC}$  values of Soxhlet extracted sediments are approximately 5~6 times of their respective original sediments, which means that under natural water conditions sorption capacity of actual river sediments for phenanthrene is much lower than that of “clean” or organic solvent extracted ones.

This study demonstrated that black carbon and coaly materials are dominant sediment organic matter in the samples tested and that the untreated sediments exhibited more linear sorption isotherms with lower  $K_D$  values at low concentrations. After extracted with organic solvents, the sediments samples displayed much more nonlinear isotherms for phenanthrene with larger sorption capacities. These observations suggested that the role of black carbon and coaly materials in the equilibrium sorption of PAHs may be dramatically diminished after aging of the carbonaceous materials in the sediments. This finding challenges the predictive means developed for quantitatively assessing the equilibrium sorption and desorption of organic pollutants from single measurements of the black carbon content in the sediments. Direct measurement of sorption equilibria with a representative organic pollutant probe is likely required for predicting contaminant distribution in environmental media.

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TABLE 1. Sediment Properties

Sediments	Source	TOC (wt %)	HA (%)	KBC (%)	BC (%)	Site description
HR	Hudson River	5.68	23.0	56.1	28.0	Date: 10/25/2004 Location: Berry's Creek (a tributary of the Hackensack river)
HR1	Hudson River	7.09	0.89	93.0	72.4	Date: 04/29/2004 Location: 40 43.297N, 74 01.680W, 2.6 km from battery
HR2	Hudson River	2.35	6.79	59.7	24.6	Date: 04/29/2004 Location: 40 53.287N, 73 56.152W, 19.7 km from battery
HR12	Hudson River	2.14	11.4	58.4	26.7	Date: 04/29/2004 Location: 25.4km from battery
HR13	Hudson River	2.29	23.2	52.6	23.0	Date: 04/29/2004 Location: 41 01.020N, 73 53.430W, 33.9 km from battery
HR15	Hudson River	1.92	14.8	65.4	18.2	Date: 04/29/2004 Location: 41 03.323N, 73 52.909W, 37.8 km from battery
HR17	Hudson River	2.31	3.58	61.6	26.6	Date: 04/29/2004 Location: 40 49.181N, 73 58.322W, 12.6 km from battery
BH	Baltimore Harbor, MD	3.91	1.58	82.2	42.6	N/A
WR	Anacostia River, Washington DC	3.26	13.82	64.8	34.5	N/A
PP	Delaware River, Philadelphia	nd				Penn's Landing area, 2 <sup>nd</sup> street

TABLE 2. Phenanthrene Sorption Isotherm Parameters

	Sediment	$n$	$\log K_F^a$	$R^2$	Single-point $\log K_{OC}^b$					
					$C_e/C_S=10^{-1}^c$	$C_e/C_S=10^{-2}$	$C_e/C_S=10^{-3}$	$C_e = 10 \text{ ng/l}$		
HR	Before Extraction	0.962	0.027	3.375	0.050	0.986	4.543	4.581	4.619	4.697
	After Extraction	0.792	0.017	3.752	0.031	0.992	4.571	4.779	4.987	5.414
HR1	Before Extraction	0.937	0.026	2.997	0.049	0.986	4.017	4.080	4.143	4.272
	After Extraction	0.673	0.017	3.755	0.029	0.989	4.234	4.561	4.888	5.558
HR2	Before Extraction	0.844	0.017	3.168	0.032	0.992	4.477	4.633	4.789	5.109
	After Extraction	0.707	0.012	3.547	0.023	0.995	4.576	4.869	5.162	5.762
HR12	Before Extraction	0.843	0.011	3.158	0.020	0.997	4.506	4.663	4.820	5.142
	After Extraction	0.705	0.012	3.548	0.022	0.995	4.613	4.908	5.203	5.808
HR13	Before Extraction	0.855	0.014	3.119	0.025	0.995	4.462	4.607	4.752	5.049
	After Extraction	0.667	0.012	3.613	0.021	0.995	4.571	4.904	5.237	5.919
HR15	Before Extraction	0.840	0.013	3.062	0.024	0.996	4.451	4.611	4.771	5.099
	After Extraction	0.675	0.019	3.500	0.035	0.986	4.551	4.876	5.201	5.867
HR17	Before Extraction	0.849	0.011	3.144	0.020	0.997	4.471	4.622	4.773	5.082
	After Extraction	0.707	0.014	3.508	0.026	0.993	4.544	4.837	5.130	5.730
BH	Before Extraction	0.934	0.009	3.467	0.016	0.998	4.740	4.806	4.872	5.007
	After Extraction	0.728	0.011	3.983	0.021	0.996	4.833	5.105	5.377	5.935
WR	Before Extraction	0.991	0.014	3.194	0.026	0.996	4.662	4.671	4.680	4.699
	After Extraction	0.814	0.015	3.595	0.028	0.994	4.701	4.887	5.073	5.454
PP	Before Extraction	0.940	0.019	3.195	0.036	0.992	nd <sup>d</sup>	nd	nd	Nd
	After Extraction	0.767	0.011	3.611	0.020	0.997	nd	nd	nd	nd

<sup>a</sup> Freundlich isotherm coefficient with units of  $((\mu\text{g}/\text{kg})/(\mu\text{g}/\text{L})^n)$

<sup>b</sup> organic carbon normalized distribution coefficient at a given aqueous phase concentration, with units of L/kg.

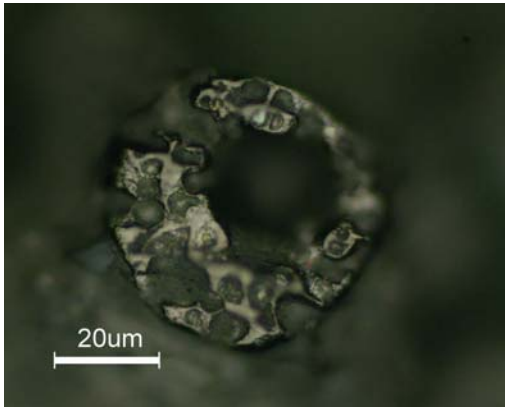
<sup>c</sup>  $C_e$  and  $C_S$  are aqueous phase phenanthrene concentration and aqueous phase phenanthrene solubility limit, respectively.  $C_S = 1.12 \text{ mg/l}$  at  $20^\circ\text{C}$ .

<sup>d</sup> nd, not calculated.

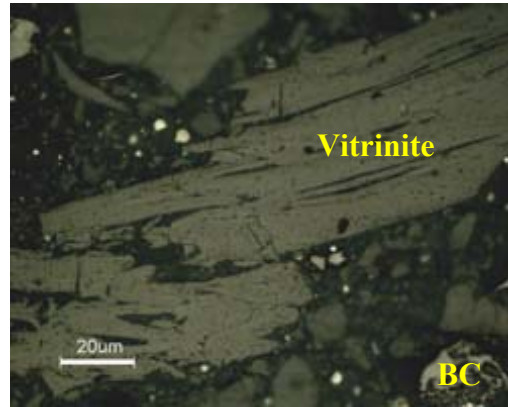


Figure 1. Microphotographs of the isolated SOM particles under the microscope of reflecting white light mode.

(a) KB (HR2)



(b) KB (HR1)



# RESISTANCE OF FRACTURED ROCK DECHLORINATING BACTERIA TO PRESSURE FROM HEAVY METALS

## Basic Information

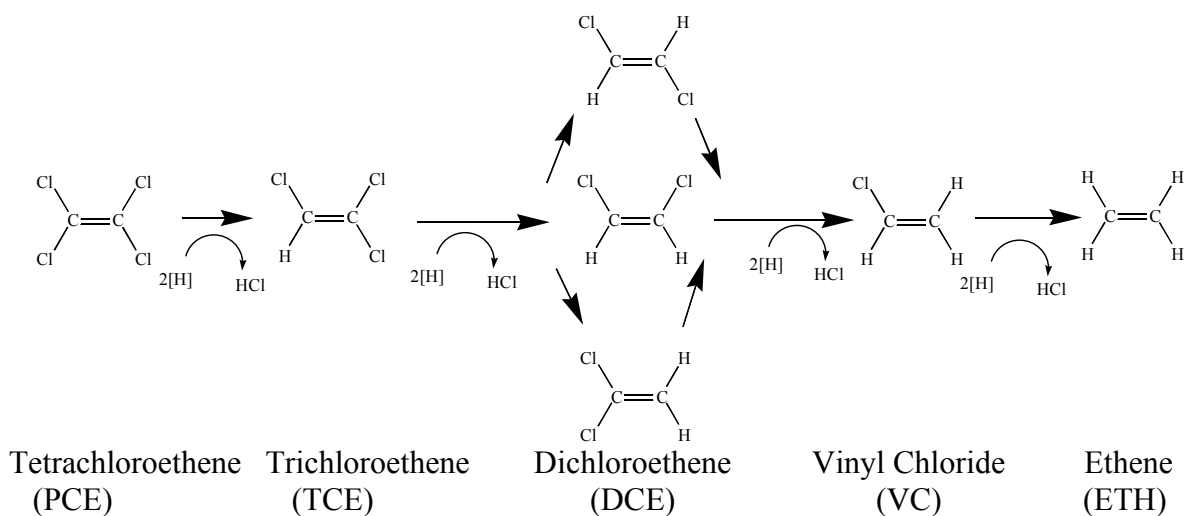
<b>Title:</b>	RESISTANCE OF FRACTURED ROCK DECHLORINATING BACTERIA TO PRESSURE FROM HEAVY METALS
<b>Project Number:</b>	2005NJ91B
<b>Start Date:</b>	3/1/2005
<b>End Date:</b>	2/28/2006
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	6
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Groundwater, Methods, Water Quality
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Eun Kyeu Son, Donna E. Fennell

## Publication

1. Son, E-K.; Lee, K. Y.; Fennell, D. E. Characterization of tetrachloroethene- and vinyl chloride-dechlorinating bacteria enriched from a tertachloroethene- contaminated site in the Newark basin. Poster presented at the 105th ASM general meeting, Atlanta, GA, June 5-9, 2005.
2. Fennell, D.E.; F. Liu; E.-K. Son; A. Zarnadze; U. Krogmann; L.Totten. Biotransformation of halogenated contaminants in sludges and enrichments from municipal anaerobic digesters. Poster presented at the SETAC North America 26th Annual Meeting, Baltimore, MD, November 13 17, 2005.
3. Son, E.-K., Fennell, D.E. : Identification of tetrachloroethene- and vinyl chloride-dechlorinating bacteria enriched from tetrachloroethene-contaminated groundwater and sediments . The 21st SSW Annual Meeting, Amherst, MA, October 17-20, 2005.

