New Jersey Water Resources Research Institute
Annual Technical Report
FY 2007

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. The funding is intended to jump−start novel and important research efforts by both faculty and students, and thus emphasizes new research ideas that do not have other sources of funding. We hope to support the acquisition of data that will enable further grant submission efforts, and, in the case of students, lead to research careers focused on cutting−edge research topics in water sciences.

Research conducted by faculty covers a wide range of topics. In a project continued from FY2006, Qiu and colleagues developed a method for combining topographic, hydrologic and land use information to designate “critical source areas” for pollution in an agricultural watershed, and used the method to demonstrate that upland as well as riparian areas may be important for creating buffers for pollutant removal. In another project continued from FY2006, Huang and colleagues have been working on methodologies for detecting estrogenic compounds in wastewater and stormwater samples. In a new project, Gimenez and colleagues have developed a novel method of analyzing water level records from urban wetlands using wavelet analysis to identify sources of variability in water levels, and have created models relating hydrological patterns to land−use patterns. In a second new project, Yee and colleagues have examined the possible role of a novel bacterium in converting lead carbonate to a more stable phosphate; results to date indicate that abiotic rather than biotic mechanisms may be responsible for the transformation.

Graduate students have similarly carried out research over a wide range of topics. Hylton and her advisor have developed a microscale liquid membrane extraction method for monitoring low concentrations of pesticides and related contaminants, by optimizing solvent types, extraction efficiency, extraction time, and solvent loss factors. Ndiba and his advisor have tested a method of stabilizing metals in contaminated dredged sediment material from regional estuaries by treating with phosphoric acid and calcinations, and have shown that the method has potential to render the material suitable for beneficial re−use in construction. MacDonald and his advisor have developed a microcosm system in which to test the effects of wetland plants on arsenic cycling, by following plant−generated changes in redox and organic carbon conditions; this research will be applicable to the development of wetland and bioretention systems to treat arsenic−contaminated waters. Taylor and her advisor have demonstrated that shell−bag reefs and oyster aquaculture racks create habitat for migratory American eels in the Delaware estuary, and also enhance biodiversity in general. Finally, Yu and his advisor have developed 14C methods to determine if carbon from methylmercury is incorporated into the biomass of demethylating bacteria in the highly Hg−contaminated rivers of northern New Jersey.

The goal of our information transfer program is to bring timely information about critical issues in water resource sciences to the public, and to promote the importance of research in solving problems. The information transfer program continues to focus on producing issues of the newsletter that provide a comprehensive overview of a particular water resource issue, as well as one issue a year that highlights water research and the role of research in solving problems, and also developing the NJWRRI website (www.njwrri.rutgers.edu) into a comprehensive portal for water information for the state. We also collaborate with other organizations in sponsoring and producing conferences.

Research Program Introduction

The New Jersey Water Resources Research Institute has had a policy, yearly re−affirmed by the Advisory Council, of using the research dollars to promote new and novel directions of research. To this end, two projects directed by research faculty at institutions of higher learning around the state are selected, and five grants−in−aid are awarded to graduate students who are beginning their research. In both cases, we expect that the research is exploratory and is not supported by other grants. The intent is that these projects will lead to successful proposals to other agencies for further support. The larger goal of the research component of the Institute's program is to promote the development of scientists who are focused on water resource issues of importance to the state.

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

Basic Information

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

Publication

Problem and Research Objectives

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

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

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

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

Methodology

LC-MS/MS Method Development

We have developed an LC-MS/MS method with collaboration of Dr. Zhiqiang Yu of Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. We used a liquid

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

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

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

GC-MS/MS Method Development

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

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

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

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

Site Selection for Water Sampling

A combination of wastewater treatment plant (WWTP) effluent and surface water samples were collected along and from the South Brach Raritan River and the upper and lower Passaic River in New Jersey between May and July 2008. A single combined sewer overflow (CSO) sample was collected during a heavy rain event in Perth Amboy in May 2008 as well. The South Branch of the Raritan River is 51 miles long with most of the land use in the watershed being agricultural. However, suburban-industrial development is rapidly increasing. Approximately 23 NJPDES permits have been issued for this watershed. The Passaic River is roughly 80 miles long with a watershed area of 935 square miles, and the Upper Passaic River serves as a significant source of drinking water for a large part of northeastern New Jersey. The lower portion of the Passaic flows mostly through urbanized and industrialized portions of the state and suffers from significant pollution. Two WWTP's and two surface water locations were chosen per stream for a total of eight sites. The WWTP's chosen were located in the townships of Flemington, Clinton, Two Bridges, and Livingston.

Three rounds of sampling were collected from each location during the summer months. Duplicate surface water grab samples were collected from a bridge at the center of flow – the choice of sites being based on accessibility and proximity to selected WWTP's in this study. 4 L of sample were transferred from a plastic bucket to amber glass bottles which contained sodium azide at a concentration of 1.25 – 4.0 g/L as a preservative. The sample bottles were kept on ice and brought the laboratory within five hours of collection and store at 4 °C until filtration and extraction.

Water Sample Filtration and Extraction

In order to avoid clogging of the extraction disk, all samples were pre-filtered using 0.7 micron glass fiber filter. The filter paper was saved and stored in the freezer for future Soxhlet extraction. After filtration, the sample was spiked with surrogate Estrone-d4 to a concentration of 50 ng/L. Samples were extracted with 47 mm SDB-XC (3M Corporation, St. Paul, MN) at a flow rate of approximately 25 ml/min. The disk was preconditioned with 10 ml DCM, 10 ml acetone, 10 ml isopropanol, and 10 ml methanol. After the disk was dried out for 30 min, it was eluted with 8 ml methanol, 16 ml DCM/methanol (50/50), and finally 8 ml DCM. The eluent from liquid phase extraction

and filtrate Soxhlet extraction (extraction to be done at later time) will be blown down to dryness under a gentle nitrogen stream, shipped to Guangzhou, China, and then reconstituted with methanol prior to analysis by LC/MS. Three matrix spike (Milli-Q water and all target analytes) and three blank samples (contained only Milli-Q water) were processed as well to correspond with the three rounds of sampling. Five hormones will be analyzed for in this study, including 17β-estradiol, estrone, 17α-ethinylestradiol, testosterone, and androstenedione.

Quantification of Hormones in Water Using LC-MS/MS

We will analyze the hormone concentrations in the water and suspended solids samples collected from the sites described above using the LC-MS/MS method delineated above. Il Kim, the PhD graduate student who works on this project, has booked the airplane ticket for her visit to China in July 2008. She will bring the processed samples to Guangzhou Institute of Geochemistry and will work with the research scientists on the quantification. The costs of her travel and chemical analysis are covered by another grant awarded internally by Rutgers University. The results will be summarized in next year's report.

Principal Findings and Future Work Plan

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

With the no-cost extension of the project, we have taken water samples from the field, which were processed in the lab for chemical analysis using LC-MS/MS method. We expect to complete the proposed work by the end of the summer semester of 2008. A complete progress report on the results will be provided in the Spring of 2009.

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

Basic Information

Title:	Integrated Assessment of Economic and Water Quality Impacts of Agricultural Best Management Practices in Upper Cohansey River Watershed
Project Number:	2006NJ118B
Start Date:	3/1/2006
End Date:	12/31/2007
Funding Source:	104B
Congressional District:	6th
Research Category:	Water Quality
Focus Category:	Water Quality, Economics, Models
Descriptors:	
Principal Investigators:	Zeyuan Qiu, Christopher Obropta

Publication

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

Project Summary:

Problem and Research Objectives

Understanding the economic and water quality impacts of agricultural best management practices (BMPs) is becoming increasingly important for achieving the desired water quality standards in watersheds in suburban settings like New Jersey. The goal of this research is to provide a science-based information analysis to policy makers who want to maximize water quality benefits while minimizing economic costs when implementing multiple conservation practices in a watershed. The supporting objectives are (1) to estimate the economic and water quality impacts of various agricultural BMPs being implemented in the Neshanic River watershed; and (2) to evaluate the potential in controlling agricultural pollution to achieve locally defined water quality goals through optimal placement of BMPs in the watershed by integrating the results of the estimated costs and water quality benefits in the first objective with an optimization programming model.

Methodology

A literature review has been conducted on hydrological theories, agro-environmental policies, effectiveness of agricultural BMPs, and modeling to develop innovative ways of managing agricultural nonpoint source pollution. Empirical evaluation of agricultural BMPs in the Neshanic River watershed went two directions. The first was to identify the critical source areas (CSAs) for the placement of conservation buffers, one of the most popular agricultural BMPs by integrating hydrological modeling with geographic information systems to improve its effectiveness. The second was to apply a watershed-scale water quality simulation model Soil and Water Assessment Tool (SWAT) and economic models to evaluating the placement of conservation buffers and other BMPs in the watershed. The Neshanic River watershed is 31 square miles in area with mixed land use in the Raritan River Basin in Hunterdon County, New Jersey. The primary water quality consideration is contamination of phosphorus and fecal coliform in its streams. This non-trout river has over 40% of its drainage area in agricultural land use, which is the highest percentage in the entire Raritan River Basin.

Critical Source Areas (CSAs) for Conservation Buffer Planning

In the previous period, we developed a methodology to identify the CSAs for conservation buffer placement following variable source area hydrology. Three spatial datasets were used to delineate the critical source areas in the watershed: a digital elevation model (DEM), a soil data and a recent land use/cover. In this extended period, we evaluated the cost-effectiveness of three buffer restoration strategies when applied to the Neshanic River watershed by assuming buffer restoration in agricultural lands was supported by the New Jersey Conservation Reserve Enhancement Program (NJCREP). The three strategies included an unconventional strategy of targeting buffer restoration in agricultural CSAs in the watershed and two conventional riparian buffer restoration strategies. The two conventional strategies were restoring buffers in the agricultural lands

within the 177-foot (which is equivalent to the CSA strategies in terms of buffer sizes) and 100-foot (which is most likely being agreed and adopted by local communities) riparian corridors of the streams in the watershed.

NJCREP supports four types of buffer practices, i.e., grass waterway, contour grass strips, filter strips and riparian buffer, in agricultural lands. Site-specific buffer types under each strategy were based on site-specific conditions. The implementation costs including sign-up incentive, installation and maintenance costs, and soil rental costs were based on the average costs of the existing enrolled CREP lands in New Jersey. The environmental benefits of different strategies were evaluated using the runoff potential of all sites measured by the modified topographic index. The cost-effectiveness was measured by the targeted average runoff potential divided by the average implementation costs.

Modeling Water Quality Impacts of Agricultural BMPs using SWAT

SWAT is a continuous, daily time-step process model that simulates the water, nutrient, chemical and sediment movement in a watershed resulting from the interaction of weather, soil properties, stream channel characteristics, land management practice, and crop growth (Arnold et al., 1994). SWAT integrates field-scale BMPs being implemented within a watershed and evaluates their water quality benefits at sub-watershed- and watershed-scales over a long period of time. This model has been widely applied to estimate water quality impacts of BMPs (Fohrer et al., 2002; Santhi, et al., 2002; Tripathi, et al., 2003) and effectiveness of alternative regulatory instruments (Qiu and Prato, 1999; Whittaker et al., 2003). The 2002 landuse data, 10-meter DEM and NRCS Ssurgo soil data and the NJDEP 1995 stream layers were used to set up the SWAT model. The SWAT modeling effort was initially delayed because of the lack of the BMP data. In the interim, we drove through the entire watershed to collect detailed information on agricultural activities, such as crop and livestock productions, in each field within the watershed. We also interviewed farmers and the Hunterdon Soil Conservation District agricultural specialists for detailed crop production practices and BMPs.

Figure 1. The Delineation of Watershed for SWAT Modeling

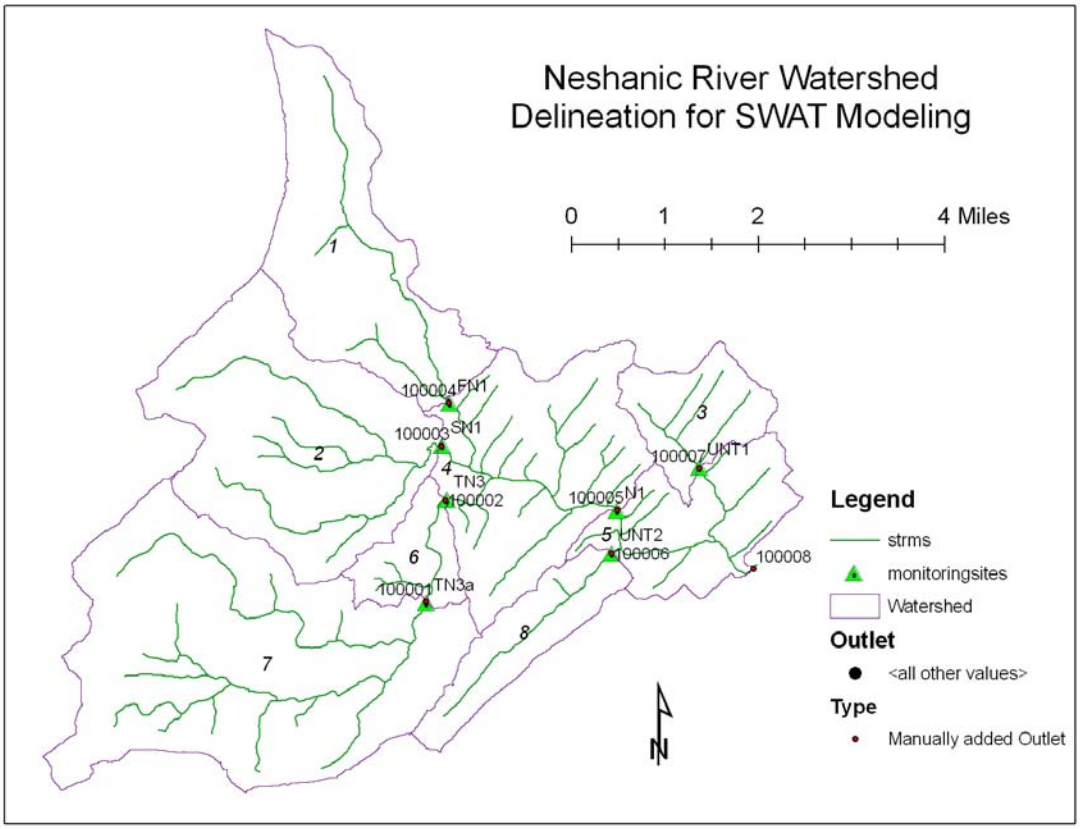

Figure 1. Presentation of the detailed delineation of the watershed for SWAT modeling. The watershed was divided into 8 subwatersheds based on the historical and current water quality monitoring activities in the watershed and each drains to one of those monitoring stations.

Table 1. The area distribution by subbasins in Neshanic River Watershed. Subbasin 7 is the largest, representing about 30 percent of the watershed.

Sub-basin ID	Acres	Percentage
1	2,896	14.84
2	3,819	19.57
3	956	4.90
4	2,851	14.61
5	1,503	7.70
6	651	3.34
7	5,838	29.92
8	997	5.11
Total	19,512	100.00

Table 2. The area distribution of different land uses in Neshanic River watershed

Land Use Type	Acres	Percentage
Residential-High Density --> URHD	93	0.48
Residential-Medium Density --> URMD	207	1.06
Residential-Med/Low Density --> URML	377	1.93
Residential-Low Density --> URLD	4,358	22.34
Commercial --> UCOM	275	1.41
Industrial --> UIDU	486	2.49
Transportation --> UTRN	161	0.83
Water --> WATR	54	0.28
Wetlands-Non-Forested --> WETN	80	0.41
Agricultural Land-Generic --> AGRL	7,926	40.62
Wetlands-Mixed --> WETL	203	1.04
Orchard --> ORCD	111	0.57
Forest-Deciduous --> FRSD	2,983	15.29
Forest-Evergreen --> FRSE	206	1.06
Forest-Mixed --> FRST	904	4.63
Wetlands-Forested --> WETF	1086	5.57

Table 2 gives the area distribution of different land uses in the watershed. Agriculture, low density residential development, and forest are the largest land use categories in the watershed. Since NJDEP didn't give a detailed classification on cropland and pasture, we divided the agricultural lands in each subbasin into the following categories based on the land use activities collected in the watershed.

Table 3. Sub classes of agricultural lands for SWAT Modeling

Sub-class	Percentage
Corn	30
Soybean	15
Timothy	20
Alfalfa	15
Oats	10
Wheat	10

During the basic run of the SWAT model, we also made the following assumptions on the lawn management activities in urban land:

- No nutrients or chemicals applied.

- For low density development, cut lawn twice a month for May, June and July, and once a month for August, September, and October.
- For other urban land use, cut lawn twice a month for May, June, July and August, and three times for September and October.

We also collected the following observed weather data for the Flemington Weather Station, which is just outside of the watershed:

- Rainfall and temperature – 1960-2006
- Others (solar radiation, relative humanity and average wind speed) – 1960-2004

The final SWAT consists of 8 Subbasins and 153 Hydrological Response Units (HRUs). We ran the model for the period from 1/1/1995 to 12/31/2004.

Principal Findings and Significance

Table 4 presents the comparison of the cost-effectiveness of the three strategies. As expected, the CSA strategy was more cost-effective, which was 57 and 51 percent higher than the 177-foot and 100-foot riparian buffer strategies, respectively. Several local conservation initiatives have incorporated the idea of targeting CSAs for agricultural BMPs. For example, a CCPI (Cooperative Conservation Partnership Initiative) grant, funded by the Natural Resource Conservation Service and led by North Jersey Resource Conservation and Development Council (RC&D) with collaborations from New Jersey Institute of Technology and NJWSA, is adopting the innovative CSA strategy to develop a riparian restoration plan for agricultural lands in the Raritan River Basin. The CSA concept is also adopted in the North Jersey RC&D's River-Friendly Farm Certification Program that seeks to promote agricultural best management practices through recognition of those farms that, through good management, help to protect water resources in Raritan River Basin.

Table 4. Cost-effectiveness of three buffer restoration strategies

	Units	CSA Strategy	100-Foot Riparian	177-Foot Riparian
Total Areas	Acres	2,643	1,508	2,654
Agricultural Lands	Acres	692	321	705
Signing Incentive Payments	$	69,207	32,138	70,475
Installation Costs	$	1,514,526	926,924	2,032,640
Annual Land Rental Costs	$	27,698	12,395	26,800
Annual Maintenance Costs	$	3,045	1,864	4,088
Total Costs	$	2,044,880	1,172,947	2,566,428
Average costs	$ per acre	2,955	3,650	3,642
Targeted Runoff Potentials	per acre	500	409	393
Cost-effectiveness		0.169	0.112	0.108

Figure 2 presents the simulated and observed stream flows at the USGS Reaville Station, monitoring station 100006 in Figure 1.