## Problem and Research Objectives

Because of the extensive use as degreasers, chlorinated ethenes such as tetrachloroethene (PCE) and trichloroethene (TCE) are the most common groundwater contaminants (1). The remediation of chlorinated ethenes-contaminated aquifers is a difficult proposition that is further complicated by the presence of heavy metal co-contaminants. Up to 60% of CERCLA sites contain heavy metals along with other contaminants (15) and the DOE has identified heavy metals and TCE as a common contaminant mixture at their sites (2). Microbial reductive dechlorination which transforms chlorinated ethenes to the benign product ethene (3) is an attractive remedial process for contaminated aquifers. Several genera of bacteria have been identified to have the ability to reductively dehalogenate the chlorinated ethenes (4, 5, 6). However, only one genus of bacteria, *Dehalococcoides*, has been identified which is capable of the complete dehalogenation from tetrachloroethylene (PCE) to ethene through serial reductive dechlorination (PCE → TCE → *cis*-DCE → VC → ethene) (7, 8).



**Figure 1. Pathway of anaerobic biological reductive dechlorination of the chloroethenes.**

Inhibition of dechlorination of organic compounds in the presence of toxic heavy metal such as Cr, Cd, Pb, Zn, Cu, and Co has been shown in sediments, sludges, and enrichment cultures (12, 13, 17). Though extensive research has been performed on reductive dechlorination of chlorinated ethenes and anaerobic biotransformation of heavy metals respectively, little work has been performed to show how the presence of mixtures of chlorinated ethenes and heavy metal co-pollutant affects dechlorination.

The primary goal of this study is to investigate the effect of heavy metals on the dechlorination potential in groundwater contaminated with both chlorinated ethenes and heavy metals under anaerobic condition using the PCE enrichment culture containing *Dehalococcoides* bacteria. Understanding the interplay between chlorinated ethenes and heavy metal mixtures will allow better description and prediction of their fate and transport.

## Methodology

**Enrichment culture and growth condition.** Highly PCE-enriched cultures which dechlorinated PCE completely to ethene at high rates have been developed in our laboratory using Busch Campus aquifer material (14). The description of enrichment development is as follows; Groundwater and fine sediments were collected from the aquifer. 100 mL of groundwater/sediment fines mixture was distributed to sterile 160 mL serum bottles in a nitrogen-purged glove bag. After determination of initial chloroethene concentrations, the bottles were then divided into different treatment sets. Autoclaved controls, live controls and bottle sets amended with PCE or VC and lactate and butyrate as electron donors were run. PCE or VC were added in corresponding bottles periodically and chlorinated ethenes (PCE, TCE, DCEs and VC), and ethene concentrations were analyzed using gas chromatography with a flame ionization detector (GC-FID). Electron donors and their fermentation products, volatile fatty acids were determined using high performance liquid chromatography (HPLC). To purify the cultures, the enrichments were transferred periodically into anaerobic basal mineral medium. The anaerobic growth medium was described in ref. (18). From the 3<sup>rd</sup> transfer 1 mg/ml of ampicillin and 5 mM of bromoethanosulfonate(BES) were applied and butyric acid and lactate were substituted with H<sub>2</sub> gas as an electron donor.

**Molecular Analysis.** By using 16S rRNA gene-based molecular methods such as PCR using primers specific for *Dehalococcoides* or universal bacteria, terminal restriction fragment length polymorphism (TRFLP) and denatured gradient gel electrophoresis (DGGE), we characterized microbial composition of our PCE enrichment culture. To identify microbial community each band from DGGE was excised and DNA sequencing was conducted.

**Anaerobic dehalogenation studies in the presence of added metals.** The most purified PCE enrichment culture was chosen for determination of metal resistance. To avoid metal sulfur precipitates, Na<sub>2</sub>S was deleted from the anaerobic growth medium described above and L-cysteine was used as a reducing agent. 10% transfer (v/v) of the PCE enrichment cultures were conducted into 60 mL serum bottles with the modified growth medium. The cultures were grown with addition of PCE and H<sub>2</sub> gas for 3 weeks for acclimation. All PCE in the cultures was completely transformed to ethene and 10% (v/v) of the adjusted cultures were transferred into the medium containing respective concentrations of heavy metals. Concentrated stock solutions of CdCl<sub>2</sub>, CuCl<sub>2</sub>·H<sub>2</sub>O, and K<sub>2</sub>CrO<sub>4</sub> were prepared with sterile water, purged with N<sub>2</sub> gas, sealed in acid-washed serum bottles, and autoclaved. An initial study monitored the dechlorination of the PCE enrichment cultures acclimated with the medium containing L-cysteine in the presence of Cr final concentrations of 0.1 to 5 ppm. Based on the initial study, **Figure 2.**, metal ions solubility and the previous experiment (data not included), three concentrations for each metal were selected (Table 1). About 35 μmole/100ml of PCE was spiked two times in metal amended enrichment bottles and chlorinated ethenes (PCE, TCE, DCEs and VC), and ethene concentrations were determined using gas chromatography with a flame ionization detector (GC-FID). Dose response graphs describing the effect of Cd(II), Cr(IV) and Cu(II) on dechlorination were obtained. All treatment cultures including control were triplicate. The cultures were incubated at room temperature in the absence of light.

**Table 1. Heavy metal treatment sets (final concentration)**

	Cd(II) : CdCl <sub>2</sub>	Cr(VI) : K <sub>2</sub> CrO <sub>4</sub>	Cu(II) : CuCl <sub>2</sub> ·H <sub>2</sub> O	Control
1	50ppm	50ppm	25ppm	No metal addition
2	100ppm	100ppm	50ppm	
3	200ppm	200ppm	100ppm	

### Principal Findings and Significance (Progress Report)

Primary results of the on-going project to date are to characterize the highly purified PCE enrichment which showed complete dechlorination activity and document the effect of three kinds of heavy metals (Cr, Cd and Cu) on dechlorination of the enrichment culture.

**Culture description.** Microbial enrichment for this study was examined by using 16S rRNA gene-based molecular analysis of genomic DNA of the enrichment culture. On the DGGE gel we had one band and this band was sequenced to turn out *Dehalococcoides*-like microorganism. TRFLP data from the reactions with two different kinds of restriction enzymes (Hae III and Hha I) also gave us one major peak in its chromatograms. To assure the purity of the culture and identify the longer sequence full 16S rRNA gene was amplified and sequenced. We obtained single chromatogram from DNA sequencing of the crude PCR amplicon which meant only one kind of DNA fragment was present in the PCR amplicon sample. From these results, we could speculate tentatively our PCE enrichment culture was highly purified (may be pure) and contained *Dehalococcoides* genus bacteria of which 16S rRNA gene sequence is most similar to *Dehalococcoides* sp. strain CBDB1. This culture showed very fast dechlorination (20 µmole/100ml of PCE to ethene within 4 days). No methanogenic activity was observed after BES (methanogen inhibitor) application.

**Effect of concentrations of metals.** Dechlorination of PCE and formation of the intermediates and final product, ethene, in the presence of added metals are presented in **Figure 3.** and **Figure 4.** Chlorinated ethenes and ethene were determined periodically. When complete dechlorination of PCE in the control set was observed, dechlorination degree of each culture in response to the heavy metal presence was monitored. The first spike of about 35 µmole/100ml of PCE was completely dechlorinated to ethene in 90 days and in the second addition of same amount of PCE complete dechlorination was shortened to 60 days. For comparison of different groups, molar fraction (%) of chloroethenes and ethene among total molar amount was used instead of absolute concentration.

**Cadmium.** The previous study in our lab revealed that the genome of *Dehalococcoides* contains *zntA/copA*-like genetic elements, known to impart resistance to Cd. Also, the mixed culture with *Dehalococcoides* sp. strain 195 has shown capability to grow under high Cd concentrations (up to 200ppm). Based on these results, relatively higher concentrations of Cd (II) were applied (50ppm, 100ppm, and 200ppm).

Dechlorination intermediates such as TCE, c-DCE and VC were detected first after 30 days incubation in the treatments of Cd (II) concentration of 50ppm and 100ppm. 50ppm of Cd (II) seemed not to affect dechlorination potential of the enrichment culture and all PCE was transformed to ethene and no other intermediates were observed 90 days after PCE addition. At 100ppm and 200ppm of Cd(II) concentrations inhibition effect was obvious and very little ethene formation and large accumulation of intermediates were detected (**Figure 3. (a)**). In the second addition of PCE, dechlorination rates of all Cd (II) treated cultures decreased and no ethene formation was observed at 100ppm and 200ppm (**Figure 4.(a)**). This inhibition effect could be explained by the accumulation of soluble Cd (II) ions inside the dechlorinating bacterial cell (16).

**Chromium.** In the preliminary study it was observed that neither increase nor decrease in dechlorination occurred by the addition of low concentrations of Cr (VI) (over the range of 0.1ppm to 5ppm) (**Figure 2.**). Thus, higher concentrations were chosen for further inhibition/resistance study for Cr (VI) (50 ppm, 100ppm, and 200ppm). First onset of dechlorination of PCE was observed on day 30th after the first PCE spike at all three concentrations. 90 days incubation data demonstrated that the addition of Cr (VI) concentration of 50ppm to 200ppm resulted in significant inhibition of chloroethenes dechlorination and ethene formation was inversely proportional to the concentrations (**Figure 3. (b)**). In contrast to Cd (II), dechlorination capability was considerably restored at 50ppm and 100ppm of Cr (VI) in incubation with the second PCE spike (**Figure 4. (b)**). It may lead to the speculation that unlike to *Dehalococcoides* sp. strain 195, our culture could have mechanisms responsible for resistance to Cr (VI).

**Copper.** Because of lower solubility of Cu (II) in the anaerobic growth medium used here, concentrations of 25ppm, 50ppm, and 100ppm were applied. 70% or more recovery in ethene formation was observed at 25ppm and 50ppm of Cu (II) in the first spiked PCE dechlorination (**Figure 3. (c)**). Dechlorination inhibition pattern after the second PCE addition was changed. Overall inhibition pattern was similar to the first spike, but, more PCE was accumulated at all three concentrations and more ethene was produced at the 100ppm (**Figure 4. (c)**).