Figure 2. The simulated and observed stream flow in Reaville USGS station

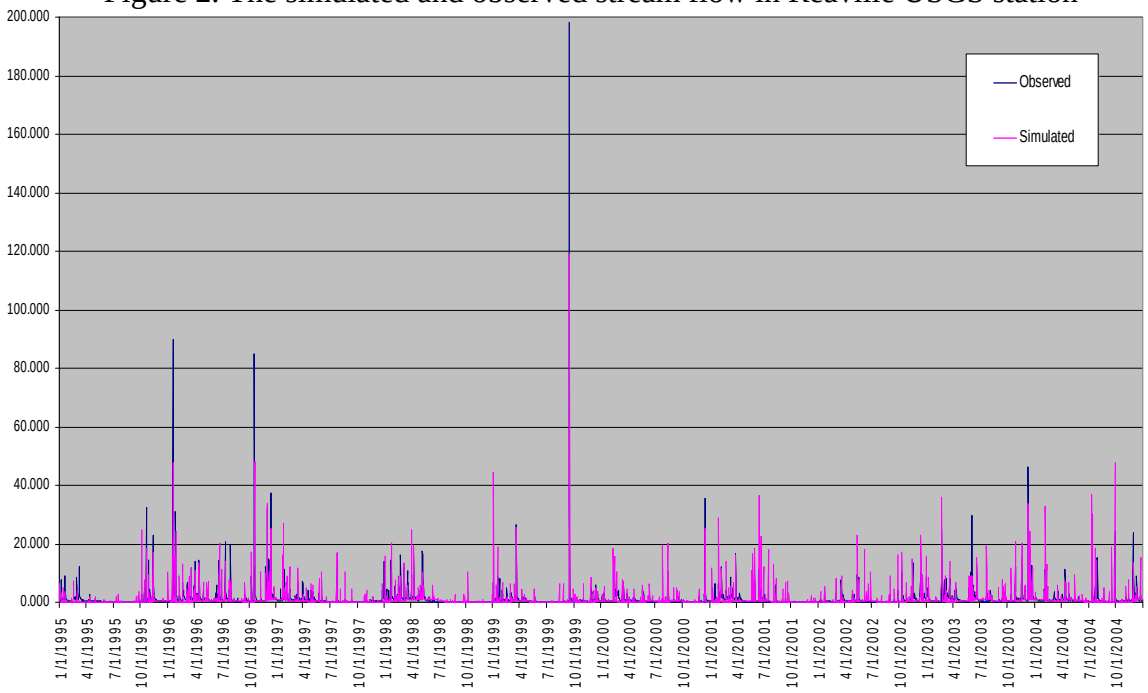

Table 5 compares the simulated crop yields with the Hunterdon County average yield and the farmers' yield goal for each crop. SWAT simulates the crop yield very well.

Table 5. Comparison of the simulated crop yield, Hunterdon County average yield and the Farmers' crop yield goal

Crops	Units	Simulated Yield	County Average	Yield Goal
Corn	Bu/ac	106.84	98.72	95 - 140
Soybean	Bu/ac	32.51	31.75	
Oats	Bu/ac	98.63		72
Wheat	Bu/ac	60.06	48.92	60 - 70
Alfalfa	T/ac	2.89	3.09	
Timothy	T/ac	2.59	1.80	2 – 2.5

We are in the process of refining the subbasin delineation and spatial distribution of crop pattern and crop rotations in the watershed. We are also going to calibrate the model using the observed stream flow and water quality data. The calibrated model will be used to evaluate the water quality impacts of the collected agricultural BMPs, which will then be integrated with the production costs of the farming practices to evaluate the spatial placement of BMPs.

Cited Literature

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The influence of flooding cycles and iron oxides on arsenic retention in contaminated, planted microcosms in comparison with phosphate retention.

Basic Information

Title:	The influence of flooding cycles and iron oxides on arsenic retention in contaminated, planted microcosms in comparison with phosphate retention.
Project Number:	2007NJ130B
Start Date:	3/1/2007
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	12th
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Toxic Substances, Water Quality
Descriptors:	
Principal Investigators:	Luke MacDonald, Peter Jaffe

Publication

(3) Project Summary:

Problem and Research Objectives

This research aims to better predict the behavior of phosphate and arsenic under changing iron and sulfur redox conditions. Accordingly, this study investigates the potential for iron oxides, sulfides, and iron sulfides to capture phosphate and arsenate, and the influence of plants and hydrology on this process.

Iron oxides and sulfide bearing minerals, ubiquitous in the environment, bind to inorganic arsenic and phosphate. Inorganic arsenic occurs in two dominant redox states, arsenate (As(V)) and arsenite (As(III)), both highly toxic and carcinogenic (Hopenhayn, 2006). The oxidized form, arsenate, behaves like phosphate (P(V)) in the environment, because the two species display similar coordination chemistry and both readily bond with soil solids like iron oxides and clay particles (Kinniburgh et al. 2003). Lab and field studies show that arsenate and phosphate sorb to iron plaques that form on plant roots found in ponds and wetlands (Blute, Brabander, Hemond, Sutton, Newville and Rivers, 2004, Liu, Jeon, Zachara, Wang, Dohnalkova and Fredrickson, 2006). Plants generate these plaques by pumping oxygen from the atmosphere to their roots, creating microoxic regimes in otherwise anoxic sediments (Lloyd, 2003).

But redox conditions change frequently and precipitously in wetlands and vegetated storm water retention ponds, after storm events or during extended droughts, shifting the system back and forth between oxic and anoxic conditions. Under oxic conditions dissolved ferrous iron will oxidize and precipitate to form new iron oxides, while existing solid ferrous oxides will transform to new ferric oxides, and sulfide-bearing minerals may oxidize and dissolve. As Figure 1 shows, both new iron oxides and transformed ferrous oxides will affect the solubility of phosphate and arsenic. In shallow groundwater, flooding and drought lead to cycles of oxic and anoxic conditions that could, based on the mechanisms presented in Figure 1, produce cyclic patterns in iron redox states and in the mobility of arsenic and phosphate. A similar scenario follows for sulfur chemistry, not shown for brevity. In both cases, in comparison with steady-state, stable redox conditions, cyclic redox patterns may lead to greater or lesser arsenic and phosphate mobility, depending on whether the arsenic and phosphate remain in solution, co-precipitate with fresh iron oxides or sulfides, or sorb to surfaces.

The problem that this research investigates is: *will iron oxides or sulfides effectively capture arsenic and phosphate under the redox conditions we expect to find in wetlands and retention ponds, how do plants impact the capture of these pollutants, and what role do wetting and drying cycles play?* As discussed above, competing redox driven processes influence the solubility and sorption of phosphate and arsenic. These dynamic redox processes may have opposite effects on the capture of these pollutants, making it difficult to determine the optimal conditions for arsenic and phosphate capture, and the goal of this research is to help unravel this mystery.

Methodology

Vertical plug-flow planted microcosms simulate groundwater upwelling, and allow the monitoring concentration profiles (Figure 2). A total of 24 five-gallon microcosms test the influence of plants, arsenic contaminated soil, sulfur cycling, and iron (Figure 3). The microcosms receive influent solution consisting of deionized water, 5ppm arsenate, 1mM sulfate, 1mM phosphate, and a minimal artificial groundwater

media. These pseudo-steady state greenhouse microcosms, which undergo significant redox changes through diurnal variation in plant root exudate concentrations, will undergo several rounds of 24-hour sampling in the upcoming months. Duplicate planted microcosms (Figure 3) help to verify the statistical similarity at flooded steady-state, and in the future one set of microcosms will undergo drying and wetting cycles while the other set remains permanently flooded, thereby studying the influence of wetting and drying cycles.

At each depth, the following variables are monitored:

i. Total dissolved organic carbon
ii. Nitrate
iii. Total dissolved sulfur and sulfate
iv. Arsenate and total arsenic
v. Total dissolved iron and dissolved Fe(II)

Principal Findings and Significance

Most of 2007 was spent constructing the microcosms, establishing plant growth, working through the hydrology, and creating the sampling protocol to best preserve the redox sensitive species. A pilot study revealed that the plants did not consume enough nitrate to allow for iron or sulfate reduction under high nitrate loads, and consequently nitrate was removed from the influent media. The preliminary results from the steady state microcosms (Figure 4) show significant arsenate retention in the presence of plants, and in the presence of soil. More detailed analysis will tease out the relative contribution of plant root exudates, iron plaques, and biomass uptake.

Figure 1: Mechanisms of phosphate and arsenate capture and release due to iron redox transformations.

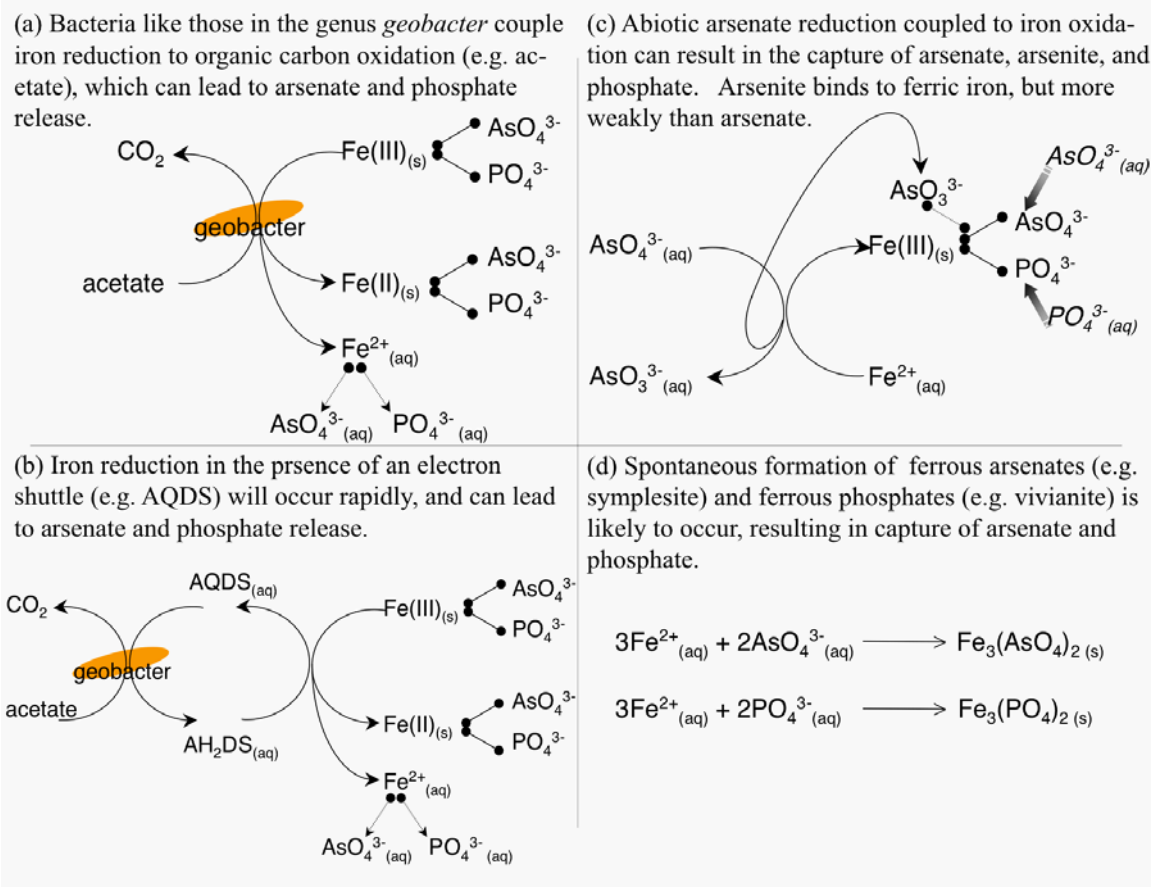


Figure 2: Photograph of the greenhouse experiment. Each microcosm receives influent water from the blue 55-gallon drums. The water enters at the bottom port, and contains nine sample ports equally spaced throughout the microcosm. The system is permanently flooded, with a free water surface. Sand is present in all microcosms to ensure adequate flow rates and sample volumes. Each port connects to four air-stone diffusers at the same depth, and sample ports are pumped simultaneously from all ports to evenly draw water.

Figure 3: Schematic showing the experimental design

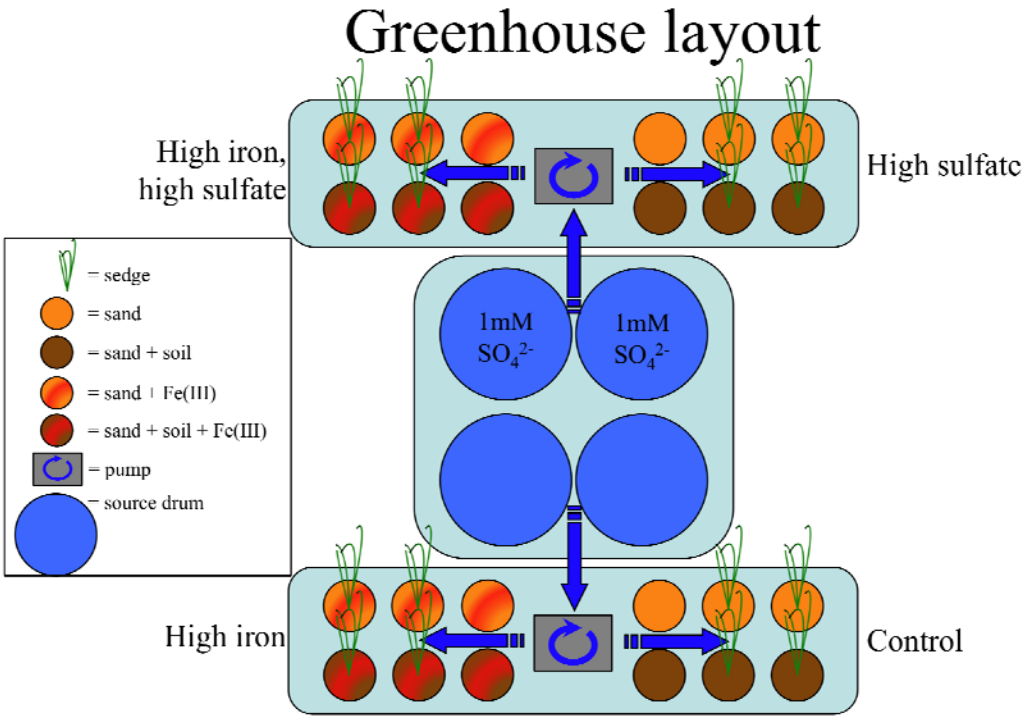
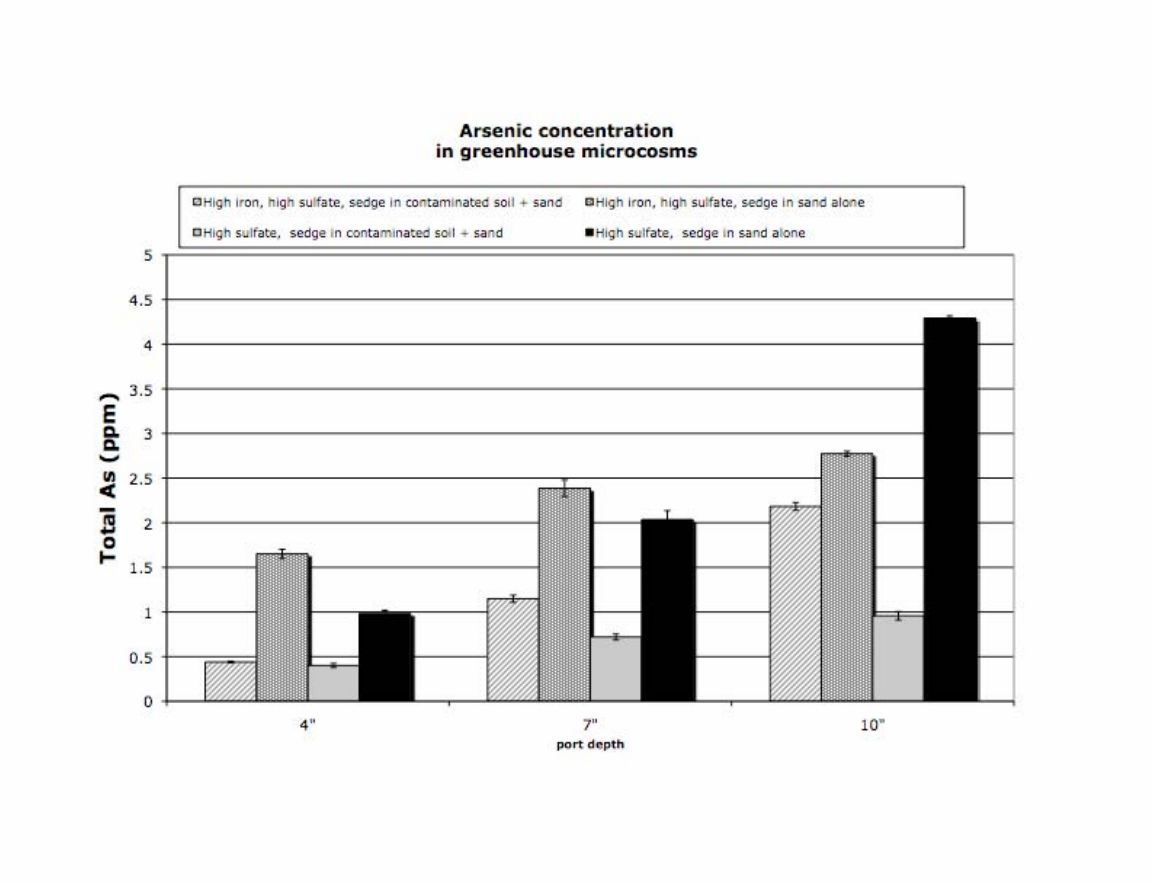


Figure 4: This figure shows the influence of iron, sulfate, and soil on arsenic retention. Adding iron oxides reduces the porewater arsenic concentrations in sand microcosms, but shows less of an effect in sand-soil mixtures.



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Development of Microscale Membrane Extraction for trace Monitoring of Pesticides and other Emerging Pollutants in Water

Basic Information

Title:	Development of Microscale Membrane Extraction for trace Monitoring of Pesticides and other Emerging Pollutants in Water
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Descriptors:	
Principal Investigators:	Kamilah Hylton, Somenath Mitra

Publication

1. Hylton, Kamilah; Somenath Mitra, 2007, Barrier film protected, and mixed solvent optimized micro−scale membrane extraction of methyl carbamate pesticides, Journal of Chromatography A, 1154, 60–65.
2. Hylton, Kamilah; Somenath Mitra, 2008, A microfluidic hollow fiber membrane extractor for arsenic (V) detection, Analytica Chimica Acta, 607 (1), 45−49.
3. Hylton, Kamilah, 2008, Micro−Scale Membrane Extraction For Monitoring Trace Water Pollutants, “Ph.D Dissertation,” Department of Chemistry and Environmental Science, College of Science and Liberal Arts, New Jersey Institute of Technology, Newark, NJ, 101 pp.

Project Summary:

Problem and Research Objectives

In a 2004 Environmental Science and Technology Article (1), a USGS study revealed the presence of a large number of "emerging contaminants," such as antibiotics and households chemicals, in the drinking water of many homes in the New York metropolitan area, including New Jersey. According to Stackleberg (1), synergism between these chemicals could increase their impacts on human health. Recent reviews include cyanobacterial and algal toxins, endocrine disrupting chemicals, pesticides, pharmaceuticals, fluorinated surfactants, and perchlorate in the list of these contaminants (2, 3). In January 2006, the U.S. EPA implemented a voluntary program for the cutback and eventual elimination of perfluorooctanoic acid (a fluorinated surfactant) when studies showed that it is toxic, persistent and has a tendency to bioaccumulate. In light of health concerns and the absence of regulation of these compounds, studies are needed that allow us to determine the amounts actually reaching the environment and consequently how much additional treatment may be required.

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are used in fire fighting foam, fast food wrappers (for grease resistance) and as a coating on certain clothing and carpeting (for water and dirt resistance). The ubiquitous use and disposal of these substances has even lead to reports of the presence of PFOS and PFOA in wildlife blood (4). Clarithromycin, azithromycin and erythromycin are macrolides used to treat a wide range of bacterial illnesses including skin infections, sinusitis, pneumonia, bronchitis, syphilis, and chlamydia. Sulfamethoxazole is usually used in conjunction with trimethoprim for traveler's diarrhea, upper and lower respiratory tract infections and shigellosis. Ciprofloxacin is a fluoroquinolone shown to be effective against *Vibrio*, *Brucella*, *Campylobacter*, and *Bacillus anthracis* (5*)*. Carbamates are esters of carbamic acid that are widely used in gardens and homes to control pests such as flies, ticks and mosquitoes. They are acetylcholinesterase inhibitors, and allow acetylcholine to build up resulting in health effects such as, headaches, vomiting abdominal cramps, uncontrolled urination or defecation, and even a comatose state. Based on their toxicity, the US EPA currently monitors eleven carbamates including aldicarb, carbaryl, carbofuran, methiocarb and propoxur.

Measurement of these trace compounds is challenging because many are acidic, basic or polar. Recent reviews (2-4) have all listed solid phase extraction (SPE) as the only sample pretreatment technique, followed by separation and detection with liquid chromatography/mass spectrometry (LC/MS), liquid chromatography/electrospray ionization/mass spectrometry (LC/ESI/MS) or gas chromatography/mass spectrometry (GC/MS). While these techniques are capable of detecting trace amounts of contaminants, they are expensive and require multiple steps, long analysis time and large amounts of solvents. Also, most SPE is done off-line which makes continuous monitoring difficult. Petrovic et. al. (3) laments that the lack of more effective methods for trace determination of these new pollutants limits their measurement. Clearly, there is a need for the development of simple, inexpensive techniques that allow for quantification of these pollutants at low levels in environmental samples with the possibility of on-line analysis.

(ii) Methodology

A. Membrane Extraction

As mentioned previously, both pesticides as well as other pollutants will be examined. This report will focus on the carbamate pesticides: alidicarb, propoxur, methiocarb, aldicarb and carbofuran. A segment of hollow fiber membrane was cut into 10 cm lengths and soaked for a few minutes in 1-octanol, which served as the barrier film. 50 µL of the extractant was withdrawn into one 50 µL syringe, which was then attached to one end of the fiber. The other end of the fiber was affixed to another syringe

which was used to withdraw the extract. The membrane was then placed into the sample and the acceptor injected into the lumen of the membrane. The experimental setup is shown in Figure 1. The sample was then stirred for a given time period at the end of which, the extract was withdrawn into a syringe and placed into a vial insert for HPLC analysis. Toluene, dichloromethane, hexane, acetone, 1-nonane, decane, and 1-octanol were investigated as extractants. The sample was stirred for 30 minutes at a stirring level of 1 (80 rpm).

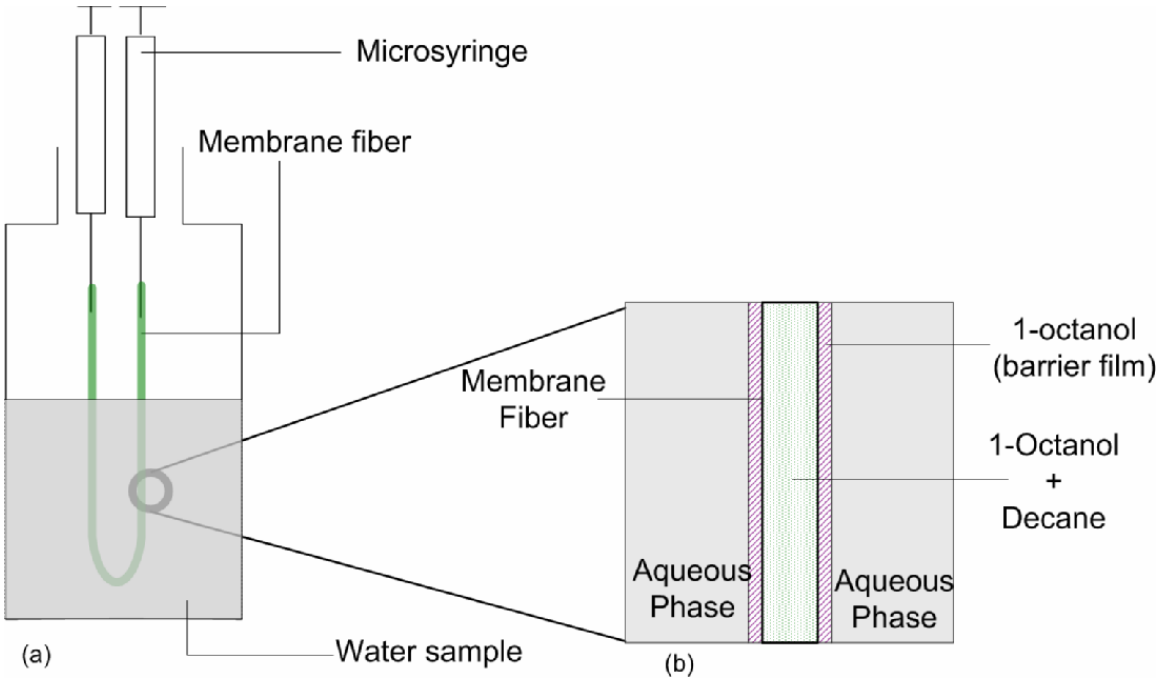

Figure 1. (a) Experimental set-up for microextraction of N-methyl carbamates; (**b)** Schematic diagram of the barrier film system. Membrane lumen contains a mixture of solvents whose loss is reduced by the presence of the 1-octanol film.

B. HPLC Analysis

The chromatographic separation was done using a Supelco C_{18} 150 x 4.6 mm column. The mobile phase was acetonitrile, water and methanol at flow rate of 1.5 ml/min in a gradient elution. The gradient program was as follows: 88% water, 12% methanol, 0% acetonitrile (t=0); 68% water, 16% methanol, 16% acetonitrile (t=5.4 minutes); 50% water, 25% methanol, 25% acetonitrile (t=16.1 minutes) and 88% water, 12% methanol, 0% acetonitrile (t=22 minutes). Detection was done at 214 nm with an injection volume of 5 µL. Separation of the five carbamates was achieved within 23 minutes.

(iii) Principal Findings and Significance

In micro-scale membrane extraction methods, membrane pores are filled with an organic liquid which only allows certain molecules to pass through. Once the analytes have passed through, they are trapped in the extractant (or acceptor phase) which must be carefully chosen to ensure that there is no reverse migration. Permeation across a membrane is usually driven by a concentration, pH or electrochemical gradient, and is dependent on the diffusivity of the analyte, and its distribution coefficient in the membrane. The two most common micro-scale membrane extraction approaches are supported liquid membrane extraction (SLME) and liquid-liquid membrane extraction (LLME). In SLME, pH dependent selective extraction is carried out in a 3-phase system, whereas in LLME the extraction is typically from an aqueous to an organic phase.

The efficiency of such a microscale membrane extraction is typically measured by the extent of the extraction efficiency (EE) and enrichment factor (EF). The EE is a measure of the fraction of the analyte that is extracted into the extractant and is determined as:

$$EE = m_a/m_d = \frac{C_a \times V_a}{C_d \times V_d} \quad \text{(1)}$$

Such that, m_a/m_d = mass ratio of analyte in acceptor and donor phases
C_a = concentration of analyte in acceptor after extraction
C_d = concentration of analyte in donor prior to extraction
V_a = volume of acceptor (organic extractant)
V_d = volume of donor (sample solution)

The EF is the ratio of the concentrations of the analyte in the extract and sample. This is given by the equation below:

$$EF = C_a/C_d \quad \text{(2)}$$

It was discovered that solvent loss, extraction time and nature of the extractant were all factors that influenced the extraction and enrichment of the pesticides.

(a) Solvent Loss

Solvent loss refers to the difference in the volume of extractant placed in the lumen and the volume retrieved at the conclusion of an extraction. This is measured by simply withdrawing the extractant into the syringe and noting the volume obtained at the end of an extraction. Here toluene, dichloromethane, hexane, acetone, n-nonane, 1-octanol, and decane were evaluated as candidate solvents. Retaining the extractant in the membrane was an important issue (6). The solvent could be lost through the membrane by diffusion and by solubilizing in water. Along with the solvent, some of the extracted analytes are also lost, reducing both EE and EF. So, in addition to partition coefficient and extractability, solvent loss is a key issue. Toluene, dichloromethane, hexane, acetone, and n-nonane were not retained in the membrane fiber for more than two minutes. This may be attributed to the fact that toluene, dichloromethane, hexane, and acetone were relatively soluble/miscible with water. Additionally, being small molecules, they have high diffusion coefficients through the membrane material. Toluene, in fact, was lost almost immediately, while the retention of decane and 1-octanol were better and were investigated further. For example, after thirty minutes, 40% of decane and 100% 1-octanol were still retained. While both decane and 1-octanol are insoluble in water, decane appears to have a higher diffusion coefficient as compared to 1-octanol, and was expected to be lost more readily. Figure 2 shows solvent loss as a function of time for these two solvents. In fact, 1-octanol loss in 24 hours was less than the decane loss in one hour. It was anticipated that dip-coating the membrane with a barrier film of 1-octanol would prevent the loss of decane. The role of the barrier film is clearly seen in Figure 2, where the loss of decane was significantly reduced in the presence of a barrier film. While all the decane was lost after four hours when no film is present, only 60% was lost in the presence of the film. Therefore, this was important for minimizing solvent loss, enabling longer extraction times, and allowing a more vigorous agitation for higher EF.

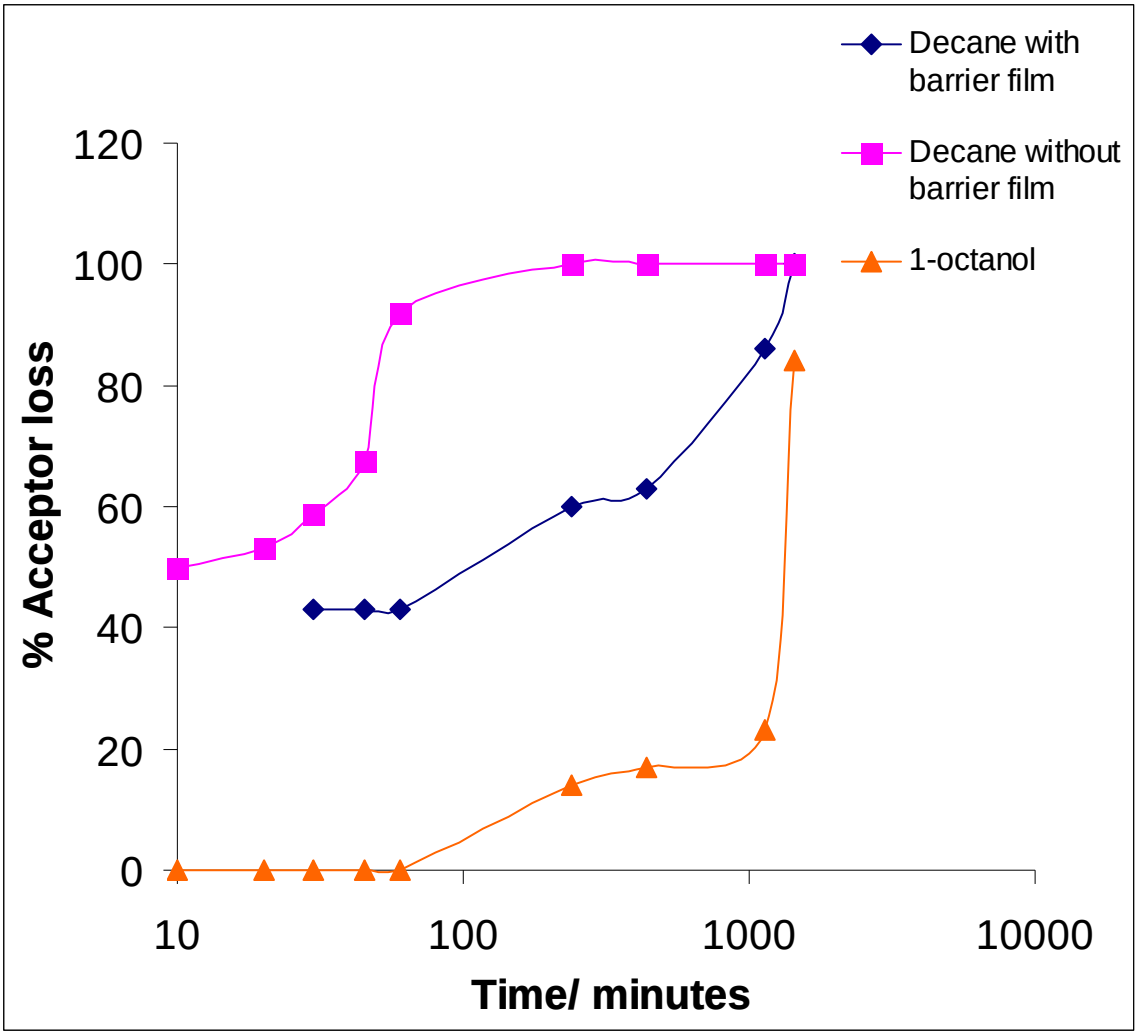

Figure 2. Effect of extraction time on acceptor loss.

(b) Solvent Selection

Since, 1-octanol and decane showed relatively lower solvent loss, they were investigated further as potential organic acceptors. It is important to note that along with solvent loss there is usually analyte loss and consequently low enrichment. Therefore, it was important that the solvents chosen have a high selectivity for the analytes as well as low volatility and low permeability through the membrane. For each experiment, the membrane fiber was dip-coated in the barrier fluid prior to the acceptor being injected into the fiber lumen. EF and EE were as high as 1600 and 45% respectively during a 30 minute extraction. Both EE and EF depended upon the solvent as shown in Figure 3.

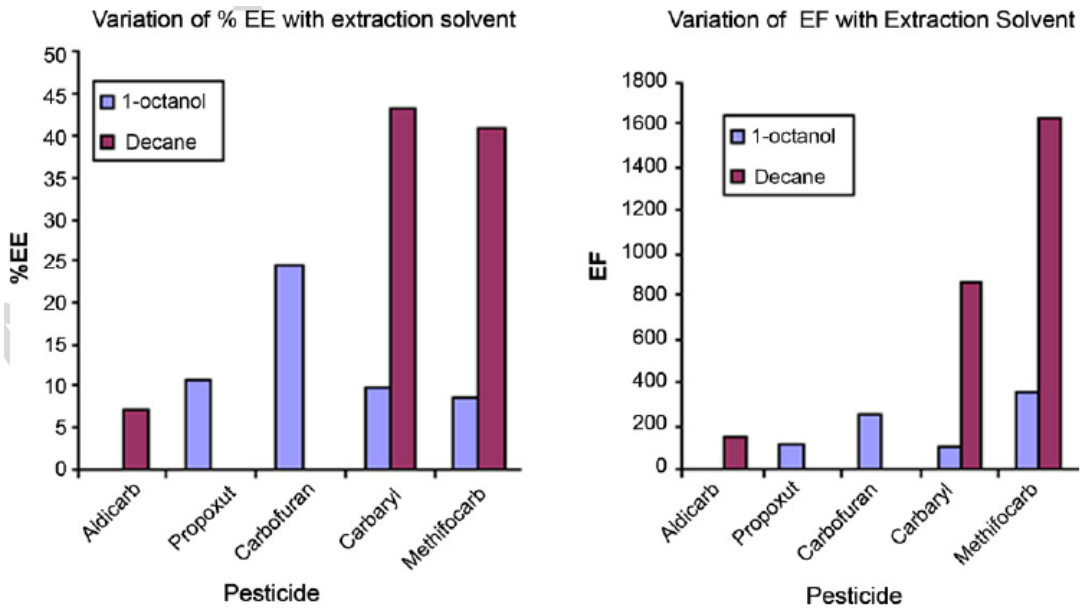

Figure 3. Extractant effect on EF and %EE.

(c) Extraction time

Previous reports (6,7) have shown that an increase in extraction time usually leads to higher EF, but also increases solvent loss which then lowers EF. The objective then is to strike a balance between these two factors. It should be noted that often equilibrium (or quantitative) extraction may take a very long time, and in the meantime most or all of the solvent would be lost from the membrane lumen, making longer extractions redundant. As shown in Figure 4, aldicarb and carbaryl achieved maximum enrichment in 30 minutes, while for propoxur it was reached in 10 minutes. Even though carbofuran and methiocarb showed an increase in enrichment after 30 minutes, equilibrium was not achieved. All the other methylcarbamates showed a decrease after 30 minutes, so this was chosen as the optimal extraction time. It should also be noted that after 30 minutes, more than 50% of decane was lost and so extraction past this point was futile.

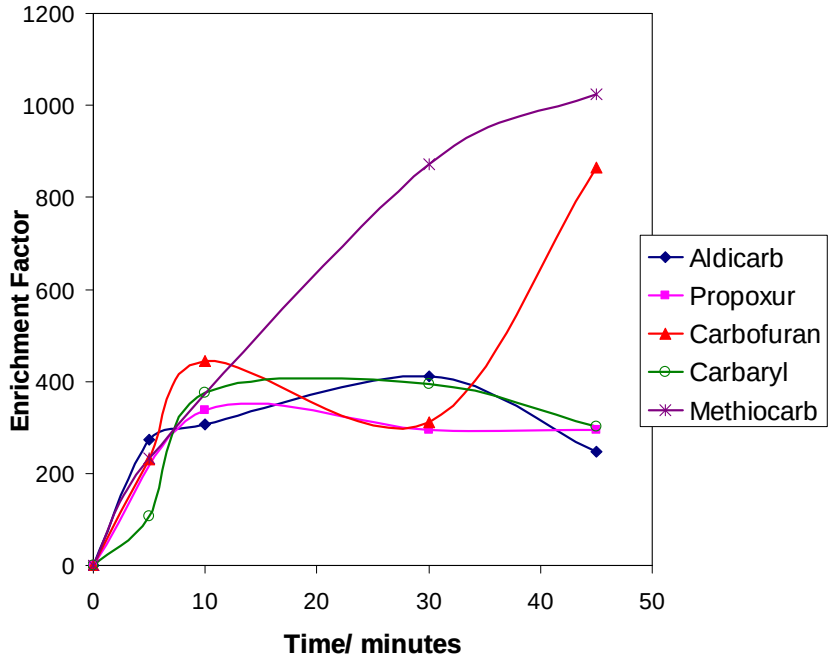

Figure 4. Effect of extraction time on enrichment factor. Sample spiked with 10ppb of pesticides and 40/60 1-octanol/decane (v/v) used as organic acceptor. Stirring speed is 80rpm.