**Discussion.** Our data suggest that our culture was highly purified with *Dehalococcoides* bacteria and they are responsible for complete dechlorination of the enrichment culture. Three heavy metals, Cd (II), Cr (VI) and Cu (II) at high concentrations showed inhibition effect on PCE dechlorination of our PCE enrichment culture. However its resistance potential and response pattern to introducing of respective heavy metals were all different. For further elucidation of mechanistic explanation, molecular analysis of metal treated cultures such as PCR specific for heavy metal resistance genes and quantification of the microorganisms interested should be followed. These findings can be directly related to design and evaluation of the remediation options and to assessment of the natural dechlorination potential of contaminated sites.

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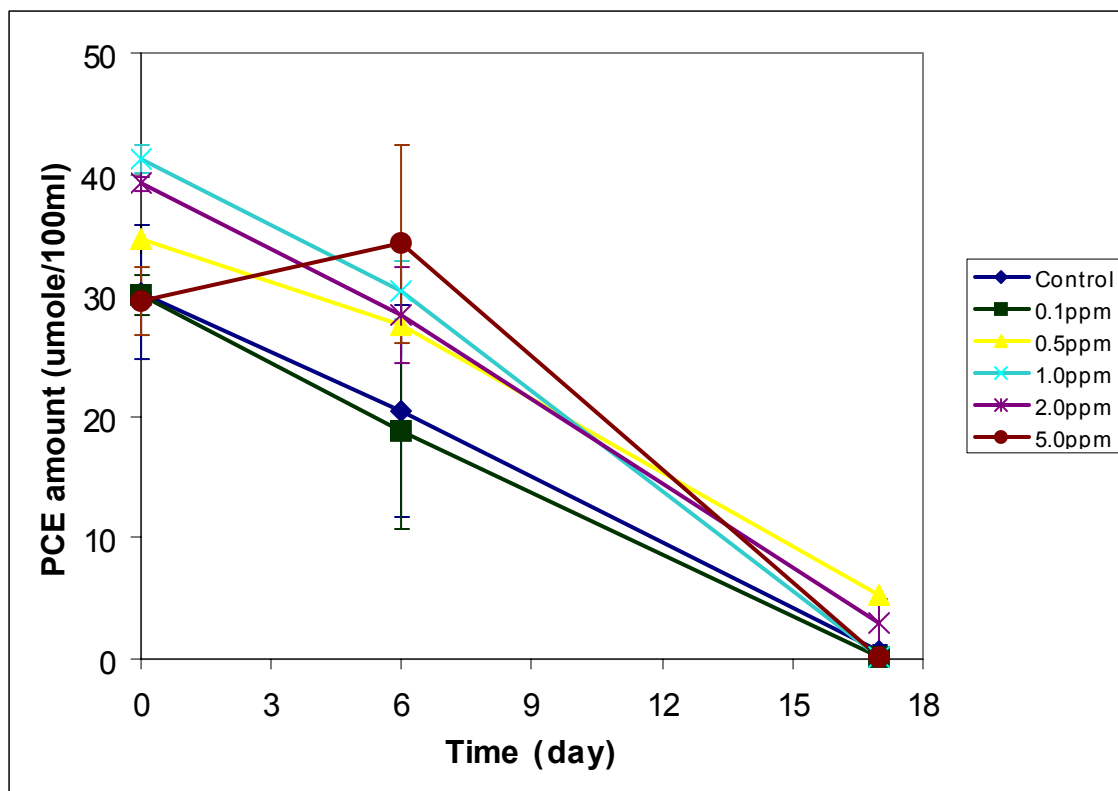
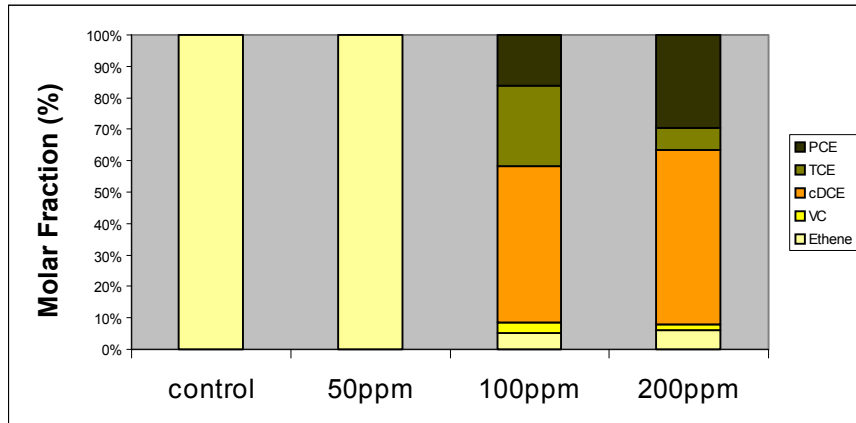
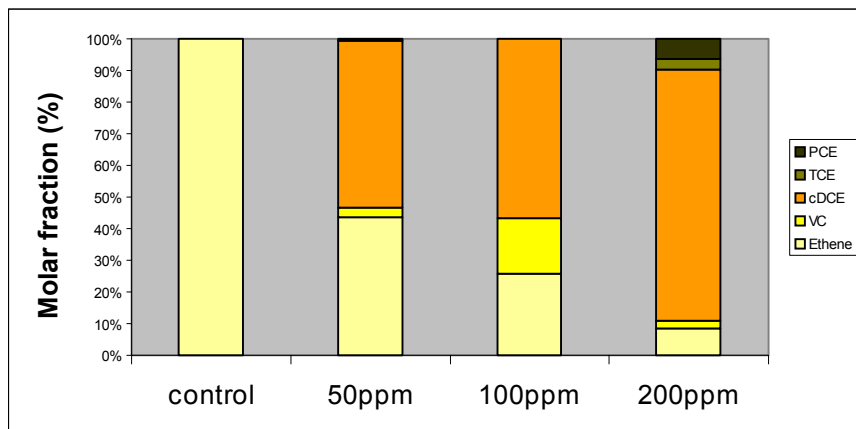


Figure 2. Dechlorination of PCE in the presence of different concentrations of Cr(VI)

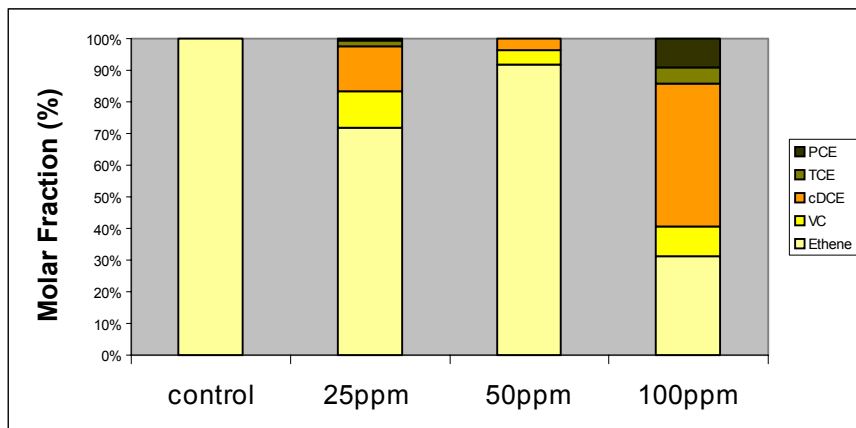
(a)



(b)

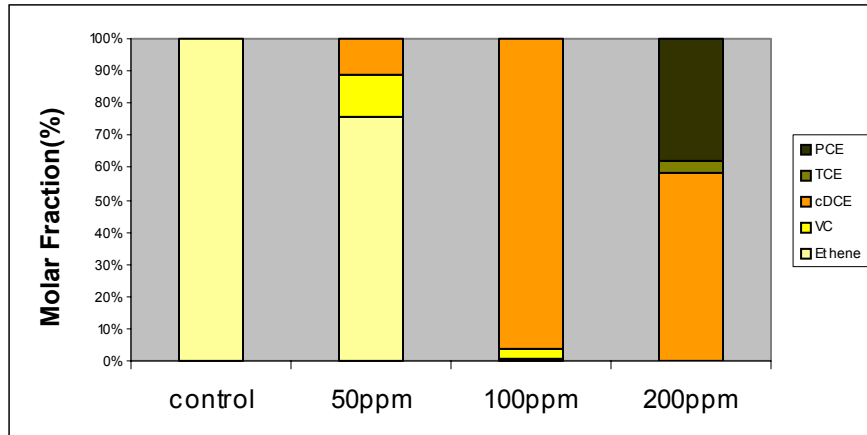


(c)

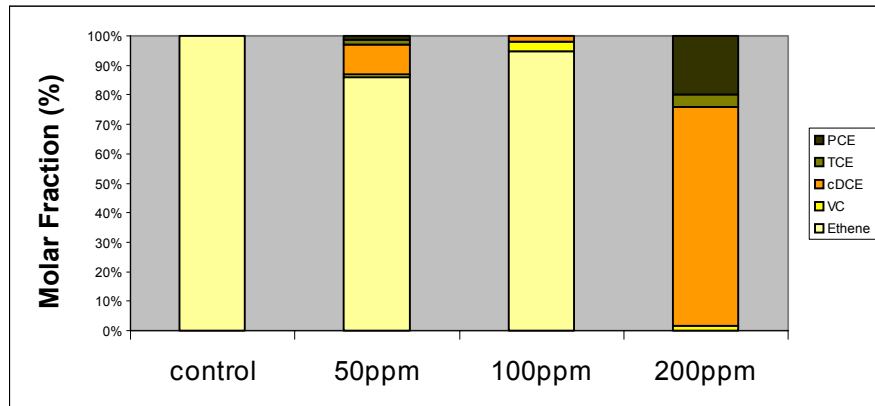


**Figure 3. Effect of added Cd(II) ; (a), Cr(VI) ; (b), and Cu(II) ; (c) on dechlorination of the first spiked PCE after 90 days incubation.**

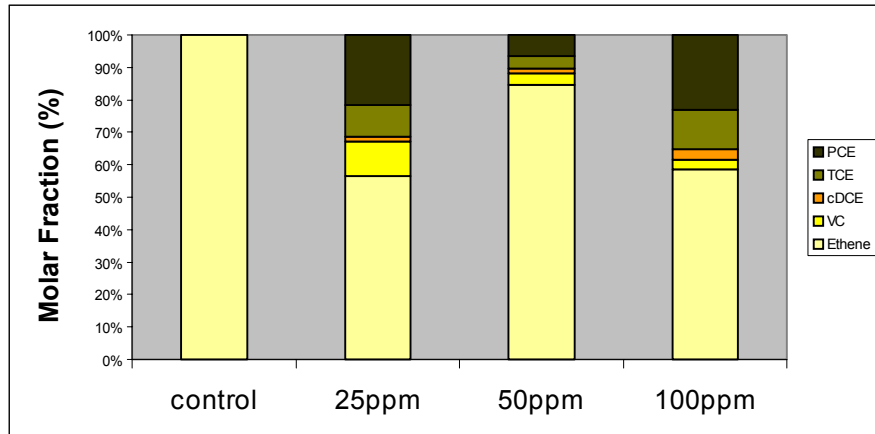
(a)