(d) Barrier film with mixed solvent

In typical LLME, a single acceptor has been used as the extractant. For example, n-hexane has been used for the extraction of PAHs (8) and isooctane for PCBs (9). Since properties may vary widely within a group of compounds, some may exhibit high enrichment, and others may not. To enhance the EF, a salt may be added to the sample solution, but even this may not provide the necessary EF. Analyte interactions may vary even within a group; while some may exhibit high EF, others may not be enriched at all. An optimized mixture of solvents may provide high EF for all the analytes. In this case, neither 1-octanol nor decane was able to significantly enrich all the carbamates simultaneously. So, mixtures of 1-octanol/decane in varying ratios were investigated. In addition, based on the data from Figure 2, the membrane was dip-coated with 1-octanol to reduce the loss of decane. The 1-octanol barrier film was formed by immersing the fiber in the solvent for 10 minutes prior to extraction. A schematic of the barrier film system is shown in Figure 1b.

A study of the variation in EF with the percentage of 1-octanol used in the solvent mixture showed that the EF for different carbamates depended upon the composition of the acceptor, and there was a maximum point in the profile. For aldicarb, propoxur and carbofuran an 80:20 1-octanol/decane mixture showed the highest EF, while for carbaryl and methiocarb, 40% 1-octanol was the best. This implies that different solvent systems would be needed for maximizing EF of different carbamates. In this study a compromise consisting of 40% 1-octanol and 60% decane was considered to be most effective in achieving the optimum extraction of all the pesticides studied. The analytical performance of this system is highlighted in Table 1.

Analyte	**EF**	**Relative Standard Deviation, RSD (%)**	**Regression Coefficient (R^2)**	**Detection Limit (µg/L)**	
				Micro- LLME with HPLC-UV	**EPA Method 531.1**
Aldicarb	410	2.14	0.9501	5.5	1.0
Propoxur	294	1.90	0.9991	0.50	1.0
Carbofuran	312	7.31	0.9745	0.024	1.5
Carbaryl	395	9.53	0.9963	0.42	2.0
Methiocarb	873	5.44	0.9841	0.0010	4.0

Table 1. Analytical performance of the micro-LLME 1-octanol/decane system

Conclusions

A mixed solvent membrane extraction in conjunction with a barrier film was developed for the analysis of N-methyl carbamate pesticides in water that precluded the need for post column derivatization. All the pesticides could not be extracted with any one solvent, so the use of a mixed solvent was absolutely necessary for extending the range of compounds studied with high sensitivity. The presence of the barrier film reduced solvent loss, allowing higher stirring rates and extraction times that led to enhanced enrichment and lower limits of detection. This used small sample volumes, and was simple and environmentally friendly.

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Phosphate and Thermal Stabilization of Dredged Sediments for Reuse as Construction Material

Basic Information

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Focus Category:	Toxic Substances, Methods, Sediments
Descriptors:	
Principal Investigators:	Peter Ndiba, Lisa Axe

Publication

1. Ndiba, Peter; Lisa Axe; Thipnakarin Boonfueng, 2008, Heavy metal immobilization through phosphate and thermal treatment of dredged sediments, Environmental Science &Technology, 42 (3), 920–926.

The Problem and Management of Contaminated Sediments

Sediments are continuously deposited in rivers, lakes, and shorelines through the natural processes of erosion, transport, and deposition. Because of their capacity to adsorb contaminants, sediments act as an important sink (Thibodeaux, 1996; Vdovic et al., 2006); their contamination can adversely affect the health of organisms impacting the aquatic food chain (Lyman et al., 1987; Peplow and Edmonds, 2005). The U.S. EPA (2004) reported that the most severely contaminated sediments in the U.S. reside in estuaries, including the Passaic and Hudson Rivers. Navigable waters and harbors are regularly dredged to maintain and sometimes extend water depths. The amount of material excavated can be enormous: for example, 55.5 million cubic meters was proposed in a NY/NJ Harbor deepening project, an estimated 75% of which was considered contaminated (Yozzo et al., 2004). Such large quantities of contaminated sediments naturally raise the question of disposal. Historically, dredged material has been relocated to open waters, estuaries, rivers, or placed in wetlands near U.S. Federal channels. Enactment of more stringent regional ocean disposal criteria under the Marine Protection, Research and Sanctuaries Act (MPRSA, 2000) has, however, reduced the volume of dredged material acceptable for open sea disposal and for disposal at the Mud Dump Site off the New Jersey coast (Jones et al., 2001). With the costs of upland placements escalating (Jones et al., 2001), disposal of dredged sediments poses a major challenge for dredging projects. However, dredged material has recently been regarded as a resource for harbor construction (Joski et al., 2004; Yozzo et al., 2004).

Treatment and reuse of dredged sediments as an alternative to disposal is highly desirable as it reduces the cost of disposal and conserves natural resources. Existing treatment technologies have been, for the most part, adopted from technologies applied on contaminated soil and in the mining industry; however, comparatively, sediment treatment is more expensive because of the high water content (over 50%) and the large quantities involved (Neville and Burt, 1998). Consequently, few existing technologies are actually commercially used (Mulligan et al., 2001). With the need for further development, a novel method is proposed for sediments dredged from the Passaic and Hackensack Rivers: phosphate addition and thermal treatment at 700^{o}C, where organics are mineralized with the off-gas treated by carbon adsorption, and heavy metals are stabilized into sparingly soluble hydroxylapatites (Kribi et al., 2004). If the treatment is found to be successful, the stabilized sediments can potentially be used as construction material.

Natural and synthetic hydroxylapatite is widely used to stabilize heavy metals in wastes, contaminated soils, and sediments (Ma et al., 1995; Yang and Mosby, 2006). Reuse of dredged sediments would be subject to the Resource Conservation and Recovery Act (RCRA), which regulates the leaching of 39 compounds, including eight metals (40 CFR, Part 261.24). As such, analyses including the toxicity characteristic leaching procedure (TCLP) (U.S. EPA, 1992) for both raw and treated sediments are warranted. More specific to the issue of leaching is the understanding of metal speciation. X-ray absorption spectroscopy (XAS) provides a method for determining the local structure around a central atom, including neighboring atoms, coordination number, bond length, and the mean square variation in distances. For heterogeneous materials such as sediments, XAS, in combination with principle component analysis (PCA), target

transformation (TT), and linear combination fit (LCF), is a meaningful approach to quantitatively determine the speciation of trace elements (Isaure et al., 2002).

Objectives

Development of effective methods for stabilization and beneficial reuse of dredged sediments, as opposed to disposal, would provide a sustainable solution for their management. Objectives of this research are to:

1. Characterize dredged sediments from the Passaic and Hackensack Rivers using a suite of analytical procedures including acid digestion for total metal concentrations, TCLP for leaching characteristics, XAS for speciation, x-ray diffraction (XRD) for mineralogy, and sequential extraction for assessing contributions of sediment phases to metal distribution.
2. Assess the feasibility of stabilizing heavy metals in dredged sediments by phosphate addition and thermal treatment for beneficial reuse in the construction industry using the standard U.S. EPA TCLP procedure.
3. Validate the treatment technology as assessed by the TCLP procedure, using thermodynamic analysis based on speciation determined by XAS, XRD, and sequential extraction data.

Methodology

Materials and Characterization. Dredged sediments were obtained from the Passaic River estuary and Dampremy, Belgium. Treatment was carried out by addition of phosphoric acid at 2.5% of sediments by dry weight followed by calcination at 700^{o}C for 3 hours (Kribi, 2004). Sediment mineralogy was characterized by XRD using a Philip's X'Pert x-ray diffractometer. Total metal concentrations were obtained by HNO_3 and HCl acid (aqua regia) digestion, while organic matter was estimated by loss on ignition at 445 ± 10°C for six hours (AASTHO, 1986).

XAS Data Collection and Analyses. X-ray absorption spectroscopy was conducted at the Zn K-edge at beamline X11A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Ground sediments were measured in fluorescence mode using a Lytle detector, while 13 reference compounds were measured in transmission mode with nitrogen gas in the ion chamber before the sample (I_0) and in the transmission chamber (I_t). The XAS spectra were analyzed using WinXAS (version 3.1) and fit with theoretical models generated using FEFF7. To identify the spectra members, PCA was used to decompose the spectra into components which were then identified by TT and quantified by LCF.

Leaching Tests. The U.S. EPA TCLP leaching procedure was conducted to determine the efficacy of the treatment as well as obtain regulatory information on the treated product. The procedure was performed on sediments: dredged, 2.5% phosphate addition, calcination at 700^{o}C, and phosphate addition followed by calcination. Extractions were carried out with 20:1 liquid to solid ratio in an acetate solution at pH 2.88 ± 0.05 based on the sediment pH, in 2L HDPE bottles tumbled at 30 rpm for 18

hours. The pH was measured and the extract filtered, acidified, and refrigerated at 4°C until analysis with flame atomic absorption spectrometer (FAA).

Principal Findings

The Zn K-edge spectra for treated sediments differed significantly from that of the dredged (untreated) sediments (Figure 1), indicating significant structural changes during treatment

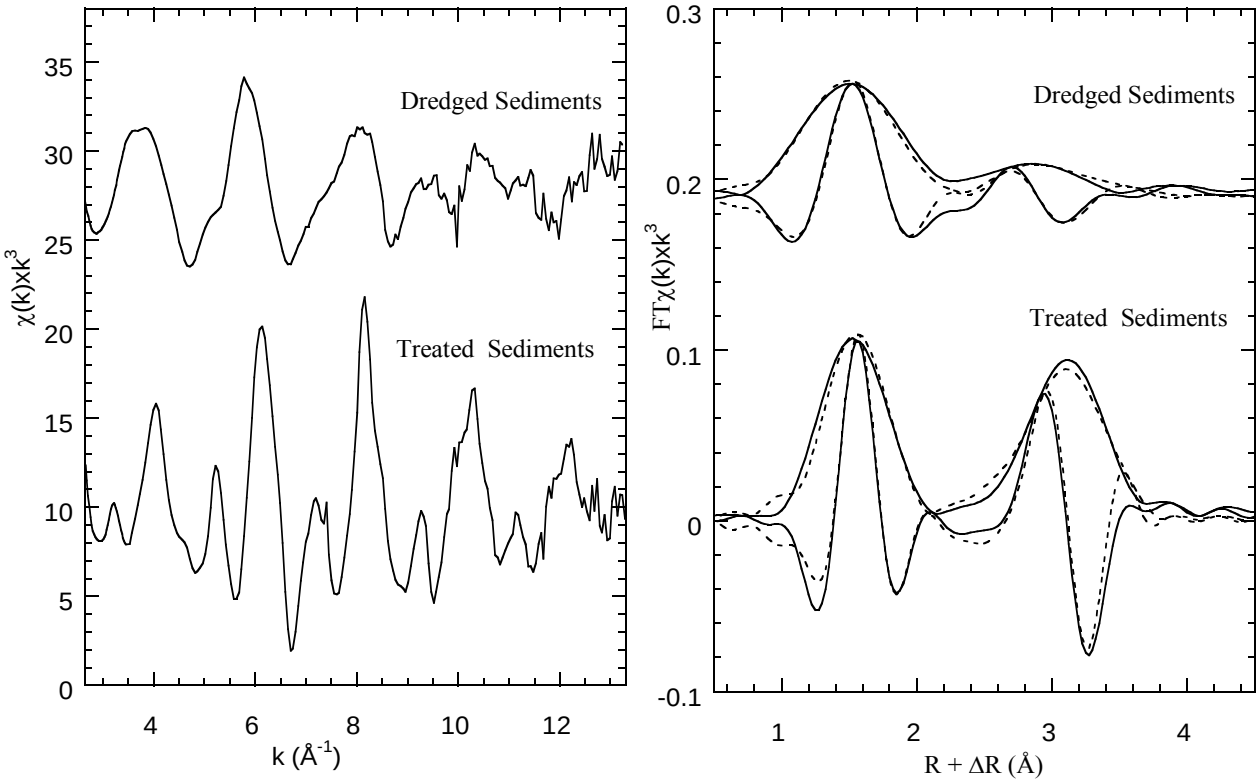

Figure 1. Dredged and treated sediments: (a) Background subtracted, normalized, and averaged $\chi(k)\cdot k^3$ spectra and (b) Fourier transformation $\chi(k)\cdot k^3$ (solid lines) over 3.0–12.5 $Å^{-1}$ and fitted (dashed lines) with models.

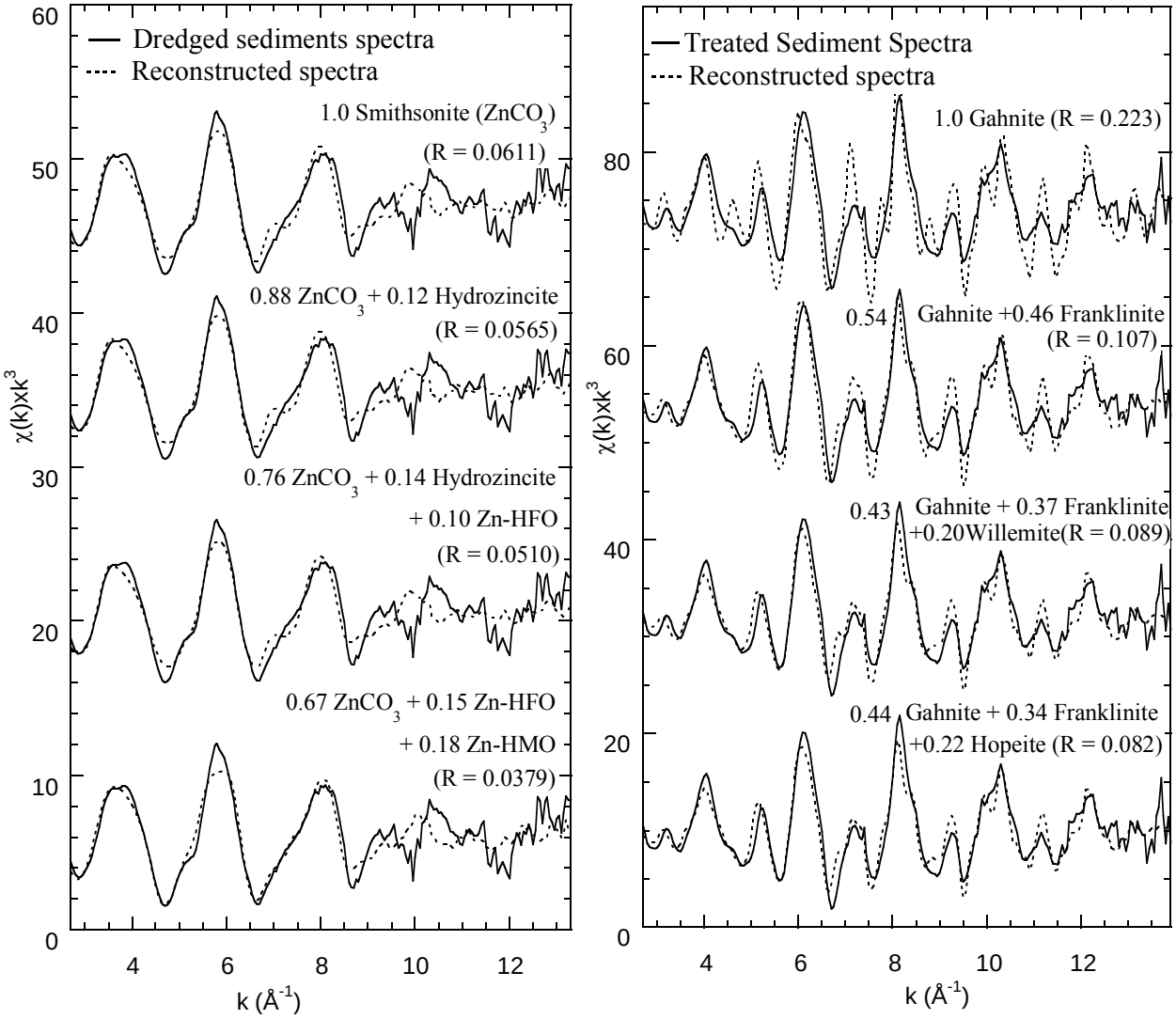

Figure 2. Experimental and LCF reconstructed $\chi(k)\cdot k^3$ spectra for dredged and treated sediments. Only spectra with more than 10% contributions are included. The fitting factor $R = \sum[(k^3\chi_{exp}-k^3\chi_{model})/k^3\chi_{exp}]^2$ where χ_{model} refers to spectra reconstruction with PCA decomposed components.

of the sediments. Using PCA, TT, and LCF (Figure 2), we found Zn in dredged sediments was precipitated as $ZnCO_3$ (64%) and adsorbed to hydrous manganese oxide (20%) and hydrous iron oxide (16%). In the treated sediments, phosphate addition resulted in hopeite ($Zn_3(PO_4)_2{\cdot}4H_2O$) (22%), while calcinations induced formation of spinels, gahnite ($ZnAl_2O_4$) (44%) and franklinite ($ZnFe_2O_4$) (34%). Thermodynamic analysis showed that these resulting minerals were sparingly soluble indicating Zn was immobilized. Leaching assessments with the U.S. EPA toxicity characteristic leaching procedure (TCLP) (Figure 3) confirmed Zn and other heavy metals were immobilized following treatment with an up to 89% reduction in leaching.