(b)



(c)



**Figure 4. Effect of added Cd(II) ; (a), Cr(VI) ; (b), and Cu(II) ; (c) on dechlorination of the second spiked PCE after 50 days incubation.**

# Delaware River Basin Commission State of the Basin Report

## Basic Information

<b>Title:</b>	Delaware River Basin Commission State of the Basin Report
<b>Project Number:</b>	2005NJ1270
<b>Start Date:</b>	8/1/2005
<b>End Date:</b>	12/31/2006
<b>Funding Source:</b>	Other
<b>Congressional District:</b>	N. A.
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Management and Planning, Water Quality, Hydrology
<b>Descriptors:</b>	watershed management, planning, watershed indicators
<b>Principal Investigators:</b>	Joan G. Ehrenfeld, Archil Zarnadze

## Publication

## **Delaware River Basin Commission: State of the Basin Report Project Summary**

### **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 is 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:**

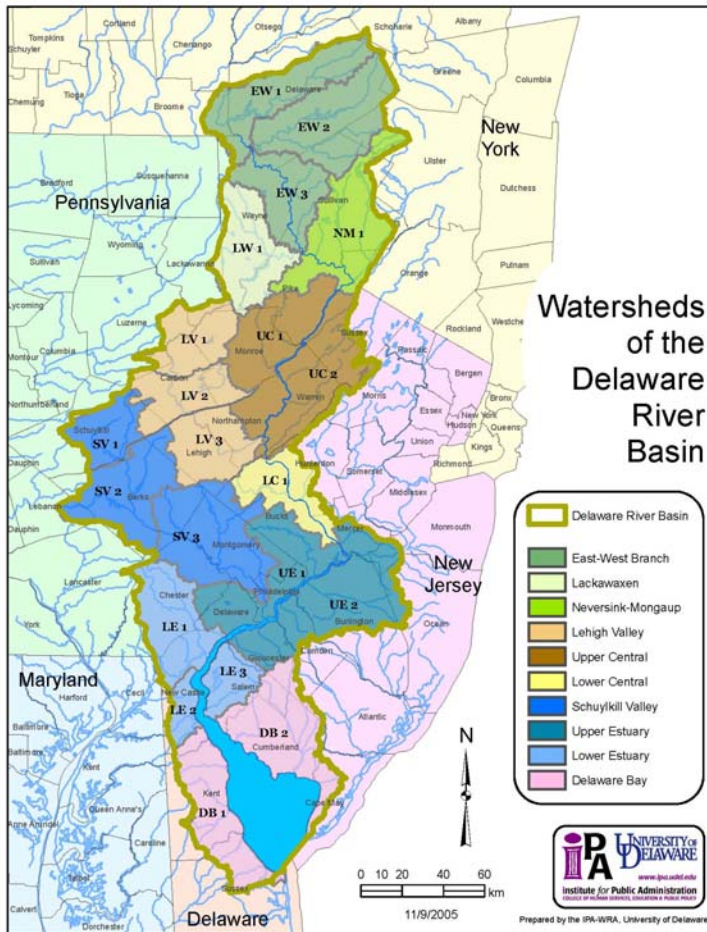
The water resources institutes from the four land grant universities of the states in the basin – Cornell, Delaware, Rutgers, and Penn State (institute partners) - are collaborating to collect appropriate and readily available water resource data and associated land-use and socio-economic information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

A Report Coordinating Team consisting of staff from the following organizations has been assembled:

- Delaware River Basin Commission
- Delaware Estuary Program
- Federal Government (U.S. Geological Survey and U.S. Environmental Protection Agency)

- University of Delaware, Delaware Water Resources Center and Water Resources Agency - Newark, DE
- Cornell University, New York State Water Resources Institute – Ithaca, NY
- Rutgers University, New Jersey Water Resources Institute - New Brunswick, NJ
- Penn State University, PA Water Resources Research Center and Center for Watershed Stewardship, State College, PA

Each of the Institutes is responsible for data collection and analysis for the portions of the basin in its state. Thus, the New Jersey WRRI is handling the analyses for the Upper Central (UC2), part of the Lower Central (LC1), Upper Estuary (UE2), Lower Estuary (LE3), and Delaware Bay (DB2) sub-watersheds, as delineated as the first product of the project.



Meetings have been held bi-monthly to review progress and to collaboratively address the format and nature of the data to be collected and analyzed.

The components of watershed status are expected to include the following (as described in the “Goals of the Water Resources Plan”):

- Water quality for human & in-stream/ecological use
- Water supply adequacy
- Riparian corridor function & condition
- Flood warning & mitigation
- Aquatic & wildlife abundance & diversity
- Aquatic & wildlife habitat

- Public health (recreation, consumption advisories, etc.)
- Water quantity and flow regime
- Land use and water resource linkages

Progress to date:

During the first three meetings and interim conference calls, a potential list of about 50 indicators was compiled and then evaluated in terms of their relevance, data availability, and interpretability. As a result of this winnowing process, a final list of potential indicators was developed. These include:

Water quality: DO, salinity, total N, total P, total suspended sediment, fish consumption advisories, metals ( Cu, Pb, Zn, Hg), organics (PCBs, atrazine, metalachlor), Sec. 303d designated use attainment/impairment lists

Water quantity: riparian corridor condition, water supply and demand

Hydrology and geomorphology: streamflow, groundwater quantity, flooding, dams (hydrologic impairment)

Living resources: macroinvertebrates, shellfish, oyster, horseshoe crab, blue crab, freshwater mussels, zebra mussels, American shad, freshwater trout, striped bass, sturgeon, Louisiana water thrush, shorebirds (red knot), bald eagle, amphibia, endangered species

Land use/landscape: tidal wetlands, tidal wetland buffers, total wetlands, impervious cover, land use, forest health, population, federal/state superfund sites

Possibly added in the future: National Wild and Scenic River designations, aquatic invasives, sea level rise, National Park, National Heritage status.

For each of these indicators, we have developed potential metrics (e.g., use of 5-year medians, maximum and minimum values for the past 40 yr of data for water quality indicators).

The metrics and indicators are being obtained for at least one subwatershed (HUC 14) within each of the sub-basins. It was agreed to collect data for one test case to ensure that the design of the metrics will accomplish the project goals. This has been completed for the LC2 sub-basin, using USGS Gage # 01477120 (RACCOON CREEK, near Swedesboro, NJ). The data were obtained from diverse sources, including the US Geological Survey on-line data bases, EPA STORET data, and data obtained directly from NJ DEP agencies. At a meeting in June, 2006, these data were discussed, and final refinements for the metrics were adopted. All data have been displayed as GIS data layers, enabling both spatial analysis and clear presentation suitable for the general public (e.g., adoption of a 'red-yellow-green' coding for water course segments and/or subwatershed units, based on the data).

Work is now proceeding to obtain and prepare the analyses of data for each of the other subbasins in our work area. It is anticipated that all data collection and analysis will be completed by August 2006, and report preparation will then be undertaken.

A presentation at the national AWRA meeting in Baltimore, MD in November, 2006, has been planned to describe the project to the water-resource public.



# Undergraduate Research Internships

## Basic Information

<b>Title:</b>	Undergraduate Research Internships
<b>Project Number:</b>	2005NJ129B
<b>Start Date:</b>	9/1/2005
<b>End Date:</b>	12/31/2005
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	N.A.
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	None, None, None
<b>Descriptors:</b>	undergraduate education, internships
<b>Principal Investigators:</b>	Joan G. Ehrenfeld

## Publication

## UNDERGRADUATE RESEARCH INTERNSHIPS

1) William J. Cromartie, Associate Professor, Environmental Studies, Richard Stockton College of New Jersey: **Assessing Subwatersheds within the Great Egg Harbor River Basin**

INTERN: Lauren Keltos

Collecting and analyzing baseline data of the existing visual, biological, chemical, and morphological features and conditions of the Great Egg Harbor Watershed is one of the most fundamental ways that we can learn about, understand and then manage to protect water quality. With 49 subwatersheds (HUC-14s) in the watershed, collecting detailed data on each one of these units is a daunting task. One ongoing problem with water quality assessment in Pinelands watersheds like the Great Egg Harbor is the assignment of all non-attainment New Jersey AMNET sites in Pinelands watersheds to 303(D) Sublist 3, "insufficient data". Present EPA and NJ metrics for measuring "aquatic-life-use-attainment" in low pH waters fail to discriminate among sites with different levels and types of impairment. This impedes our ability to address the causes of water quality degradation, including habitat, benthic community and hydrologic alterations, along with sedimentation and nonpoint chemical pollution in Pinelands waters. There is an urgent need to develop eco-region specific metrics for aquatic life attainment and reference condition identification in the Great Egg Harbor River and other Pinelands watersheds. Without sufficient, unambiguous data, it is very difficult to obtain meaningful water quality measurements, plan and implement remediation and restoration, and improve water quality for the long term.

Visual, chemical, stream morphological, and biological data for two subwatersheds were collected to identify both natural conditions and alterations or stressors that impact water quality. One possible reference subwatershed (Gravelly Run, already studied in spring and summer 2005) and one other subwatershed (upper Babcock Creek) were studied. Sampling will be done fall 2005 through spring 2006. Parameters tested included pH, specific conductance, temperature, redox potential and abundance of selected taxa of aquatic macroinvertebrates (insects, snails, etc.).

The student researcher assisted in all phases of the work, supervised in field work experience by Fred Akers, Great Egg Harbor Watershed Association (GEHWA) Administrator, and by Dr. Cromartie. The same portable instruments used in earlier studies will be employed to measure pH and Specific Conductance (SC) and temperature, along with a set of lightweight electronic probes for pH, SC, redox, and temperature. For macroinvertebrates, we sampled woody debris, following the protocol developed at Stockton College in 2003-2005. For all sampling stations, replicate samples will be obtained on the same date to determine within site variability as well as differences between sampling stations and subwatersheds. Specimens were identified to the lowest taxonomic level necessary to obtain an unambiguous categorization of the watersheds. All samples are retained in the collection at Stockton College. All parameters are incorporated into the GEHR database at Stockton.

### **Data analysis**

Collected data were tabulated and analyzed using PC-ORD, CANOCO 4.5 and ArcGIS software. The relationship of landuse to stream parameters in the data obtained in 2005-06 is strong (see [Cromartie, et al. 2005](#)) and can be demonstrated using these multivariate methods. Gravelly Run, the potential reference site, compares well to other known high-quality subwatersheds in both the Great Egg Harbor and Mullica drainages (Zampella et al. 2001). The student researcher developed a preliminary geodatabase design for the project data, along with data from earlier studies, the GEHWA and the NJ DEP. This will allow continuous incorporation of data from the current sites and from additional subwatersheds as the project proceeds.

### **Dissemination of Results**

The student presented the results to the Stockton Day of Scholarship in February 2006 and the Ecological Society of America, Mid-Atlantic Region meeting in April 2006. Results will be presented in a poster to the Ecological Society of America annual meeting in August 2006. Results are also being prepared for publication by Dr. Cromartie. Stockton also plans to begin serving the geodatabase online as soon as possible, so that state and local planning agencies can view the results directly.

### **FURTHER SOURCES OF PROJECT SUPPORT**

To collect and document watershed wide data sooner rather than later, watershed scientists need more resources and more partners. Based on the partnership between Stockton College and the Great Egg Harbor Watershed Association (GEHWA) on Adams Branch and Babcock Creek (*Adams Branch Stormwater Remediation Plan - Phase One, NJ DEP, Division of Watershed Management, contract to Stockton College and GEHWA, May 2004 to September 2005*), we believe doing more baseline subwatershed assessments on the Great Egg will help achieve the goal of a fully documented watershed. GEHWA recently awarded a grant to the Richard Stockton College for \$3,000 to assess selected subwatersheds of the Great Egg Harbor River in the summers of 2005/06. These funds were used to pay student interns who are currently pursuing coursework in Environmental Studies and to cover the costs of administration by the college.

### **PRESENTATIONS OF PROJECT RESULTS FROM PREVIOUS WRRI UNDERGRADUATE INTERNS**

- Revised macroinvertebrate criteria for the Great Egg Harbor River. Oral presentation. NJ Academy of Sciences annual meeting, 2003. (with [Jason Gliddon](#))
- Biomonitoring in New Jersey blackwater streams: recalibrating an invertebrate bioassay. Poster presentation. Annual Meeting of the Ecological Society of America, Savannah, Georgia, 2003 (with [Jason Gliddon](#), [Lynn Maun](#), Julie Akers, Tamica Johnson and James Grimes)
- Stream biomonitoring using macroinvertebrates in the New Jersey Pinelands: Consistency with water chemistry and landuse. Mid Atlantic Chapter of the Ecological Society of America Conference on Sustainable Landscapes. Lancaster PA, March 2004 (with [L. Maun](#), J. Akers, T. Johnson, [J. Gliddon](#), J. Grimes and D. Monzo.)

Using Stream Insects on Woody Debris to Assess Water Quality in the New Jersey Pinelands, at the NJ Academy of Sciences' annual meeting, April 2004, Fairleigh Dickinson University, Madison NJ. (with **L. Maun**, J. Akers, T. Johnson, **J. Gliddon**, J. Grimes And D. Monzo )

Adams Branch Restoration: Macroinvertebrates and Water Chemistry. Poster session. Joint meeting, American Entomological Society and Entomological Society of Pennsylvania. Newark, DE. 20 October 2004. (with **Lynn Maun**, Julie Akers, Denis Cummings, Justine Cook, Jordan Leckenbush, and Bob Fromtling)

Aquatic Macroinvertebrates in the Great Egg Harbor River Watershed. Newark Entomological society, New Brunswick, NJ. 23 October 2004. Poster session. (with **Jason Gliddon**, Tamica Johnson, **Lynn Maun**, Julie Akers, Denis Cummings, Justine Cook, Jordan Leckenbush, and Bob Fromtling)

Macro-invertebrates, landuse and chemistry in an urbanizing watershed. Poster session. Mid-Atlantic Region, Ecological Society of America, Baltimore MD, 12 March 2005 (with Julie Akers, Justine Cook, Denis Cummings, Jordan Leckenbush and Graeme Millar)

Stream ecology of an urbanizing watershed in the New Jersey Pine Barrens. Poster presentation, International Congress of Ecology, Montreal, Quebec, August 2005 (with J. Akers, D. Cummings, J. Cook, J. Leckenbush and G. Millar)

<http://www.stockton.edu/~cromartw/GEHR/handouts%20esa%2005.ppt>

Determination of biological, hydrological and chemical reference sites in a New Jersey Pinelands watershed. Poster session. Mid-Atlantic Region, Ecological Society of America, NJ School of conservation. 9 April 2006. ( with **Keltos, L.**, Dwyer, A., Mott, K. and F. Akers)

**ABSTRACT:** As part of a program to assess subwatersheds in the Great Egg Harbor River, Stockton College faculty and students have been working with the Great Egg Harbor Watershed Association on a study of Gravelly Run, a stream which may be among the least disturbed HUC-14 watersheds in the GEHR basin. The chemical, physical and biological characteristics of several sites along Gravelly Run were studied in 2005-06. The first year's results indicate this watershed is suitable as a reference site for pH, specific conductance, snag-dwelling macroinvertebrates and hydrologic flow regime. We are continuing to assess additional parameters. Gravelly Run compares favorably with reference sites in the adjacent HUC-14 unit we studied from 2003-2005. Our result supports the utility of macroinvertebrates on woody debris as a target for biological assessment.

Reference site characterization for ecological monitoring in the Great Egg Harbor River New Jersey. Poster presentation, Annual Meeting of the Ecological Society of America, Memphis TN, August 2006. (With **Keltos, L.**, Dwyer, A., Mott, K., Akers, F. and T Chirenje)

**ABSTRACT:** The Great Egg Harbor River, in Atlantic County NJ is a low gradient, acid-water river system, located largely within the Pinelands National Reserve. Stockton College faculty and students have been working with the Great Egg Harbor Watershed Association on a study of Gravelly Run, a stream which may be among the least disturbed Hydrologic Unit Code14-digit (HUC-14) watersheds in the GEHR basin. The chemical, physical and biological characteristics of several sites along Gravelly Run were studied in 2005-06. The first year's results indicate this watershed is suitable as a

reference site for pH, specific conductance, heavy metals, snag-dwelling macroinvertebrates and hydrologic flow regime. We are continuing to assess additional parameters and to extend the monitoring program to more impacted HUC-14 watersheds. Gravelly Run compares favorably with reference sites in the adjacent HUC-14 unit we studied from 2003-2005. Our result supports the utility of macroinvertebrates on woody debris as a target for biological assessment of low-gradient coastal plain streams.

## **LITERATURE CITED**

Robert A. Zampella, John F. Bunnell, Kim J. Laidig, and Charles L. Dow. 2001. *The Mullica River Basin: A Report To The Pinelands Commission On The Status Of The Landscape And Selected Aquatic And Wetland Resources*. NJ Pinelands Commission. New Lisbon NJ. 371 pp.

2) Dr. John Hasse, Department of Geography and Anthropology, Rowan University: Evaluating **Water Quality Relationships to Urbanization Patterns in Gloucester County, New Jersey**  
**Research Intern: Donna Moffett**

This report documents the work performed by Donna Moffett, a senior geography major at Rowan University supported by funding from New Jersey Water Resources Research Institute under the directorship of Dr. John Hasse, Rowan University.

### **Work Accomplished: Research Question I**

Under an EPA-funded program, an engineering team at Rowan is evaluating the potential feasibility for wastewater recycling within Gloucester County, NJ. Donna has assisted this team in developing a GIS database in which the location of potential sources and potential users have been identified. Donna's data development assistance has resulted in the completion of an engineering student's Masters thesis and on going research related to wastewater recycling in Gloucester County.

### **Work Accomplished: Research Question II**

In phase II, Donna conducted research in evaluating relationships between smart growth, urban sprawl and water quality. Utilizing the NJ DEP Land Use/Land Cover GIS database which contains information on impervious surface coverage, Donna's analysis performed GIS overlay analysis to determine whether or not and to what degree there is a relationship between impervious surface, smart growth and sprawl. Donna's work culminated in the presentation of the research at the Association of American Geographer's Annual Conference in Chicago, IL in March 7-11, 2006 (figure 1).

### **Summary Statement: Research Question II**

This research examined the relationship between urban form and impervious surface. Smart growth development (compact, mixed-use, pedestrian friendly, etc) has been held up as a solution to the negative consequences of urban sprawl (low density,

scattered and poorly coordinated urbanization). For example, smart growth has been hailed as a solution to traffic congestions, the loss of open space, the consumption of open space and other environmental impacts attributed to sprawl. This analysis explores the relationship of sprawl/smart growth to one very widely used indicator of water quality, impervious surface.

The study first graded development in Gloucester County, NJ on a smart growth/sprawl scale utilizing housing-unit density (Hasse 2004) as a proxy for sprawl. The analysis evaluated impervious surface at three watershed levels (HUC-11, HUC-14 and a smaller sub-watershed level produced by the research team utilizing GIS) by utilizing the impervious surface values contained in the NJ DEP land use/land cover data. A correlation evaluation was then made between the urban density value and the gross as well as percentage amounts of impervious surface for each watershed scale throughout the county.

## **Results**

Our results show that a significant correlation exists between intensities of impervious surface and sprawl although the correlation varied depending on the scale of the watershed. The strongest correlation for total percent impervious surface versus urban density was at the basin-level (HUC-11), the largest scale. These results indicate that spread out, sprawling development is generally located within watersheds that have lower intensities of impervious surface. In other words, watersheds with sprawling urbanization have lower percentages of total impervious surface and thus are indicated to have less impacted water quality than high density urbanization. In contrast, when looking at a per capita basis, watersheds with sprawling urbanization have substantially larger quantities of impervious surface per person than higher urban-density watersheds. The strongest correlation of the impervious surface per capita analysis was at the sub-watershed level, the smallest scale.

## **Conclusion**

Sprawl has a complex relationship with impervious surface and thus water quality. Watersheds with high-density development (smart growth) actually have higher percentages of impervious surface (i.e. more degraded water quality) than sprawling watersheds at the local sub-watershed level. These finding may suggest that sprawl is actually good for water quality compared with high-density growth. However, when normalizing by the number of people that occupy sprawling development, our findings show that substantially more impervious surface is produced overall with sprawl than with high-density growth. Sprawl has a larger impervious footprint consuming more watersheds than smart growth but the impact is less intense.