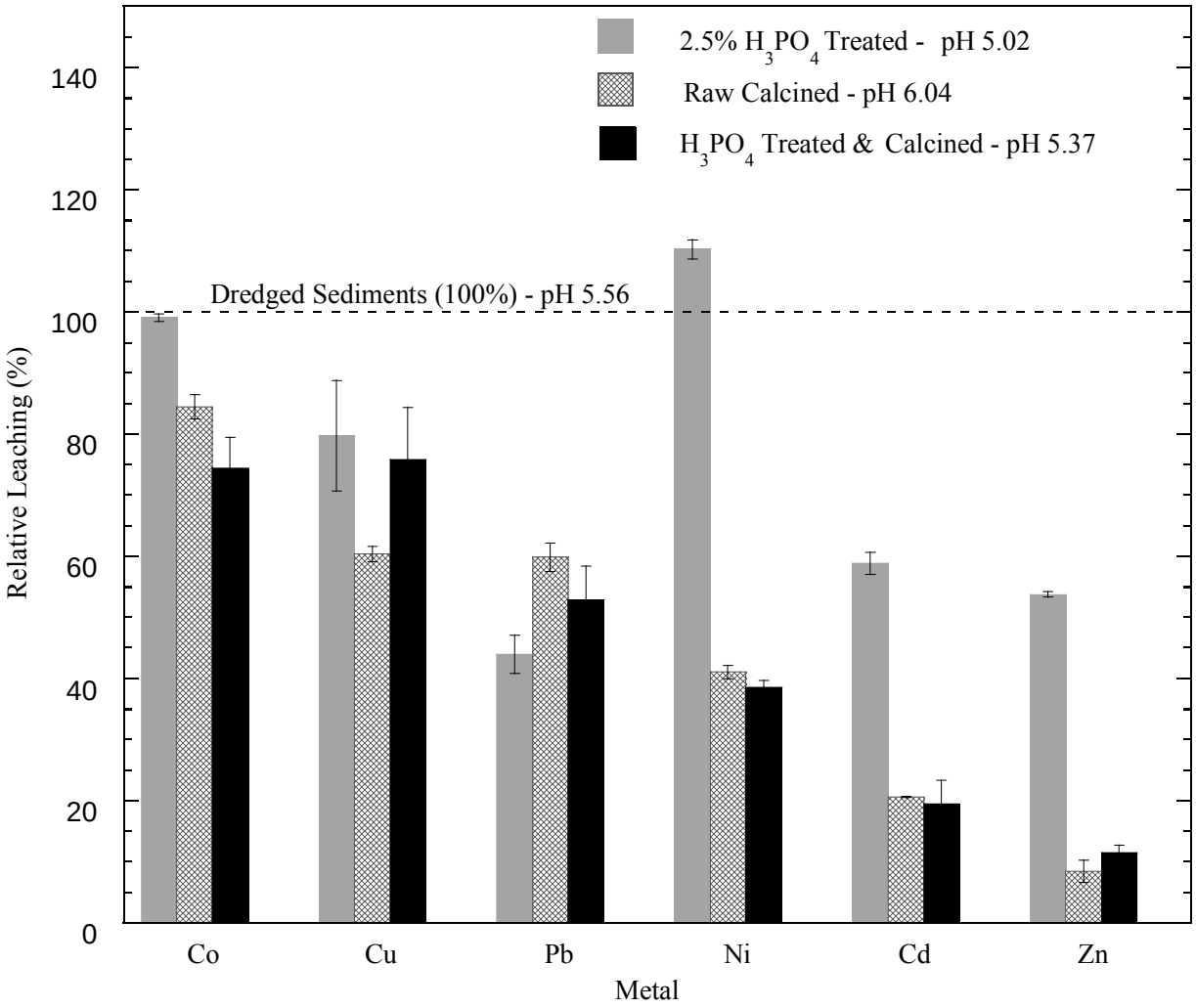

Figure 3. TCLP metal leaching for sediment treatments relative to amount leached from dredged sediments. Percent of leaching from calcined sediments are adjusted for loss of organic matter. Error bars indicate 2 × standard error. Lower pH after phosphoric acid treatment increased Ni leaching as compared to dredged sediments.

Significance of Findings

The aim of phosphate addition followed by calcination treatment is to stabilize dredged sediments for beneficial reuse in construction. Examination of Zn speciation showed that treatment results in structural changes to more thermodynamically stable crystalline phases: heat induced spinels, gahnite and franklinite, and the phosphate mineral, hopeite. The treatment resulted in substantial reduction in leaching of metals by TCLP when adjusted for loss of 16.8% by dry weight of organic matter (potentially mineralized or captured through carbon adsorption). Although TCLP results showed that the sediments were not hazardous for the metals studied, several states in the U.S. require further testing with the synthetic precipitation leaching procedure (SPLP) for beneficial reuse (Townsend et al., 2003). Alternative phosphate sources for treatment are being evaluated

for compliance based on state regulations for reuse of waste materials; methods include the SPLP, field emission scanning microscopy (FESEM), and energy dispersive x-ray analysis (EDX).

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Restored oyster reef habitat use by the American Eel (Anquilla rostrata) in the Lower Delaware Bay

Basic Information

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Descriptors:	
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3. Taylor, J and D. Bushek. Nekton utilization of constructed intertidal oyster reefs and aquaculture structures in Delaware Bay, USA. 28th Milford Aquaculture Seminar. February 25−27, 2008. Meriden, Connecticut USA. (Oral presentation)
4. Taylor, J and D. Bushek. Nekton utilization of constructed intertidal oyster reefs and aquaculture structures in Delaware Bay, USA. ERF 2007. November 4−8, 2007. Providence, Rhode Island USA. (Oral presentation)
5. Taylor, Jaclyn. 2008. Evaluation of the Ecological Value of Constructed Intertidal Oyster Reefs and Aquaculture Structures in Delaware Bay: Habitat Utilization by Motile Macrofauna. M.S. Thesis, Department of Ecology and Evolution, Rutgers University, New Brunswick, NJ. 77pp.

Project Summary:

Problem and Research Objectives:

A preliminary small-scale oyster restoration project was funded in summer 2006 through a Rutgers University Research Council grant, and demonstrated the potential for creating oyster habitat in the intertidal zone of the lower Delaware Bay. Preliminary minnow trap sampling data showed an increase in macrofauna abundance associated with the shell bag reefs compared to adjacent control sand areas. Of the 27 total fish caught on the shell bag reefs, the American eel (*Anguilla rostrata*) accounts for 25% of this total, while no eels were caught on the adjacent sand areas. Interestingly, the total length of *A. rostrata* increased from 35cm to 55 cm during the June through October sampling season. The preliminary catch and length data from the Cape Shore reefs reported above corresponds with the predicted migration time of *A. rostrata*. These findings imply that oyster reef habitat use by American eels in the lower Delaware Bay is important for successful migrations.

The present study was designed to test the hypothesis that yellow phase American eels, *Anguilla rostrata*, utilize oyster reefs and oyster aquaculture racks in the intertidal zone of lower Delaware Bay during their migration season. The objectives were as follows: 1) Provide novel documentation on the ecological importance of restored oyster beds as habitat for yellow phase *Anguilla rostrata* in the lower Delaware Bay, 2) Determine abundance and length-weight relationship of *A. rostrata* associated with shell restoration and aquaculture sites, 3) Determine the relationship between period of maximum abundance of *A. rostrata* and their migration season, and 4) Determine if *A. rostrata* are resident or transient species associated with restoration sites and aquaculture racks through mark-recapture efforts.

Methodology:

The study was conducted on the intertidal sand flats at the Rutgers University Cape Shore Hatchery Facility near Green Creek, NJ in the lower Delaware Bay. On 9 May 2007, six shell-bag reefs were constructed on the sand flats at Cape Shore. Mesh bags (14.3 mm opening) were filled with 19L of oyster shell and arranged to form 1.5 m x 3 m x 0.3 m reefs. The corners of six sand plots (1.5 m x 3 m) were marked with rebar poles and six oyster aquaculture rack and bag structures were marked with wooden stakes.

Motile macrofauna were sampled every other week with 18 galvanized steel 6.35-mm mesh minnow traps (length = 45 cm, diameter = 23 cm, 25.4 mm funnel entrances at each end), 18 galvanized steel 6.35-mm mesh eel traps (length = 79 cm, diameter = 23 cm, 25.4 mm funnel entrances at each end) and 6 double funnel 4-cm mesh crab traps (length = 62 cm, width = 25 cm, height = 30 cm). Using a randomized block design, unbaited traps were secured to the base of shell-bag reefs, aquaculture racks and control sand plots during low tide. At the following low tide, all individuals captured were bagged and taken back to the laboratory for analysis. Species were identified,

enumerated and measured for total length (TL) and biomass (g). Thirty-nine collections were conducted from 20 May to 16 October 2007.

An American eel, *Anguilla rostrata,* mark-recapture study was conducted during bi-weekly trap sampling from 20 May to 16 October 2007. Subcutaneous acrylic paint injections were used to mark eels. All *A. rostrata* captured were measured for TL (cm) and weighed for biomass (g), then anaesthetized by placing them on ice for a short period of time prior to injection. Non-toxic Liquitex® soft body professional acrylic artist paints were injected ventrally behind the anus using a 1cc syringe with a 30 gauge needle. Paint marks were unique for each individual captured. Six paint colors were used in varying combinations and injected on the right side (Reef), left side (Aquaculture) and both sides (Sand) of the body in order to identify habitat residency when recaptured. To assess mark retention, three eels were marked in the lab and held in an aquarium for seven days.

Principal Findings and Significance:

A total of 30 species were collected during the trap sampling period with species richness lowest on the sand (n=17) and highest on the aquaculture racks (n=25) (Table 1). Of the 30 species collected, seven were unique to the aquaculture habitat, while one species was unique to sand and shell-bag reef habitats, the Asian shore crab, *Hemigrapsus sanguineus,* and the Black sea bass, *Centropristis striata,* respectively. The most abundant trap species for all three habitats was *Palaemonetes pugio*. Thirteen of the trap species were only collected as juveniles: *Limulus polyphemus, Bairdiella chrysoura, Menidia menidia, Lagondon rhomboides, Etropus microstomus, Morone saxatilis, Micropogonias undulates, C. striata, Paralichthys dentatus, Alosa pseudoharengus, Lutjanus griseus, Leiostomus xanthurus, Cynoscion regalis*. The eight most abundant species were associated with all three habitat types in varying abundances and of these eight species only two species, *Crangon septemspinosa* and *Callinectes sapidus*, were more abundant on the sand habitat (Table 1).

Species abundance box plots indicate average species abundance was highest on the aquaculture racks (44.98) and was more than five times greater than sand average species abundance (8.697) (Fig. 1A). Also, average shell-bag reef species abundance of 31.09 is over three times greater than the sand habitat. Even though the greatest average species abundance was associated with the Aquaculture racks, median abundance values for shell-bag reef and aquaculture rack habitats were comparable (Fig. 1A). Box plots of traps species biomass reveal that the highest average biomass was also associated with the Aquaculture racks and average biomass for both shell-bag reef and aquaculture racks was three times greater than biomass on the Sand flats (Fig. 1B). Average species richness was comparable for all three habitat types, ranging from 2.18 species on the sand and 3.29 species on the aquaculture racks (Fig. 1C).

Three-factor ANOVA and Tukey's post-hoc comparison results revealed sand species abundance is significantly less than reef ($p = 0.008$) and aquaculture ($p < 0.0001$)

treatments, while there was no difference detected between reef and aquaculture (Table 2 and Fig. 1A). Time significantly affected abundance with higher species abundances occurring during nighttime sampling. In addition, trap type significantly affected species abundances. There was no difference in abundances for minnow and eel traps, but crab traps collected significantly less individuals than both minnow and eel traps ($p < 0.0001$). There was a significant Treatment * Trap interaction, largely in part that minnow and eel traps collected five times fewer animals on the sand flats than on the reef and aquaculture treatments.

Species biomass for sand treatments was significantly less than reef ($p = 0.001$) and aquaculture ($p < 0.0001$) treatments and there was no difference between reef and aquaculture biomass (Table 2 and Fig. 1B). There was no effect of time or trap time on species biomass. The only significant interaction effect on biomass was the trap * time interaction. Crab trap biomass was greater during daytime collections while minnow and eel traps had higher biomass yields during night sampling, which contributed to the significant interaction.

Three-factor ANOVA results for trap species richness indicated sand species richness was significantly less than species richness on aquaculture racks ($p = 0.036$) (Table 2 and Fig. 1C). There was no difference in species richness between sand and shell-bag reef habitats as well as reef and aquaculture racks. Day and night sampling showed no differences in species richness. The type of trap used for sampling significantly influences the number of species that were collected. While there was no difference between eel and minnow traps, the number of species collected using crab traps was significantly less than those in minnow and eel traps ($p < 0.0001$). On the sand flats, the number of species collected in minnow and eel traps was lower than shell-bag reef and aquaculture racks which contributed to the significant interaction effect of treatment * time (Table 2).

A total of 52 American eels, *A. rostrata*, were marked during the May to October 2007 trap sampling period. During this sampling period, *A. rostrata* was the most abundant finfish species collected (Table 1). Two-factor MANOVA results confirmed that there were significantly more *A. rostrata* associated with the aquaculture racks (42 eels) than both reef (15 eels) and sand (2 eels) habitats (Fig.2A). Despite only two eels being captured on the sand flats, there was no difference in *A. rostrata* abundance between reef and sand habitats. A similar pattern was evident for *A. rostrata* biomass. Aquaculture eel biomass was significantly greater than reef and sand, and there was no difference in biomass between reef and sand habitats (Fig.2B). *A. rostrata* average biomass was highest on reefs (72 g), followed by aquaculture racks (59 g), and lowest on the sand (55 g).

Seven *A. rostrata* were recaptured during the mark-recapture study period resulting in a 13.5% recapture rate. There were not any eels recaptured on the sand flats. Recaptured eels exhibited no preference between reef and aquaculture habitats, four eels were recaptured around the aquaculture racks and 3 eels were recaptured on the shell-bag

reefs (Fig.2A). One eel originally marked on an aquaculture rack was recaptured twice on Reef 6.

Seasonal abundance of *A. rostrata* increased from May to July on reef and aquaculture racks, and aquaculture *A. rostrata* abundance reached a peak in August with 17 eels captured (Fig. 3A). Following the peak in August, *A. rostrata* abundance leveled off through October for all three habitats.

Average seasonal biomass of *A. rostrata* for reefs was equal to or greater than aquaculture racks every month during the sampling period except for May (Fig. 3B). In May, two eels weighing 3 g and 140 g were captured, which is causing the unusually large SE. From July to October, average reef biomass was greater than racks. Eel abundance peaked in August on the aquaculture racks, and average eel biomass also peaked in August but on the shell-bag reefs (Fig. 3B). In August, there was a greater abundance of smaller eels associated with the aquaculture racks.

Intertidal constructed shell-bag reefs and oyster aquaculture operations support an increased species abundance and biomass of motile macrofauna than the adjacent sand flats. Abundances of species utilizing these two habitat types were more than triple that of the sand habitat. The habitat created by shell-bag reefs and oyster aquaculture structures also maintains high species richness and fauna communities similar to natural oyster reef habitats (Maurer & Watling 1971, Lenihan et al. 2001, Rodney & Paynter 2006).

During the mark-recapture study, American eels, *A. rostrata,* were most commonly associated with aquaculture racks. Also, *A. rostrata* biomass was significantly greater on aquaculture racks. However, this may be an artifact of the high abundances captured since average monthly biomass was consistently higher on shell-bag reefs. *A. rostrata* has been previously associated with subtidal and intertidal oyster reefs (Coen et al. 1999, Harding & Mann 1999). Despite the lack of statistical significance, eels were seven times more abundant on shell-bag reefs than sand flats.

Eels were recaptured on both oyster habitats but not on the sand flats. While the recapture rate is high (13%), the total number of eels marked was low for this mark-recapture study. Recaptured eels demonstrated no preference between shell-bag reef and aquaculture habitats and appeared to be traveling between the two. Previous mark-recapture studies have shown that when estuarine environmental conditions are favorable, yellow phase American eels exhibit a limited home range (Bozeman et al. 1985, Ford & Mercer 1986, Morrison & Secor 2003). Yellow phase eels prefer dark areas where they can be in constant contact with their surroundings which is why they often hide in hollow crevices or burrow in the mud (Tesch 1977). Off-bottom aquaculture operations provide dark areas and access to sediment under the racks while constructed shell-bag reefs provide a multitude of crevices for hiding. Anecdotally, during shell-bag sampling, eels were found hiding under shell-bags at low tide. A more comprehensive mark-recapture study is necessary to determine home range and residency. Nonetheless, the American eel is a species utilizing intertidal shell-bag reefs and oyster aquaculture racks as habitat.

Table 1. Species captured with minnow, eel and crab traps on the three habitat types: sand, shell-bag reefs and aquaculture racks. Values denote total number of individuals collected. Fish species and common names referenced from (Nelson et al. 2004). Invertebrate species and common names referenced from (Turgeon et al. 1998, McLaughlin et al. 2005). Superscripts indicate if species are a = adult and juvenile or b = juvenile.

Common Name	**Species Name**	**Sand**	**Reef**	**Aquaculture**	**Total**
Daggerblade grass shrimp	*Palaemonetes pugio*	541	1890	3534	5965
Eastern mud snail	*Nassarius obsoletus*	117	869	840	1826
Longwrist hermit crab	*Pagurus longicarpus*	235	867	658	1760
Blue crab	*Callinectes sapidus*	60[a]	53[a]	58[a]	171
Seven spine bay shrimp	*Crangon septemspinosa*	70[a]	30	33[a]	133
American eel	*Anguilla rostrata*	2	15	42	59
Atlantic horseshoe crab	*Limulus polyphemus*	13[b]	16[b]	1[b]	30
Silver perch	*Bairdiella chrysoura*	1[b]	2[b]	17[b]	20
Estuarine mud crab	*Rhithropanopeus harrisii*	3	12	4	19
Atlantic silverside	*Menidia menidia*	3[b]	6[b]	7[b]	16
Striped cusk-eel	*Ophidion marginatum*	5	3	2	10
Flatback mud crab	*Eurypanopeus depressus*	3	10	1	14
Naked goby	*Gobiosoma bosc*	0	6	5	11
Atlantic mud crab	*Panopeus herbstii*	2	2	2	6
Pinfish	*Lagondon rhomboides*	0	2[b]	2[b]	4
Smallmouth flounder	*Etropus microstomus*	3[b]	1[b]	0	4
Oyster toadfish	*Opsanus tau*	0	2	1[b]	3
Green crab	*Carcinus maenas*	0	1	1	2
Striped bass	*Morone saxatilis*	1[b]	1[b]	0	2
Asian shore crab	*Hemigrapsus sanguineus*	1	0	0	1
Atlantic croaker	*Micropogonias undulatus*	1[b]	3[b]	0	4
Black sea bass	*Centropristis striata*	0	1[b]	0	1
Summer flounder	*Paralichthys dentatus*	0	1	1[b]	2
Alewife	*Alosa pseudoharengus*	0	0	2[b]	2
Bay anchovy	*Anchoa mitchilli*	0	0	2[a]	2
Gray snapper	*Lutjanus griseus*	0	0	1[b]	1
Spot	*Leiostomus xanthurus*	0	0	1[b]	1
Striped killifish	*Fundulus majalis*	0	0	1	1
Weakfish	*Cynoscion regalis*	0	0	1[b]	1
White perch	*Morone americana*	0	0	1	1
Total		**1061**	**3793**	**5218**	**10072**
Species Richness		**17**	**22**	**25**	**30**

Table 2. Summary of three-factor ANOVA testing differences in trap species abundance, biomass and species richness among habitat types. Multiple comparisons of the means were analyzed using Tukey's post-hoc comparisons ($\alpha = 0.05$). Treatments are S, sand; R, reef and A, aquaculture. Time is D, day or N, night. Traps are E, eel; M, minnow and C, crab.

	Source	df	MS	F	P	Multiple Comparisons
Abundance	Treatment	2	5181.97	28.97	**<0.0001**	S < R = A
	Time	1	1662.47	9.29	**0.003**	D < N
	Trap	2	9110.77	50.94	**<0.0001**	C < E = M
	Treatment*Time	2	312.59	1.75	0.18	
	Treatment*Trap	4	1298.21	7.26	**<0.0001**	
	Time*Trap	2	441.44	2.47	0.0905	
	Treatment*Time*Trap	4	108.76	0.61	0.6579	
	Error	90	178.87			
Biomass	Treatment	2	10852.74	12.48	**<0.0001**	S < R = A
	Time	1	416.58	0.48	0.4906	D = N
	Trap	2	310.70	0.36	0.7005	E = C = M
	Treatment*Time	2	460.88	0.53	0.5903	
	Treatment*Trap	4	1905.35	2.19	0.0762	
	Time*Trap	2	4073.98	4.69	**0.0116**	
	Treatment*Time*Trap	4	301.67	0.35	0.8455	
	Error	90	869.27			
Richness	Treatment	2	5.66	21.79	**<0.0001**	S = R, S < A, R = A
	Time	1	0.60	2.32	0.1316	D = N
	Trap	2	69.88	269.01	**<0.0001**	C < E = M
	Treatment*Time	2	0.07	0.29	0.7515	
	Treatment*Trap	4	1.45	5.59	**0.0005**	
	Time*Trap	2	0.51	1.97	0.1453	
	Treatment*Time*Trap	4	0.21	0.80	0.5303	
	Error	90	0.26			

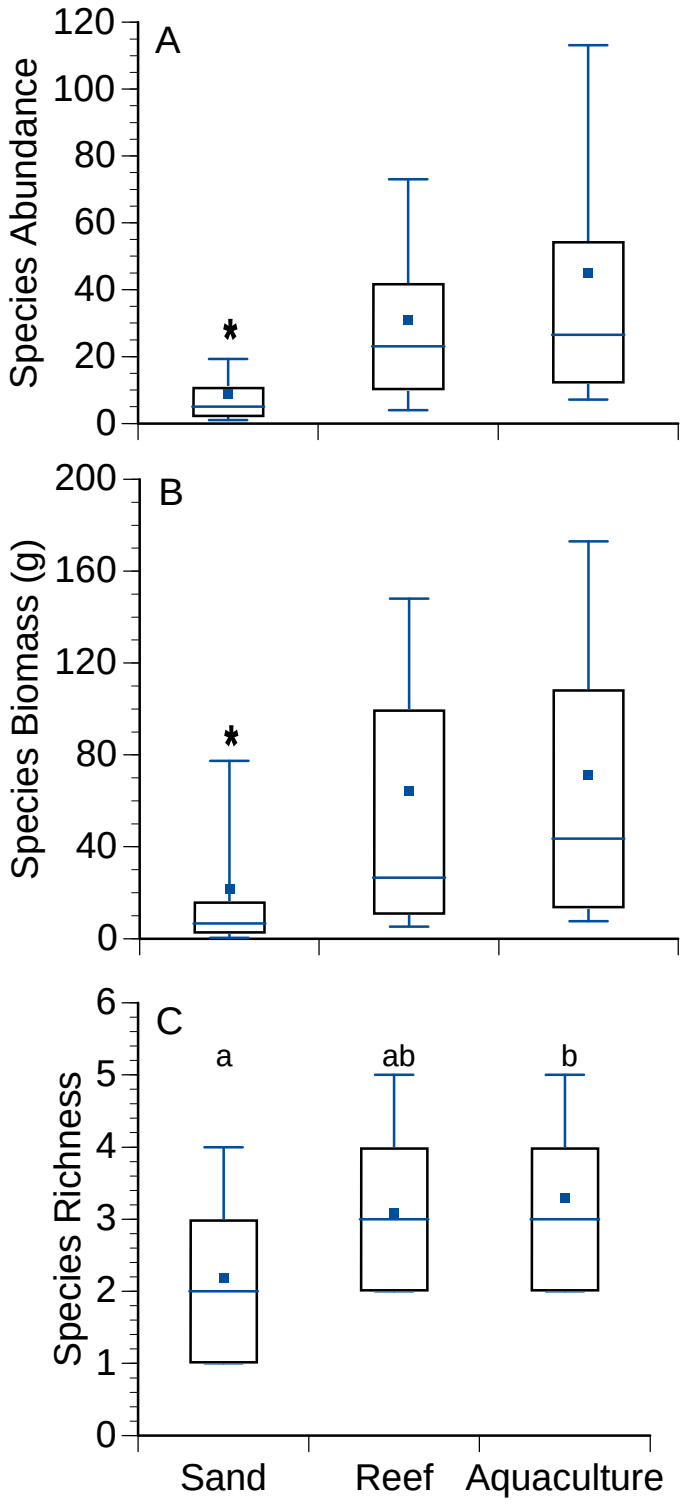

Fig. 1 Trap Species Box Plots. Trap species Box plots for A) species abundance, B) species biomass (g) and C) species richness collected via trap sampling from May to October 2007. Squares indicate mean values. * and letters indicate $p < 0.05$ for Tukey's post-hoc comparisons.

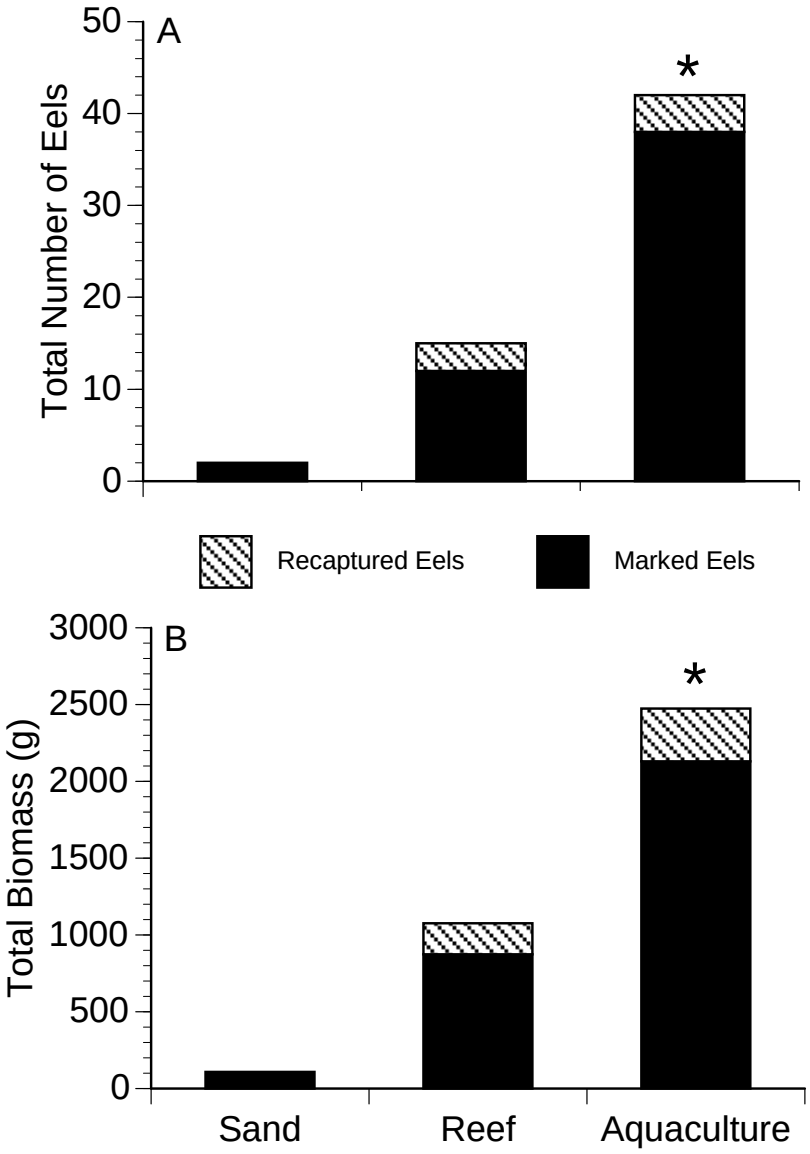

Fig. 2 *A. rostrata* Abundance and Biomass. A) Total number of *A. rostrata* marked and recaptured during trap sampling from May to October 2007. B) Total biomass (g) of marked and recaptured *A. rostrata*. * indicates $p < 0.05$ for Tukey's post-hoc comparisons.

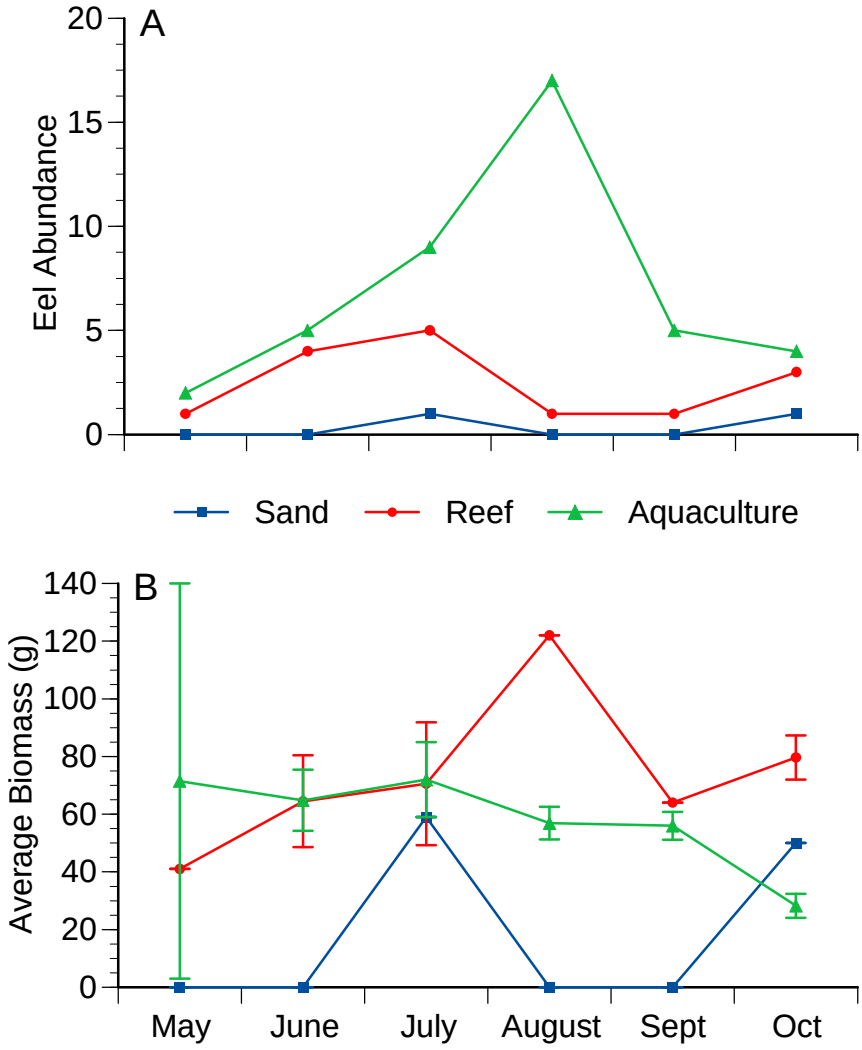

Fig.3 *A. rostrata* Seasonal Trends. A) Monthly total abundance of *A. rostrata* for sand, shell-bag reef and aquaculture habitats from May to October 2007. Totals include marked and recapture eels. B) Average monthly biomass (g) ± SE of *A. rostrata* for sand, shell-bag reef and aquaculture habitats.

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Using assimilated C−DNA to fingerprint active microorganisms in methylmercury demethylation by stable−isotope probing

Basic Information

Title:	Using assimilated C−DNA to fingerprint active microorganisms in methylmercury demethylation by stable−isotope probing
Project Number:	2007NJ144B
Start Date:	3/1/2007
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	6th
Research Category:	Biological Sciences
Focus Category:	Hydrogeochemistry, Toxic Substances, Methods
Descriptors:	
Principal Investigators:	Riqing Yu, Tamar barkay

Publication

1. Yu, Ri−Qing, Tamar Barkay, Jeffra K. Schaefer, Christopher DiPasquale, Isaac Adatto, Mark E. Hines. 2007. Molecular characterization of microbial communities in a methylmercury−contaminated Adirondack Lake wetland. 107th American Society for Microbiology General Meeting, Toronto, Canada. May 21−25, 2007 (Poster session)

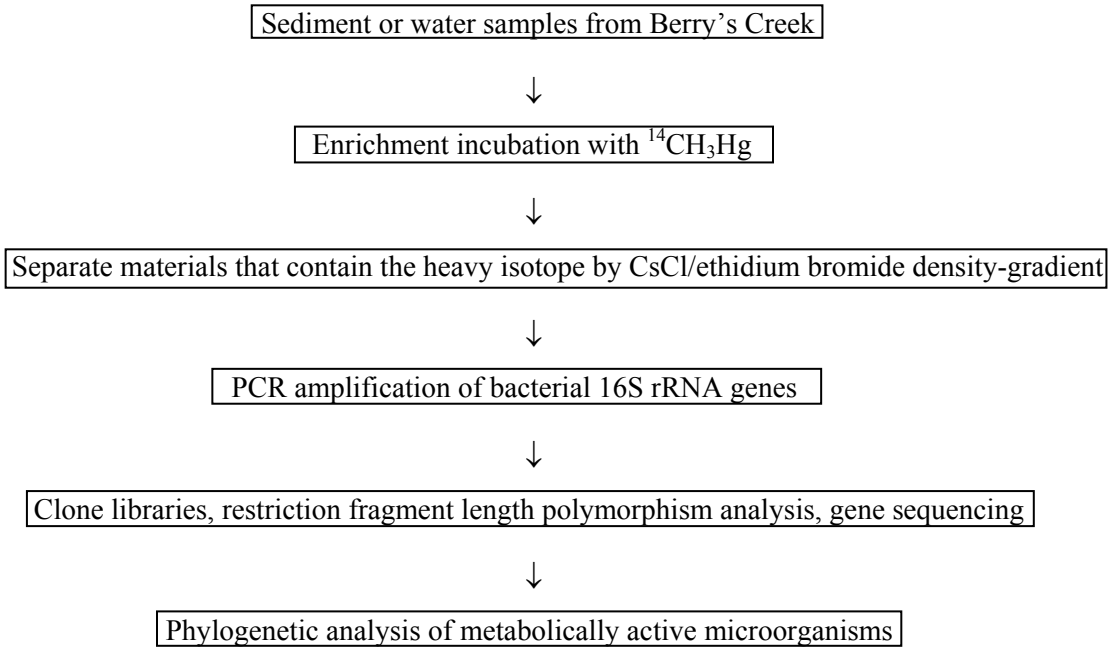
1. Problem and research objectives.

Methylmercury (CH_3Hg or MeHg), a lipophilic form of Hg that is a potent neurotoxin, could be readily accumulated by aquatic organisms and severely affect public health via food chain accumulation. The New Jersey Mercury Task Force (NJMTF, 2002) reported that mercury levels in water (e.g. the Hudson-Raritan Estuary) and sediment (e.g. 75% of the NY-NJ Harbor sediment) were found to exceed the related criteria or effect range, respectively. They also found that 43–56% of freshwater fish contained Hg concentrations higher than the FDA Action Level of 0.5 ppm.

Microbial degradation of MeHg (demethylation), a naturally occurring process of which little is known, plays an important role in mercury biogeochemical cycling and detoxification. To date, two pathways for the degradation of MeHg have been documented (Oremland *et al*., 1991; Marvin-Diapsquale *et al*., 2000; Barkay & Wagner-Dobler, 2005). Both pathways imply the conversion of the C1 moiety to gaseous products, either methane or carbon dioxide. The possibility that MeHg is degraded by microbes which utilize the C1 as a carbon source has not been examined and may be a major pathway for MeHg degradation. The proposed approach will explore this possibility by applying stable-isotope probing (SIP), a recently developed method to taxonomically and functionally characterize microbial species that are active in degradation and bioremediation processes of organic pollutants (Madsen, 2006). Thus, this project will investigate if microorganisms that are grown in the presence of $^{13}CH_3Hg$ assimilate the heavy carbon isotope into their DNA during demethylation and can consequently be distinguished by SIP. From the $^{13}CH_3Hg$ enrichment with environmental samples, ^{13}C–DNA (or RNA) extracted from the target group of microbes that actively participate in $^{13}CH_3Hg$ demethylation could be characterized taxonomically by SIP. This study will first test if and how the C1 group from MeHg is assimilated into nucleic acids in the cell. If this approach is feasible, identification of the specific groups of microorganisms that degrade MeHg will be possible.

2. Methodology.

Berry's Creek is a tidal tributary of the Hackensack River bordered by three current or former Superfund sites. The sites have contributed to the heavy Hg contamination of the creek. To examine the feasibility of the proposed approach, an experiment was set up to determine the fate of ^{14}C-MeHg in incubation with environmental samples. The change in concentrations of CH_3Hg, traced by radioactivity retention in aliquot of different samples, served as an indication of the demethylation process. Samples were taken from Berry's Creek in July and October, 2007 and included creek sediment, bottom water, and surface water. One saltmarsh sediment sample was taken from Cheesequake State Park, NJ in July 2007 and served as a control with low Hg contamination. After flushing out the gaseous products (CO_2 or CH_4) from the MeHg degradation, the remaining radioactivity, i.e., from ^{14}C-MeHg, was determined by scintillation counting (Fig. 1). At this experiment stage, ^{14}C-MeHg (rather than ^{13}C-MeHg) is employed in the isotope probing and the experimental design is slightly modified. The outline of the experimental design is listed as follows:



3. Principal finding and significance.

This study indicated that Berry's Creek sediment had 10273.19 and 32.35 ng g^{-1} dry wt of total Hg and MeHg, respectively, for the samples taken in July 2007. The preliminary incubation experiments on samples taken in October 2007 showed that significant demethylation activities only occurred in microbial consortia from the creek surface water (Fig. 1). No obvious microbial demethylation activities were detected for both the samples of creek sediment and anaerobic bottom water. Sulfate additions on the later two samples also did not cause apparent MeHg degradation responses. Thus, the project is focusing on the microbial consortia from the creek surface water. DNA from the samples was extracted (Fig. 2) and the SIP analysis is currently being processed using the DNA of the archaeon *Methanospirillum hungatei* as a carrier in the CsCl/EtBr DNA separation. Because successful SIP analysis generally needs a large amount of ^{14}C or ^{13}C-assimilated DNA extracted from the environmental microbial biomass, and our incubations (Fig. 1) consisted of small volumes, there may be a need to set new incubation with MeHg (^{14}C) to obtain more microbial biomass as a source for the DNA.

The project examines if the C1 group of CH_3Hg is assimilated into nucleic acids of exposed cells and how much of the carbon is assimilated. This is important for the understanding of MeHg demethylation and for correctly calculating demethylation rates. Phylogenetic surveys of metabolically active species or groups of microbes involved in CH_3Hg demethylation will suggest strategies for further enrichment isolation of specific strains. Future studies with such microbial strains will add to knowledge that is relevant to CH_3Hg bioremediation.