Figure 1 – Research Intern – Donna Moffett, at the 2006 Association of American Geographer’s Annual Conference

### **Future Outcomes: Research Question II**

The results of this research are currently being written up for submission to the *Middle States Geographers Journal*. The results of this research are also expected to be building blocks to further research.

### **Acknowledgements**

Donna Moffett and Dr. Hasse would like to express our gratitude and appreciation for the support provided by the NJ WWRI, Dr. Joan Ehrenfeld, and Priscila Walsh.

### **3. Dr. Kenneth Lee, Dept. Civil Engineering, Rutgers University: Measuring the Viscosity of Two-phase Nonaqueous Phase Liquid-water Systems in the Presence of a Cosolvent**

#### **Intern: Jessica Bernardini**

The main objective of this research is measure the viscosities of two-phase nonaqueous phase liquid (NAPL) – water systems in the presence of a cosolvent. In order to present accurate and publishable data, an apparatus that will be efficient in measuring the viscosities of the two separate phases will be created. The acquiring of these measurements will lead to a greater understanding for groundwater modeling of contaminated waters.

At the beginning of the research time, no apparatus existed or still exists that can simultaneously measure the viscosities of a two-phase NAPL- water system accurately. Due to the absence of a specific instrument to obtain these measurements, past research is somewhat inaccurate and can be misleading. The development of a viscometer with the

ability to do the aforementioned tasks was the first step in my research. Several plans were drawn up and considered for assembly. Balls that have little to no friction and are non-reactive with the NAPL- water systems were obtained and much needed to aid in the accuracy of my results. A magnetic ball dropping system was the final design. The balls were dropped for a known distance and controlled in the viscometer with an outside magnet.

Once an acceptable viscometer was decided upon, measurements of the viscosities began. Past research regarding NAPL- water systems was obtained and used to help prepare various concentrations of NAPL- water systems in the presence of a cosolvent. The different concentrations were tested each several times and an average time and viscosity being calculated from the various tests. Due to the fact that the lab was insufficiently stocked with the various items that were needed to accurately obtain data, the tests are still being done.

When concluded, this research will provide information regarding the effects that NAPL's pose on contaminated groundwater and the change in viscosity that occurs with the interaction of water and the tested contaminants. Some contaminants that were tested include PCE, benzene and toluene with cosolvents of ethanol and methanol.

**4). Sean X. Liu, Ph.D. Department of Food Science, Cook College: Biogenic Ice Nucleators in Lowering Energy Cost of Water Recovery from Impaired Waters Using CO<sub>2</sub> Gas Hydrate Technology  
Intern: Kristina Carl**

Gas hydrate desalination is an emerging water recovery technology that could be implemented to reduce the costs of desalination and other water recovery from impaired water sources by reducing the energy requirement. Gas hydrates are crystalline solids of hydrogen bonded water molecules around a small, hydrophobic gas molecule such as CO<sub>2</sub> molecule. They can be formed at above the freezing temperature of water as least as high as 12 °C under modest elevated pressures, thereby reducing the energy requirement associated with the phase change in thermal water recovery technologies. Several gases have been known to form gas hydrates with water under certain temperature and pressure conditions. However, due to economical and safety concerns, CO<sub>2</sub> seems to be a better former agent of gas hydrates for water recovery (including desalination) than other gases. The basic approach of the gas hydrate desalination can be envisioned to be very similar to the direct freezing desalination with a secondary refrigerant: a water jet is injected into a container with gas under pressure (3-4 M Pa) and subsequently the icelike gas hydrates are formed and once the gas hydrate formation reaction is completed, the gas hydrates are washed and de-pressurized and melted to produce pure water as CO<sub>2</sub> releases and is captured.

The gas hydrate formation temperature at a given hydrate formation pressure, though above the freezing temperature of pure water, is dependent of not only the gas molecule but also the composition of the untreated water. Some substances such as salts, are known



to inhibit the formation of gas hydrate resulting in lower formation temperature and contribute to the formation of sludge-like aggregates of small-size gas hydrate crystals that are difficult to be separated from the concentrated brine and require large amount of fresh water to wash off the residual salts and other impurities from the surfaces of the gas hydrates. It is believed that the formation of gas hydrates, like formation of ice crystals, needs nuclei to initiate the growth of crystals and the earlier the gas hydrates start to form with added nuclei, the less energy it requires to complete the hydrate formation reaction **and** the larger the hydrate size.

Biogenic ice nucleators, which are certain species of bacteria, were discovered to cause frost damage to the crops (Army et al, 1976; Upper and Vali, 1995). The biochemistry studies of ice nucleation-active bacteria revealed that it was the ice nucleation protein that provided ice nucleation by arranging water molecules in an icelike configuration or “lattice” (Phelps et al., 1986; Ruggles et al., 1991; Kozloff et al., 1993). These discoveries have led several studies on utilizing ice nucleators, either intact bacteria or isolated ice nucleation proteins, in food freezing (Watanabe et al., 1989; Watanabe and Arai, 1995; Li et al., 1997; Hwang et al., 2001). The discovery of ice nucleation bacteria and its successful applications in food freezing have a very important implication in the proposed work. Since the formation of gas hydrate is, in many ways, similar to that of ice, and the antifreeze additives such as glycol and methanol have been used to prevent water from both freezing and forming gas hydrate in the gas and oil industry (Sloan, 1998; Koh, 2002), it is logical for us to deduce that the biogenic ice nucleators will also work on the same principle of promoting gas hydrate formation. This inference will form the basis of the hypothesis in this proposed project.

In this study, we developed and set up a laboratory scale gas hydrate that was used to characterize CO<sub>2</sub> gas hydrates formed under the elevated pressures and above-freezing temperatures. In the early months of the project, we spent majority of our efforts on testing and modified the experimental setup based on a high pressure Soxhlot oil extractor cylinder, a thermal couple with electronic recorder, and a cooling bath with a mixture of automotive antifreeze and distilled water. We overcame numerous gas leaks and temperature fluctuations and finalized the experimental procedure by the end of 2005.

At the first part of the experimental project, we filled the cylinder with distilled water and submerged the testing cylinder in the cooling liquid mixture. High pressure CO<sub>2</sub> was injected into the cylinder until the pressure reached a pre-set value (2MP, 3MP, and 4 MP). The CO<sub>2</sub> inside the test cylinder was used both as reactant with water to form gas hydrate and to maintain the pre-set pressure. Once the experiment started, we recorded the changes in temperature with the thermal couple and pressure drop from the gauge reading. The relationships of temperature vs. time and pressure vs. time were used to infer the formation of CO<sub>2</sub> gas hydrates and supercooling of CO<sub>2</sub> and water mixture. The temperature history during the experiment was examined for any indication of existence of supercooling and its profile was used to assess the energy requirement for the formation of gas hydrates.

The second part of the project was to examine whether the addition of biological ice nucleators would result in faster and more energy-efficient gas hydrate formation. We repeated the experiment under the conditions of the previous experiment with the exception of adding some quantity (5 g) of ice nucleator proteins. To our disappointment, we did not observe any difference between the experimental results from the first part of the project and those from the second part.

There were several reasons that might contribute to the disappointing results if the hypothesis of the project was sound: (1) the setup (apparatus) was too elementary to detect the subtle difference between the results from the two experiments in the project; (2) the high-pressure cylinder in which the gas hydrates were formed does not have any transparent “window” so the direct observations of formation of the gas hydrates were impossible (the commercial cylinder for gas hydrate experiments costs \$37,000), which further complicated the data comparison between two experiments.

Throughout the project, the undergraduate intern was able to learn how to conduct a real-world experiment from beginning to the end and to understand the challenge and excitement of doing scientific research.

## Information Transfer Program

The information transfer program for FY2005 was hampered by the extended illness of the Administrative Assistant, Jeannine Der Bedrosian, who normally handles this component of the WRRIs activities. However, we were able to produce two issues of our newsletter, collaborate with the New Jersey Department of Environmental Protection on a major conference on water monitoring and a small conference on wetland management for wildlife values. We also sponsored a program of supporting graduate student attendance at national meetings to communicate water resource research findings.

The two newsletter issues included 1) an issue devoted to the Kirkwood-Cohansey Project, and 2) an issue highlighting the presentations at the water monitoring conference. The Kirkwood-Cohansey Project is a large, multi-investigator research efforts involving a collaboration among scientists at The Pinelands Commission, the US Geological Survey Water Science Center of New Jersey, and Rutgers University, to evaluate the potential impacts of water withdrawals from the Kirkwood-Cohansey aquifer on aquatic resources of the Pinelands National Reserve. The project has a high public profile, as development in the region is constrained by water availability and the water resources of the Pinelands are viewed as a potential source of water to out-of-basin development projects. Our newsletter allowed each of the participating scientists to explain in simple terms their component of the overall research effort. The newsletter was widely circulated by other organizations in southern New Jersey, including both the Pinelands Commission and advocacy groups (NGOs) involved in Pinelands protection.

We collaborated with the NJDEP in organizing the New Jersey Water Monitoring and Assessment Technical Workshop; the primary organizer was the NJ Water Monitoring Coordinating Council, and funding was obtained from the US EPA to support the meeting. This workshop, a two-day meeting, involved a one-day hands-on session for macroinvertebrate identification, and a one-day meeting at which over 30 invited speakers presented information on water monitoring technology and approaches to a diverse audience of over 100 professionals from the water management community of New Jersey. Brief papers from a selection of the speakers were assembled for the newsletter issue, bringing information about water monitoring to a broad public audience.

Finally, we have extensively expanded our website (<http://njwrrri.rutgers.edu/>) by adding many pages of linking information, including, for example, links to real-time data sources on both hydrology and water quality, links to state, federal, local and international agencies, links to information for K-12 teachers and students, pages with all past annual reports and newsletters, pages describing ongoing and recently-funded research and ongoing research at both state, federal, and other academic institutions in New Jersey, and actively-maintained information about upcoming meetings and conferences. We have also developed email lists targeting various stakeholder groups (e.g., water resource scientists in academia and agencies, water managers, members of the public in water-related NGO such as watershed associations, legislators, etc.) are using these lists to keep these groups up to date on group-specific information. Given the limited funding available from both the university and the absence of funding from the state, we view the website as our primary means of information transfer, and are devoting much of our effort to its enhancement and utilization in keeping the NJ public informed about water issues.

# Dissemination of Graduate Student Research Results

## Basic Information

<b>Title:</b>	Dissemination of Graduate Student Research Results
<b>Project Number:</b>	2005NJ128B
<b>Start Date:</b>	10/1/2005
<b>End Date:</b>	1/3/2006
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	N. A.
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	None, None, None
<b>Descriptors:</b>	information transfer, graduate education
<b>Principal Investigators:</b>	Joan G. Ehrenfeld

## Publication

## Dissemination of Research – Graduate Student Travel Awards

We used some of the Federal dollars to support an enhanced ability for graduate students throughout the state to present results of water-related research at national scientific meetings. Through a competitive application process, we invited students to apply for travel grants to assist them in presenting and disseminating research results. Applications were evaluated on the basis of their relevance to priority research topics, prominence of the meeting, senior authorship of the student, and a lack of other funds to support the travel. We also attempted to ensure that a broad range of water resource topics were represented. About 50% of applications were funded. Following is a table of the students, meetings, and presentation titles that were funded. The students represented four institutions.

Haibin Li	Rutgers U. - Env. Sci	Amer. Geophysical Union	Evaluation of IPCC AR4 Soil Moisture Simulations for the Second Half of the 20th Century
Allison Candelmo	Rutgers U. - Ecol & Evol	Estuarine Research Federation	Behavior and condition responses of young-of-the-year bluefish ( <i>Pomatomus saltatrix</i> ) to contaminants via trophic transfer
Litman & Ware	Rutgers U. - Entomology	Entomology Soc. Amer.	Cytochrome P450 CYP6BB1 and CYP6P10 in the eastern salt marsh mosquito <i>Ochlerotatus sollicitans</i> (Diptera: Culicidae).
Sean Michael Bugel	Seton Hall University	Soc. Environ.Toxic. and Contam.	Assessing Genetic Diversity of Chironomids in the NJ Meadowlands Using Randomly Polymorphic DNA
Michelle DaCosta	Rutgers U. - Plant Bio	Crop Sci Soc Amer- Soil Sci Soc Amer	Physiological and Morphological Characteristics Associated with Drought Resistance in Bentgrass Species
Walter Walker	Stockton State College - Civ Eng	Amer Water Resources Assoc	Exploring Wastewater Reuse Alternatives in Southern New Jersey
Diana Garcia & Jesse Dougherty	Stockton State College - Civ Eng	Amer Water Resources Assoc	Assessing Impacts of Dam Removal on Regional Stormwater Management
Shen Yu	Rutgers U. - Ecol & Evol	Soil Sci Soc Amer	Effects of hydrological disturbance on nitrogen cycling in Pinelands wetlands
Junu Shrestha	Princeton U. - Civ Eng	Amer. Geophysical Union	Ammonium Oxidation by Ferric Compounds in Continuous-Flow Microcosms and Verification Using Batch Experiments with <sup>15</sup> N-NH <sub>4</sub> Tracer

## Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	4	0	0	0	4
Masters	1	0	0	0	1
Ph.D.	17	0	0	0	17
Post-Doc.	1	0	0	0	1
<b>Total</b>	23	0	0	0	23

## Notable Awards and Achievements

The project entitled "A Study to Link Atmospheric N Deposition with Surface and Ground Water N and Denitrification Capabilities in an Urban New Jersey Wetland" is one component of the Teaneck Creek Restoration Project. Teaneck Creek Conservancy, a non-profit organization, with assistance from Rutgers University, USGS, and TRC Omni Environmental Corporation is working to restore and enhance 20 acres of urban wetlands within the Bergen County Parks system. The Teaneck Creek Restoration Project has won the following awards:

1. Environmental Excellence Award: States and Healthy Communities, Brownfield to Greenfield, NJ DEP, November, 2005
2. NY-NJ Baykeeper Award, September 2005

Work supported in part by the NJ WRRI (Youngster and Haggblom, and colleagues) establishing a new method for identifying microorganisms that degrade MTBE was highlighted in news releases throughout the state. This research is expected to lead to methods of enhancing the use of microbes to remove this chemical from ground water.

## Publications from Prior Projects

1. 2004NJ70B ("Efficiency of Bioretention Systems to Reduce Fecal Coliform Counts in Stormwater") - Dissertations - Rusciano, Gregory M., 2006, An Evaluation of the Ability of Bioretention Columns to Manage Fecal Coliform in Simulated Stormwater, MS Dissertation, Bioresource Engineering, Graduate School New Brunswick, Rutgers, The State University of New Jersey, New Jersey, 114 pages.
2. 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; Kou, Dawen; Mitra, Somenath; 2005, Continuous monitoring of haloacetic acids via membrane extraction,

Journal of Chromatography A, 1089, 39-44.

3. 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; Saridara, Chutarat; Mitra, Somenath; 2005, Microfluidic supported liquid membrane extraction, *Analytica Chimica Acta*, 543, 92-98.
4. 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 - Kou, Dawen; Wang, Xiaoyan; Mitra, Somenath; 2004, Supported liquid membrane microextraction with high-performance liquid chromatography-UV detection for monitoring trace haloacetic acids in water, *Journal of Chromatography A*, 1055, 63-69.
5. 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") - Dissertations - Wang, Xiaoyan; 2005, DEVELOPMENT OF MICRO-SCALE AND AUTOMATED MEMBRANE EXTRACTION SYSTEMS FOR WATER ANALYSIS, "Ph.D. Dissertation," Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ.
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") - Other Publications - Wang, Xiaoyan; Kou, Dawen; Mitra, Somenath; November 14-17, 2005, Continuous, On-line Monitoring of Haloacetic Acids via Membrane Extraction, 44th Annual Eastern Analytical Symposium, Somerset, NJ. (Oral presentation)
7. 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") - Other Publications - Wang, Xiaoyan; Saridara, Chutarat; Mitra, Somenath; March 13-17, 2005, Microfluidic Supported Liquid Membrane Extraction, 229th ACS National Meeting, San Diego, CA. (Poster)
8. 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") - Other Publications - Mitra, Somenath; Wang, Xiaoyan; Kou, Dawen; March 28-April 1, 2004, Supported Liquid Membrane Micro-Extraction (SLMME) for Monitoring Trace Acidic Analytes, 227th ACS National Meeting, Anaheim, CA. (Poster)
9. 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") - Other Publications - Mitra, Somenath; Kou, Dawen; Wang, Xiaoyan; November 17-20, 2003, Supported Liquid Membrane Micro-Extraction (SLMME) with HPLC detection for Monitoring Trace Haloacetic Acids in Water, 42nd Annual Eastern Analytical Symposium, Somerset, NJ. (Oral presentation)
10. 2003NJ38B ("Investigation of Design Parameters for Engineered Rhizoremediation Systems to Treat Contaminated Sediments In Situ") - Articles in Refereed Scientific Journals - Fleming MA, Kukor JJ, Häggblom MM (2003) Plant-mediated effects on polycyclic aromatic hydrocarbon (PAH) degradation by bacteria in the rhizosphere of the salt marsh grasses *Spartina alterniflora* and *Phragmites australis*. Abstract Q-030, American Society for Microbiology 103rd General Meeting, Washington, DC, May 18-22, 2003.
11. 2003NJ48B ("Automated Identification and Quantification of VOCs Using Electronic Nose

- Systems") - Articles in Refereed Scientific Journals - Polikar R., Jahan K. and Healy B., 2006, A combined pattern separability and two-tiered classification approach for identification of binary mixtures of VOCs, *Sensors & Actuators (B)*, vol. 116, no:1-2, pp. 174-182.
12. 2003NJ48B ("Automated Identification and Quantification of VOCs Using Electronic Nose Systems") - Conference Proceedings - Polikar R. and Healy B., 2005, A two-tiered classification algorithm for identification of binary mixtures of VOCs, in *Proc. of 11th Int. Symp. on Olfaction and Electronic Nose (ISOEN2005)*, Barcelona, Spain, pp. 89-92.
  13. 2002NJ1B ("Effects of the Biopollutant, *Phragmites australis*, On the Nutritional Status (Biochemical Condition) of Juvenile Weakfish, *New Directions Incorporating Otolith Chemical Signature Analysis*") - Articles in Refereed Scientific Journals - Litvin, Steven and Michael P. Weinstein, April 2003, *Life History Strategies of Estuarine Nekton: The Role of Marsh Macrophytes, Benthic Microalgae, and Phytoplankton in the Trophic Spectrum Estuaries*, Vol. 26, No. 2B, p. 552562.
  14. 2002NJ1B ("Effects of the Biopollutant, *Phragmites australis*, On the Nutritional Status (Biochemical Condition) of Juvenile Weakfish, *New Directions Incorporating Otolith Chemical Signature Analysis*") - Articles in Refereed Scientific Journals - Litvin, Steven and Michael P. Weinstein, 2004, Multivariate analysis of stable-isotope ratios to infer movements and utilization of estuarine organic matter by juvenile weakfish (*Cynoscion regalis*) *Can. J. Fish. Aquat. Sci.* Vol. 61 p. 1851-1861.
  15. 2002NJ1B ("Effects of the Biopollutant, *Phragmites australis*, On the Nutritional Status (Biochemical Condition) of Juvenile Weakfish, *New Directions Incorporating Otolith Chemical Signature Analysis*") - Dissertations - Litvin, Steven, 2005, *Trophic Linkages, Movements, Condition and Energetics of Juvenile Weakfish in the Delaware Bay Estuary: Implications for the Role of Habitat in Secondary Production*, Ph.D. Dissertation, Institute of Marine and Coastal Sciences, Cook College, Rutgers University, New Brunswick, NJ.
  16. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Articles in Refereed Scientific Journals - Schaefer, J.K., J. Yagi, J. Reinfelder, T. Cardona, K. Ellickson, S. Tel-Or, and T. Barkay. 2004. The role of the bacterial organomercury lyase in controlling methylmercury accumulation in mercury contaminated natural waters. *Env. Sci. Technol.* 38:4304-4311.
  17. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Articles in Refereed Scientific Journals - Barkay, T. and I. Wagner-Döbler. 2005. Microbial transformations of mercury: potentials, challenges, and achievements in controlling mercury toxicity in the environment. *Adv. Appl. Microbiol.* 57:1-52
  18. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Articles in Refereed Scientific Journals - Wiatrowski, H.A. and T. Barkay. 2005. Monitoring of microbial metal transformations in the environment. *Curr. Opin. Biotechnol.* 16:261-268
  19. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Articles in Refereed Scientific Journals - Ní Chadhain, S., J.K. Schaefer, S. Crane, G.J. Zylstra, and T. Barkay. Analysis of mercuric reductase (*merA*) gene diversity in an anaerobic mercury-contaminated sediment enrichment. *Environ. Microbiol.* In press
  20. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Dissertations - Schaefer, J.K. 2005. "The role of mercury resistance genes in the environment and the factors controlling their expression" Ph.D. Dissertation, Dept. of Biochemistry and Microbiology, Rutgers University, New Brunswick, NJ, pp. 199
  21. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Dissertations - Cardona-mareck, Tamara. 2005. "The mercury cycle in two estuarine ecosystems: the Delaware River Estuary and Berry's Creek Estuary" Environmental Science, Rutgers University, New Brunswick, NJ
  22. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference