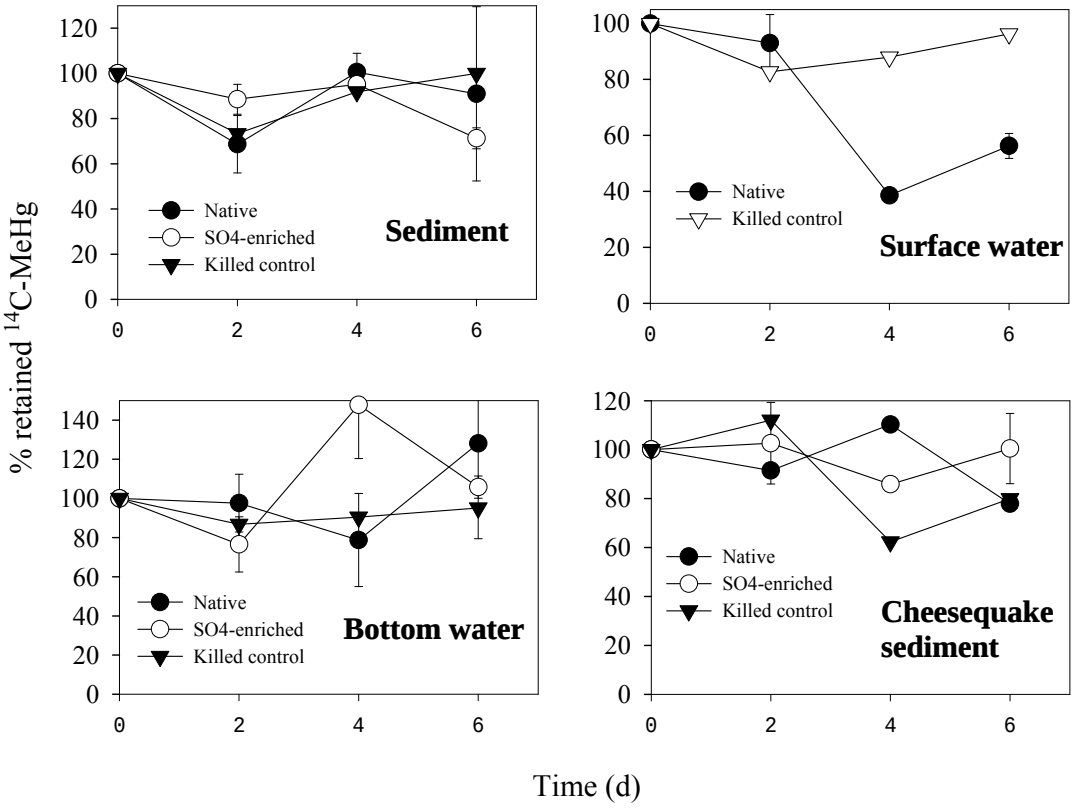


Fig. 1. Demethylation of spiked ^{14}C-MeHg in incubated samples (native and 0.1mM sulfate-enriched) from Berry's Creek, Newark (Oct. 2007). Saltmarsh sediment from Cheesequake State Park, NJ was employed as one environmental control. ^{14}C gases (CO_2 and CH_4) produced during demethylation were flushed before taking 2 ml slurry per vial for counting of retained radioactivity.

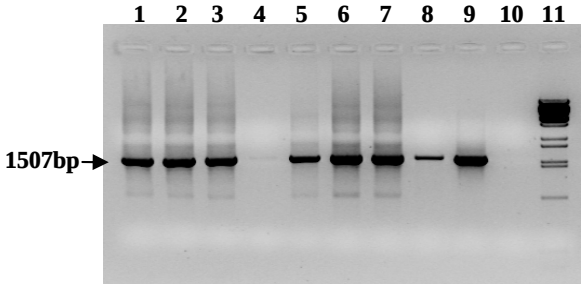


Fig. 2. 16S rRNA genes in Berry's Creek samples spiked with ^{14}C-MeHg after six days' incubation by using touchdown PCR with universal bacterial primers of GM3F and GM4R. Lanes marked as: 1. Creek sediment; 2. Creek sediment-SO_4^{2-}; 3. Bottom water; 4. Bottom water-SO_4^{2-}; 5. Surface water; 6. Cheesequake saltmarsh sediment; 7. Cheesequake-SO_4^{2-}; 8. *Desulfovibrio desulfurican* G200; 9. *E. coli.*; 10. Blank; 11. λ DNA-BstE II digest (ladder).

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A Quantitative Approach to Linking Temporal Variations of Groundwater Level with Nitrogen Cycling in New Jersey Wetlands

Basic Information

Title:	A Quantitative Approach to Linking Temporal Variations of Groundwater Level with Nitrogen Cycling in New Jersey Wetlands
Project Number:	2007NJ145B
Start Date:	3/1/2007
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	6th
Research Category:	Climate and Hydrologic Processes
Focus Category:	Hydrology, Wetlands, Groundwater
Descriptors:	None
Principal Investigators:	Daniel Gimenez, Joan G. Ehrenfeld

Publication

Project Summary

Problem and Research Objectives

Wetlands are considered one of the most valuable terrestrial ecosystems because of their multiple functions, including as regulators of biogeochemical cycles. Previous research has demonstrated that New Jersey wetlands located in developed areas experience rapid and frequent wet/dry periods (Golet et al. 1993, Ehrenfeld et al. 2003). At the core of this proposal is the hypothesis that data analysis techniques in combination with site-related information can separate and identify the factors determining the dynamics of groundwater fluctuation at a site. Furthermore, we hypothesized that these factors interact with spatial variation in soil properties to determine N cycling in wetland soils. Specific hypotheses of the research are: 1) wavelet and multifractal analyses of wetland hydrographs can provide statistical descriptions of flashy signals, and identify short- and long-frequency components of water table dynamics, and 2) temporal patterns of nitrification and denitrification ("hot moments") are better explained by the hydrological patterns elucidated and quantified in objective 1 than they are by spatial variability in soil properties alone.

Our goal is to apply multifractal and wavelets analyses to an existing database of long hydrograph records from wetlands in New Jersey, and carry out new analyses of soil conditions and N cycling in two sites selected on the basis of the hydrograph analyses. This is considered a pilot study to demonstrate the feasibility and environmental significance of the method, and as a basis for proposals for more comprehensive examination of these objectives.

Methodology

Data on groundwater levels collected with continuously recording wells at a six-hour interval was available for four wetlands located in northeastern New Jersey, a densely urban part of the New York metropolitan region (Table 1 and Fig. 1). Data from a period spanning two to three months during the years 2003-2005 were selected for this study (Fig. 2). Daily rainfall data and maximum and minimum temperature were obtained from the National Weather Service Cooperative Network (http://climate.usurf.usu.edu/) for nearby locations (Fig. 1).

Multi-resolution analysis with wavelets (MRA) was applied to groundwater level and rainfall data using the wavelet *Haar* as implemented in MatLab 7.0. The wavelet transform expresses a finite function $f(t)$ as a linear combination of a base signal $B(t)$ and noise $A(t)$ to the signal. The step from $f(t)$ to $B(t) + A(t)$ is known as *decomposition* and the opposite process is known as *reconstruction*. Precipitation and groundwater level data were decomposed and a multifractal analysis (Gupta and Waymire, 1990; Das and Mohanty, 2008) of the base signals was used to characterize both processes. Finally, a preliminary model of groundwater level fluctuation was formulated using the base function from precipitation data and the noise function from groundwater level.

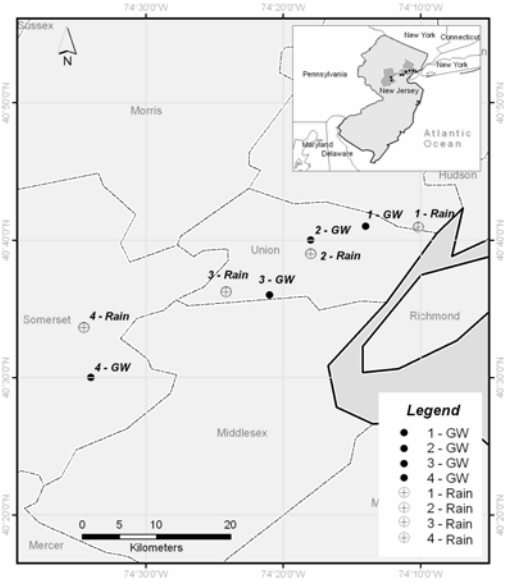

Table 1. Coordinates of groundwater (GW) and rainfall (Rain) recording sites.

Site	Latitude- Longitude of Measuring Stations	
	Groundwater	Rain
1	40°41'N -74°14'W	40°40'N -74°10'W
2	40°36'N -74°21'W	40°36'N -74°24'W
3	40°40'N -74°18'W	40°33'N -74°52'W
4	40°30'N -74°34'W	40°33'N -74°52'W

Fig. 1. Location of groundwater (GW) and rainfall (Rain) recording sites.

Table 2. Values of indicators of watershed urbanization for available sites.

Urbanization Indicator	*1*	*2*	*3*	*4*
Impervious cover (%)	46.2	na	23.6	na
Forested land cover (%)	4.25	na	6.39	na
Urban land cover (%)	92.7	na	79.2	na
Wetland land cover (%)	2.39	na	13.5	na
Residential land cover (%)	59.9	na	66.0	na
Transportation land cover (%)	1.05	na	0.45	na
Industrial land cover (%)	8.34	na	0.42	na
Population density (people/km^2)	3931	na	1262	na
Road density (km/km^2)	33.1	na	14.9	na

Principal Findings and Significance

Precipitation data from common periods and multiple years were grouped for analysis (Fig. 2). Of the selected sites, two sites exhibited groundwater levels close to the surface and two sites deeper ones. Those differences may be related to land use (Table 2) and or wetland size. So far, we developed the methodology with data from site 1 during the period May-July 2003-2005 (Fig. 2a).

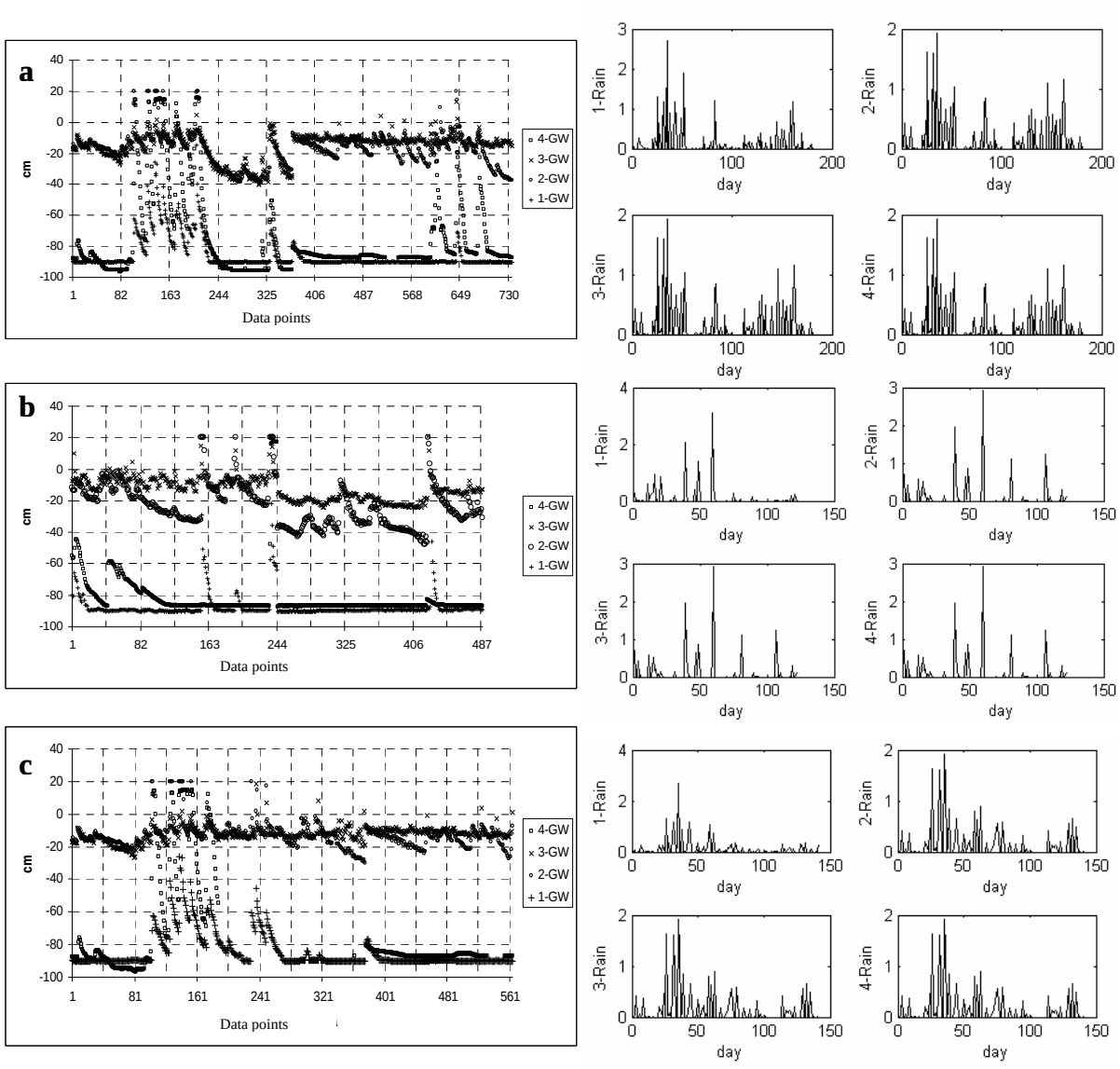

Fig. 2. Groundwater level and precipitation data for the studied sites for the periods May-July 2003-2005 (a), August-September 2004-2005 (b), and May-June 2003-2005 (c).

Decomposition of water level and rainfall data with MRA

The original 'signal' of groundwater level (taken every six hours) and precipitation (taken daily) were decomposed using wavelet transform (WT) into components of different

scales by powers of 2 (Fig. 3). Because of the differences in measurement frequencies, comparison between rainfall and groundwater level signals are done among components separated by scale differences of $2^2 = 4$. In addition, the groundwater level data was shifted forward by time steps that were multiples of 6 hours (6, 12, 18 ...hr) to account for any lag in the response of the groundwater level to a precipitation event. Linear relationships were found between the base functions (*B(t)*) and noise (*A(t)*) of precipitation and groundwater level signals (Table 3). These relationships will be used to reconstruct the fluctuation of the groundwater level.

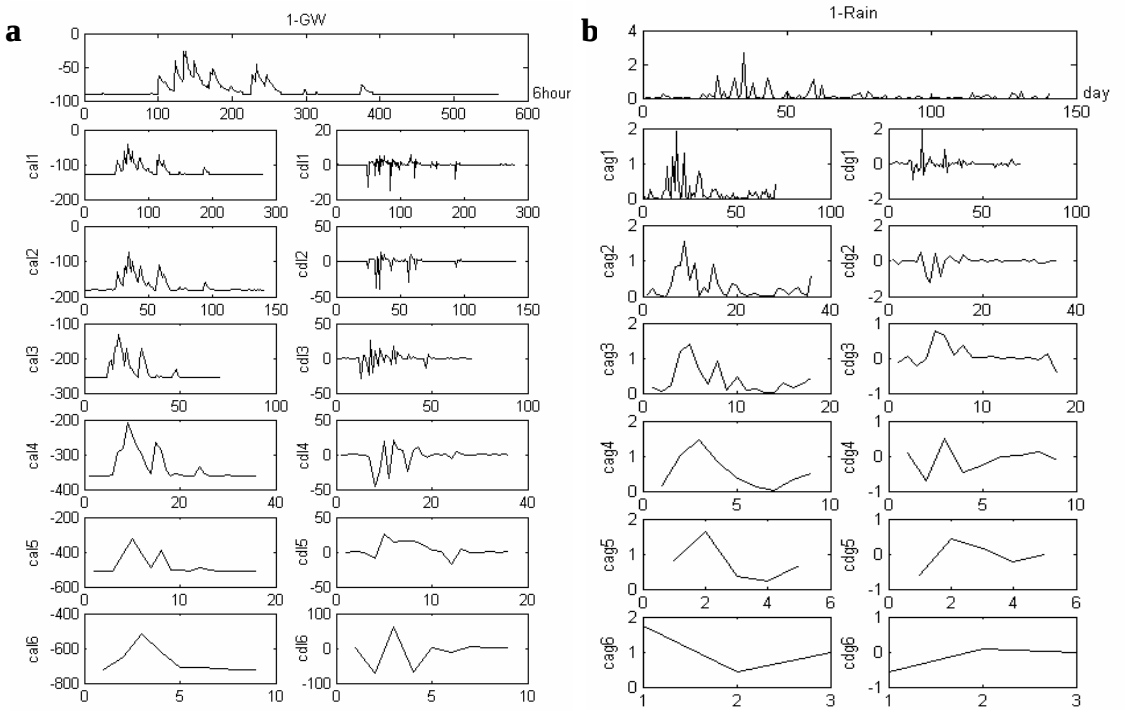

Fig. 3. Decomposition with wavelet Haar of a) groundwater level and b) rainfall of site 1. Symbols in the y-axis:, 'ca' and 'cd' refer to the low frequency signal (base, *B(t)*) and the high frequency signal (noise, *A(t)*), and l and g stand for rainfall and groundwater, respectively. The numbers represent the levels or number of applying wavelet transformation.

Table 3. Statistics R^2 for linear relationships between the base functions (*B(t)*) and noise (*A(t)*) of precipitation and groundwater level signals at different wavelet decomposition levels. The best relationship between precipitation and groundwater level is found when both *B(t)* and *A(t)* have strong linear relationship.

B(t)		R^2	*A(t)*		R^2	*Scale(λ)*
cal2	EZrainMJ	0.429	-----	-----	-----	2^0=1
cal3	cag1	0.558	cdl3	cdg1	0.493	2^1=2
cal4	cag2	0.670	cdl4	cdg2	0.619	2^2=4
cal5	cag3	0.845	cdl5	cdg3	0.481	2^3=8
cal6	**cag4**	**0.856**	**cdl6**	**cdg4**	**0.856**	2^4=16
cal7	cag5	0.880	cdl7	cdg5	0.826	2^5=32
cal8	cag6	0.775	cdl8	cdg6	0.998	2^6=64

Scaling and multifractal analysis for water level and rainfall

The scaling properties of the groundwater level fluctuations and precipitation were characterized with a multifractal technique (Das and Mohanty, 2008) using the base functions *B(t)* at various decomposition levels (see Fig. 3) raised to moments h and averaged to produce a single value for each level of decomposition and moment ($E[cal^h]$ and $E[cag^h]$ for groundwater level and precipitation, respectively). The results indicate that *B(t)* is fractal in the case of groundwater level and multifractal for rainfall (Fig. 4 and Fig. 5). A fractal signal is easier to simulate than a multifractal one. The same analysis will be performed on the noise functions *A(t)*.