- Proceedings - J.K. Schaefer, J. Reinfelder, J. Yagi, and T. Barkay. The Potential Role of mer-mediated Resistance in Controlling Methylmercury Accumulation in Freshwater Ecosystems in New Jersey. 102th Annu. Meet. Am. Soc. Microbiol. Salt Lake City, May 19 - 23, 2002.
23. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference Proceedings - Barkay, T., and J. Schaefer. Microbe-mercury interactions: old paradigms, new frontiers. Bioremediation and Biodegradation: Current Advances in Reducing Toxicity, Exposure and Environmental Consequences. Asilomar Conference Center, Pacific Grove, CA, June 9 - 12, 2002.
  24. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference Proceedings - J.K. Schaefer, J. Reinfelder, J. Yagi, S. Tel-Or, and T. Barkay. The Potential role of mer-mediated resistance in controlling methylmercury accumulation in freshwater ecosystems in New Jersey. The 34th Mid-Atlantic Industrial & Hazardous Waste Conference, Rutgers University, New Brunswick, NJ, Sept. 20-21, 2002.
  25. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference Proceedings - Barkay, T. The role of microbial transformations in controlling methylmercury accumulation in aquatic environments. The 34th Mid-Atlantic Industrial & Hazardous Waste Conference, Rutgers University, New Brunswick, NJ, Sept. 20-21, 2002. Invited talk.
  26. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference Proceedings - Yagi, J., J. Schaefer, J.-C. Bonzongo, K. Duddleston, K. Haase, M. Hines, and T. Barkay. Factors controlling methylmercury production in bank soils of the Carson River, Nevada. 103th Annu. Meet. Am. Soc. Microbiol. Washington DC, May 18 - 22, 2003.
  27. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference Proceedings - Ní Chadhain, S. M., S. Hicks, J. Schaefer, T. Barkay, G. J. Zylstra. Novel Mercuric Reductase Genes Found in Anaerobic Communities of Mercury Contaminated Sediments. 104th Annu. Meet. Am. Soc. Microbiol. New Orleans, May 19 - 23, 2004.
  28. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference Proceedings - Schaefer, J. K., J. Yagi, T. Cardona-Marek, K. Ellickson, S. Tel-Or, J. Reinfelder, and T. Barkay. The role of the bacterial enzyme, organomercurial lyase, in controlling methylmercury accumulation in mercury contaminated natural waters. 7th International Conference on Mercury as a Global Pollutant. Ljubljana, Slovenia, June 27 - July 2, 2004.
  29. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference Proceedings - Barkay T, Schaefer, J, Poulain, A. and, Amyot M. Microbial transformations in the mercury geochemical cycle. 15th Goldschmidt Conference. Moscow Idaho, May 20 - 25, 2005. Invited talk
  30. 2000NJ02 ("Factors controlling methylmercury degradation in Pine Barrens lakes") - Conference Proceedings - Schaefer, J., and T. Barkay. Diversity of Mercuric Reductase (MerA) Genes and Transcripts in Mercury Contaminated Waters 105th Annu. Meet. Am. Soc. Microbiol. Atlanta, June 5 - 9, 2005.
  31. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Other Publications - University of Florida, March 2006, Department of Pathobiology College of Veterinary Medicine, Parasitism, Food Webs and Biomass Patterns in Stream Ecosystems Invited Seminar.
  32. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Other Publications - University of Florida, January 2006, Department of Wildlife Ecology & Conservation, Parasitism, Food Webs and Biomass Patterns in Stream Ecosystems Invited Seminar.
  33. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Other Publications - Cornell University, October 2000, Aquatic Lunch Bunch Department of Entomology, Parasites in food webs Invited Seminar.
  34. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Conference Proceedings - Hernandez, A.D., Trexler, J.C., Huxham, M. and Sukhdeo, M.V.K. 2006. Parasitism, food

webs and biomass patterns in natural ecosystems. 4th Ecology & Evolution of Infectious Disease Conference, Penn State University, University Park.

35. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Conference Proceedings - Hernandez, A.D. and Sukhdeo, M.V.K. 2005. Food webs and parasites: Biomass patterns in a freshwater community. Ecological Society of America, Montreal.
36. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Conference Proceedings - Hernandez, A.D. and Sukhdeo, M.V.K. 2004. Parasite alteration of biomass and ecosystem function of hosts. American Society of Parasitologists, Philadelphia.
37. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Conference Proceedings - Hernandez, A.D. and Sukhdeo, M.V.K. 2003. Eltonian pyramids and parasitism in food webs. American Society of Parasitologists, Halifax, Nova Scotia, Canada.
38. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Conference Proceedings - Hernandez, A.D. and Sukhdeo, M.V.K. 2002. Isopod detritus processing is decreased in infected individuals. North American Benthological Society Annual Meeting, Pittsburgh
39. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Conference Proceedings - Hernandez, A.D. and Sukhdeo, M.V.K. 2001. Environmental disturbance and the incidence of parasitism in local and invasive fish species. 4th International Symposium on Monogenea. Brisbane, Australia.
40. 2000NJ05 ("NJ Pinelands Native Fish Biology: Parasites as Biological Tags") - Conference Proceedings - Hernandez, A.D. and Sukhdeo, M.V.K. 2001. Environmental disturbance and the incidence of parasitism in local and invasive fish species. American Society of Parasitologists, Albuquerque.
41. 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") - Articles in Refereed Scientific Journals - Somsamak P, Richnow HH, Häggblom MM (2005) Carbon Isotopic fractionation during anaerobic biotransformation of methyl tert-butyl ether and tert-amyl methyl ether. Environ. Sci. Technol. 39:103-109.
42. 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") - Articles in Refereed Scientific Journals - Somsamak P, Richnow HH, Häggblom MM (2006) Carbon isotope fractionation during anaerobic degradation of methyl tert-butyl ether (MTBE) under sulfate-reducing and methanogenic conditions. Appl. Environ. Microbiol. 72:1157-1163.
43. 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") - Dissertations - Somsamak, P (2005) Anaerobic biotransformation of methyl tert-butyl ether (MTBE) and related fuel oxygenates under different anoxic conditions. Ph.D. Thesis, Graduate Program in Environmental Science, Rutgers University.
44. 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") - Conference Proceedings - Somsamak P, Cowan RM, Häggblom MM (2002) Anaerobic biotransformation of fuel oxygenates under sulfate-reducing conditions. 34th Mid-Atlantic Industrial & Hazardous Waste Conference, Sept. 20-21, 2002, New Brunswick NJ.
45. 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") - Conference Proceedings - Somsamak P, Häggblom MM (2003) Anaerobic degradation of methyl tert-butyl ether (MTBE) under methanogenic conditions Abstract Q-039, American Society for Microbiology 103rd General Meeting, Washington, DC, May 18-22, 2003.
46. 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") - Conference Proceedings - Somsamak P, Richnow HH, Häggblom MM (2004) Carbon isotope fractionation during anaerobic MTBE biodegradation. Abstract Q-354. American Society for Microbiology 104th General Meeting, New Orleans, May 23-27, 2004.
47. 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") - Conference

- Proceedings - Häggblom MM, Somsamak P (2004) Anaerobic biotransformation of methyl tert-butyl ether (MTBE) and related fuel oxygenates. International Petroleum Environmental Conference, Albuquerque, NM, Oct. 12-15, 2004.
48. 2002NJ6B ("Anaerobic biodegradation of MTBE under different anoxic conditions") - Conference Proceedings - Häggblom MM (2005) Anaerobic metabolism of xenobiotic compounds - biotransformation of MTBE and related fuel oxygenates International Union of Microbiological Societies (IUMS) Conference, San Francisco, July 23 - 28, 2005.
  49. 2003NJ42B ("Microbial respiration of arsenic and selenium") - Articles in Refereed Scientific Journals - Narasingarao P, Häggblom MM (2006) *Sedimenticola selenatireducens*, gen. nov., sp. nov., an anaerobic selenate-respiring bacterium isolated from estuarine sediment. *Systematic and Applied Microbiology*, in press.
  50. 2003NJ42B ("Microbial respiration of arsenic and selenium") - Conference Proceedings - Narasingarao P, Häggblom M (2003) Isolation of microorganisms capable of dissimilatory selenate reduction. Abstract Q-457, American Society for Microbiology 103rd General Meeting, Washington, DC, May 18-22, 2003.
  51. 2003NJ42B ("Microbial respiration of arsenic and selenium") - Conference Proceedings - Narasingarao P, Häggblom M (2004) Physiological characterization of a dissimilatory selenate reducing bacterium, strain AK4OH1. Abstract Q-153. American Society for Microbiology 104th General Meeting, New Orleans, May 23-27, 2004.
  52. 2003NJ42B ("Microbial respiration of arsenic and selenium") - Conference Proceedings - Narasingarao P, Häggblom MM (2005) Dissimilatory selenate reducing bacteria are diverse and ubiquitous in nature. Abstract Q-054. American Society for Microbiology 105th General Meeting, Atlanta, June 5-9, 2005.
  53. 2003NJ42B ("Microbial respiration of arsenic and selenium") - Conference Proceedings - Narasingarao M, Häggblom MM (2006) Bacterial respiration on selenium. AXIOM-Virtual Institute Spring School Microbial Activity at Biogeochemical Gradients, Leipzig, Germany, April 3-6, 2006.
  54. 2003NJ42B ("Microbial respiration of arsenic and selenium") - Conference Proceedings - Narasingarao P, Häggblom MM (2006) Anaerobic reduction of selenate and selenite by a novel bacterium, Strain KM. Abstract Q-108. American Society for Microbiology 106th General Meeting, Orlando, May 21-25, 2006.