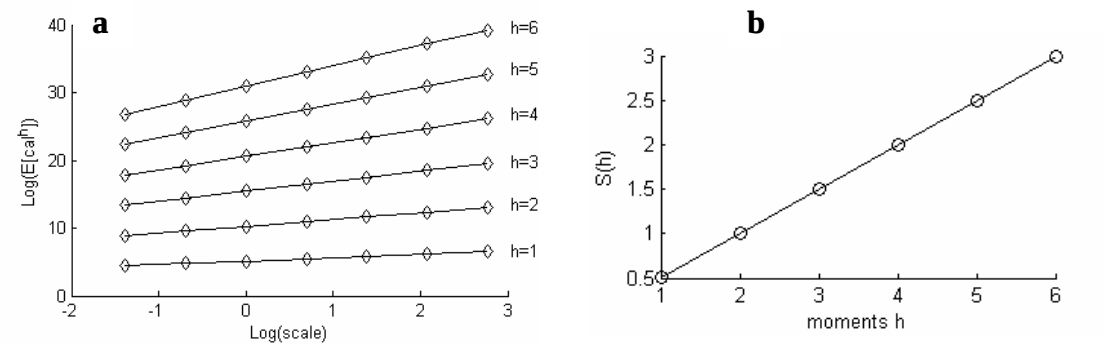

Fig. 4. Scaling of groundwater level (a) and the linear structure function indicative of a fractal process (b).

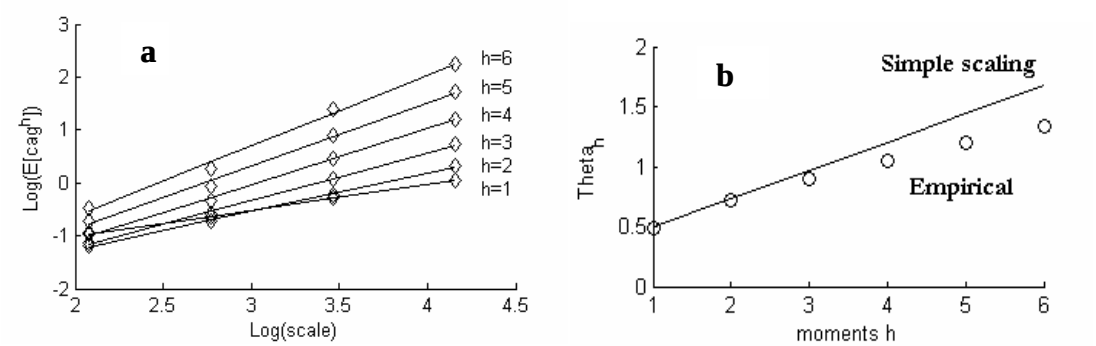

Fig. 5. Scaling of precipitation (a) and the non-linear structure function indicative of a multifractal process.

Linear empirical model for reconstructed water level

The linear relationship between the base functions *B(t)* of precipitation and groundwater level (see bolded in Table 3) can be used to predict the latter function from the former one. An inverse wavelet transform is then used to reconstruct the fluctuation of groundwater level from the predicted base function and the original noise of the groundwater table levels (see Fig. 3). The resulting model predicts reasonably well the dynamics of the groundwater table fluctuations (Fig. 6). In other words, the low

frequency fluctuations (peaks) can be predicted from rainfall. A complete model should also predict the properties of the noise function (*A(t)*).

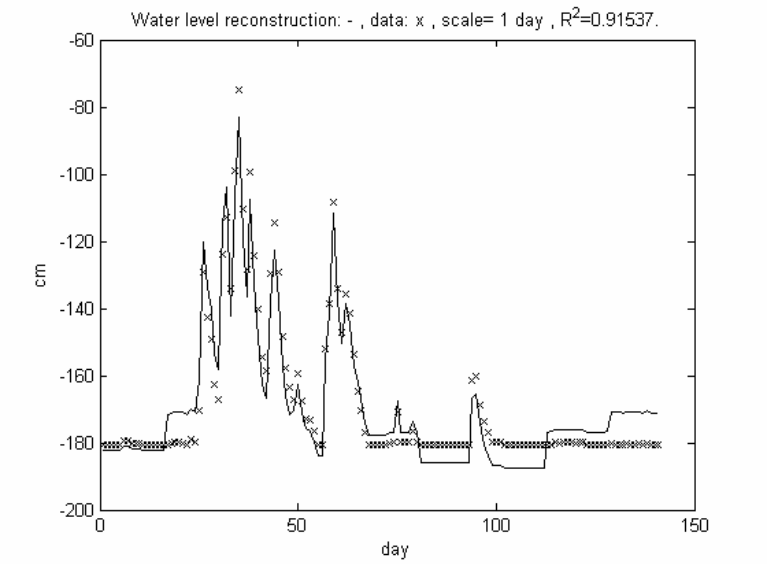

Fig. 6. Groundwater level fluctuation reconstructed with an inverse wavelet transform using precipitation data to predict the base function of groundwater at decomposition level 6 (see Fig. 3 and Table 3).

Future work

The following tasks are scheduled for completion: 1) complete the analysis for all four sites, 2) characterize the properties of the noise function at each site, 3) correlate the noise function to physical properties of the site (soil type, land use, etc), and 4) investigate N mineralization in two contrasting sites.

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Biogeochemistry of Pb transformations mediated by phosphate−releasing bacteria

Basic Information

Title:	Biogeochemistry of Pb transformations mediated by phosphate−releasing bacteria
Project Number:	2007NJ146B
Start Date:	3/1/2007
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	6th
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Hydrogeochemistry, Toxic Substances
Descriptors:	None
Principal Investigators:	Nathan Yee

Publication

Project Summary:

Problem and Research Objectives

Lead (Pb) is a toxic heavy metal found in many contaminated sites in New Jersey. The subsurface transport of Pb in groundwater is strongly affected by its chemical speciation. In order to accurately predict the fate and transport of Pb in contaminated aquifers, a detailed understanding of the biogeochemical processes that affect Pb transformations in soils and sediments is required.

A common Pb mineral found in Pb contaminated soils is cerussite ($PbCO_3$) (Evans et al., 1992; Harrison, 1981). Under atmospheric CO_2 partial pressures, cerussite is the dominant weathering product of anglesite ($PbSO_4$) and lead bullets (Lin et al., 1995; Cao et al., 2003; Vantelon et al., 2005). Thermodynamically, the most soluble Pb mineral phase will determine the aqueous Pb concentration in soil and sediment porewaters (Traina and Laperche, 1999). Because cerussite is not stable under acid pH conditions, it will naturally dissolve over time. Therefore, the solublization of cerussite in soils and sediments can release Pb ions into the solution phase and facilitate Pb mobilization. This process poses a serious risk to Pb contaminated groundwater and associated water resources.

Recently, we have isolated a bacterium from a contaminated soil in New Jersey that appears to transform cerussite into highly insoluble Pb-phosphate minerals. The mechanisms controlling this mineral transformation process are currently unknown. In this study, we employed X-ray diffraction and scanning electron microscopy to examine the biotic/abiotic transformation of $PbCO_3$ into insoluble Pb-phosphate minerals. The objective of this study was to resolve microbial and chemical contributions involved in the Pb mineral transformation process.

Methodology

Pb mineral transformation experiments were conducted with a bacterial isolate, designated as GP-19S, cultivated from Pb contaminated soils at Ringwood State Park, NJ. For the $PbCO_3$ experiments, analytical regent cerussite powder was obtained from Sigma-Aldrich. Experiments were performed by adding cerussite powder to LB medium inoculated with GP-19S. The flasks were continuously shaken at 30^{o}C. At periodic intervals, samples were collected from the culture medium to analyze the precipitates formed by the bacterium. Scanning electron microscopy (SEM) was conducted to image the dissolution of the cerussite particles, and X-ray diffraction (XRD) was used to identify the major mineral phases in the samples. The SEM images were collected with a LEO 1530VP field emission scanning electron microscope operating at an accelerating voltage of 2.0 kV. X-ray diffraction patterns were collected with a Philips PW3040-MPD X-ray diffractometer (XRD) operated at 40 kV and 20 mA using Cu Ka radiation with a graphite diffracted-beam monochromator. Step scans were made over the range of 5–75 º2θ at step sizes of 0.1 º2θ and 1 sec counting per step. Samples were mounted on zero-background quartz plates with care taken to ensure that the X-ray beam remained on the sample at all angles.

Principal Findings

- **Preliminary results suggest that cerussite ($PbCO_3$) undergoes solid-phase transformation during incubation with GP-19S.**

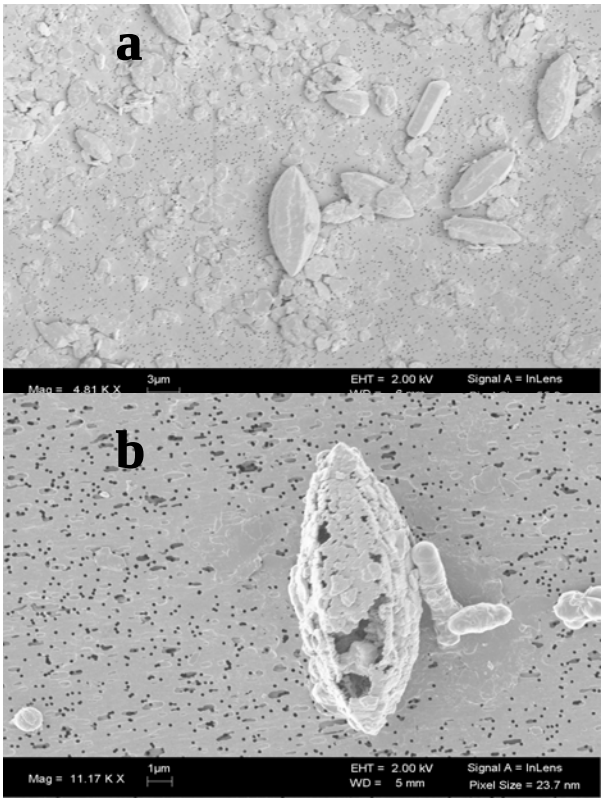

Figure 1. SEM images of cerussite ($PbCO_3$) before and after reaction in a culture medium with the soil bacterium GP-19S. a) cerussite particle at the beginning of the experiment; b) cerussite particle at the end of a two week incubation.

Figure 1a shows a SEM image of cerussite crystals prior to the experiment. These particles exhibit orthorhombic crystal morphology and a highly ordered internal atomic structure as determined by X-ray diffraction. For the mineral transformation experiment, the cerussite particles were added to a culture of GP-19S in LB media and shaken aerobically for two weeks. At the end of the experiment, SEM images of the cerussite particles show extensive dissolution features (Figure 1b). Attachment of cells onto the mineral surface was observed, although a majority of the bacteria remained suspended in the media. SEM images of the planktonic cells reveal the presence of fine-grained precipitates that are associated with the outer cell membrane but also dispersed throughout the culture media. These precipitates are acicular in morphology and approximately 50 nm in length.

X-ray diffraction analysis of the precipitates indicated that cerussite is completely dissolved by the end of the experiment and a secondary crystalline phase had formed (Figure 2a). The XRD pattern exhibited peak positions that correspond to the Pb-phosphate mineral hydroxy-pyromorphite [$Pb_5(PO_4)_3OH$].

- **Control experiments show that abiotic reactions can also induce cerussite transformation.**

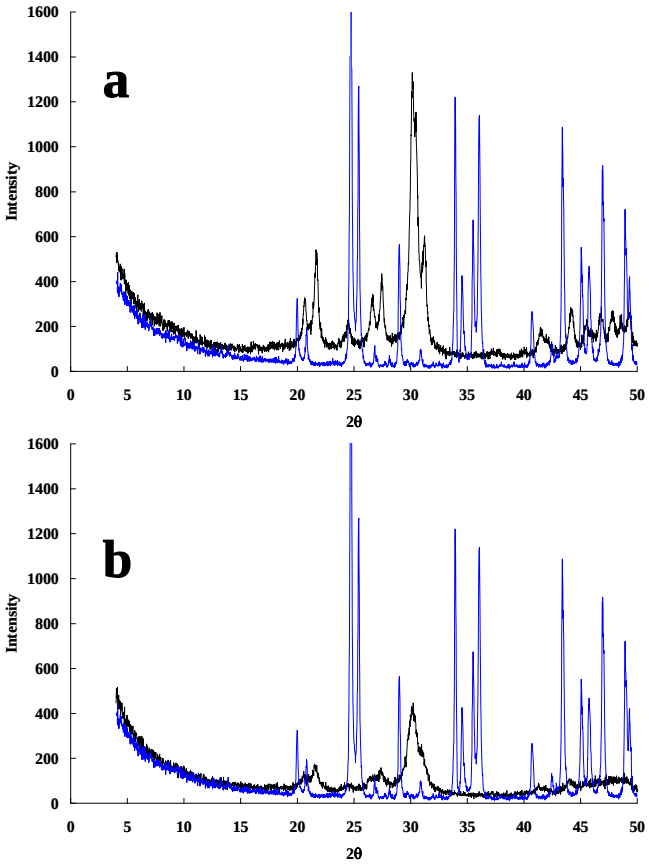

Figure 2. X-ray diffraction patterns collected for Pb minerals before (blue line) and after (black line) the reaction. The X-ray diffraction patterns in blue and black correspond to cerussite ($PbCO_3$) and hydroxy-pyromorphite [$Pb_5(PO_4)_3OH$], respectively. a) experiment with culture medium and soil bacterium GP-19S; b) control experiment with culture medium alone.

Control experiments were conducted by adding cerussite crystals to uninoculated culture medium to determine the abiotic effects of cerussite mineral transformation. After two weeks of reaction, X-ray diffraction analysis of the crystalline solids showed that cerussite was no longer present in the control experiment, and a secondary precipitate had also formed in the media (Figure 2b). The XRD pattern of the precipitate indicated that the secondary mineral was possibly hydroxy-pyromorphite. The results of the control experiment suggest that the culture medium can interact with the cerussite particles, and abiotic reactions can result in the dissolution of cerussite and re-precipitation of a secondary mineral phase. Additional experiments conducted using a defined minimal salt medium yielded the same result.

Based on these data, we cannot conclude that the solid phase transformation of cerussite observed in Figure 1 is strictly induced by bacterial activity. Further work is required to resolve the abiotic reactions involved in this mineral transformation process.

Significance

The results of this work suggest that abiotic chemical reactions rather than direct microbial processes control microbial Pb mineral transformations. Previously published studies in the literature may be erroneously reporting biogenic Pb mineral formation due to the lack of rigorous control experiments. We are currently conducting additional experiments to resolve the abiotic reactions involved in cerussite dissolution and hydroxy-pyromorphite re-precipitation in our experimental system.

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Information Transfer Program Introduction

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

Three issues of the newsletter were produced. The Spring 2007 issue examined the issue of beneficial re−use of wastewater. Articles by managers from the New Jersey Department of Environmental Protection explaining the state's program of beneficial re−use were complemented by articles from environmental organizations and county agencies discussing the impacts of re−use on wetlands, the coastal ocean, and the Pinelands, and description of a pilot demonstration project. The Summer 2007 issue highlighted a recent symposium held at and about the New Jersey Meadowlands, the largest and most prominent wetland and river complex in a highly urbanized region of the country. Selected papers presented at the meeting described the current status of the Meadowlands system, discussed novel methods of pollutant tracking (some supported by NJ WRRI research funding), the impact of climate change and sea level rise on the wetland and river system, and the subject of air−water interchange and monitoring of PCBs in the Meadowlands region. The Winter 2008 issue allowed WRRI−funded and agency researchers to describe their research on water resource issues; topics covered included the development of new technology for monitoring arsenic contamination, the economic analysis of BMPs, the development of a high school−based climate monitoring network, and a summary of on−going NJDEP research projects. Our annual research update issue is intended to illustrate the importance of water research in solving water−related problems. We are currently developing an issue for FY2008 on the use of wastewater residuals; other planned topics include papers from a recent conference on rain gardens, and an issue on methods of monitoring water flow regimes for ecological assessment.

Each issue was eight pages, and was primarily distributed via our e−mail lists to approximately 2,000 people throughout the state and as hard copies, to all members of our state legislature and Congressional delegation.

We have continued to manage the New Jersey Water Blog (http://njwrri.blogspot.com/). We regularly post articles about recent events, publications, and issues, as they arise.

Our website (http://njwrri.rutgers.edu/) was extensively revised and re−formatted this year, in order to bring it into conformity with new Rutgers University requirements for uniform appearance of all information materials distributed to the public, including websites. As part of this revamping, each of the pages was updated and revised to make it more user−friendly and informative. The home page and ‘events' pages are regularly updated to highlight upcoming events, publications and other water –related news.

We continue to expand and use targeted, group−specific e−mail lists to bring relevant information to specific audiences. Targeted lists include a list of scientists/principal investigators, water resource managers, non−governmental organizations and people affiliated with NGOs, and policy−makers. The lists are continuously updated and expanded, and are used to keep these groups informed of events, conferences, publications, and funding opportunities. These lists enable us to initiate and maintain frequent contact with stakeholder groups (rather than passively waiting for individuals to contact us). We believe these lists are an excellent method of keeping the water−related public aware of the WRRI, as well as informed about water−related news and information.

We also continue to participate in the New Jersey Water Monitoring Council, a statewide body representing both governmental and non−governmental organizations involved in water quality monitoring. We co−sponsored and helped organize the Sixth National Monitoring Conference in May 2008.

Finally, we took a leadership role in a new initiative at Rutgers, the Climate and Environmental Change Initiative, as chair of the water and ecosystem committee. This committee organized and planned a one−day symposium on climate change and water resources (held in April, 2008); the NJ WRRI is the lead organization for this meeting.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR−USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	0	0	0	0	0
Masters	1	0	0	0	1
Ph.D.	6	0	0	0	6
Post−Doc.	1	0	0	0	1
Total	8	0	0	0	8

Notable Awards and Achievements

Several awards resulted from the project "Restored Oyster Reef habitat use by the American Eel (Anquilla rostrata) in the Lower Delaware Bay" (2007NJ141B):

2008 Dean John A. Knauss Marine Policy Fellow − NOAA Sea Grant

2007 Estuarine Research Federation Conference Travel Award − ERF

2007 Dupont Clear into the Future Graduate Fellow Recipient

2007 Rutgers University Graduate Program in Ecology and Evolution Academic Excellence Fund − Demonstrating the habitat value of oyster aquaculture in Delaware Bay

2007 Honorable Mention Michael Castagna Student Research Award – NSA

Publications from Prior Years

1. 2001NJ941B ("A Continuation Proposal: Factors controlling methylmercury degradation in Pine Barrens lakes and the Meadowlands") − Articles in Refereed Scientific Journals − Cardona−Marek, T., J. K. Schaefer, K. Ellickson, T. Barkay, and J.R. Reinfelder. 2007. Mercury speciation, reactivity, and bioavailability in a highly contaminated estuary, Berry's Creek, New Jersey Meadowlands, U.S.A. Env. Sci. Technol. 41:8268−8274.
2. 2004NJ70B ("Efficiency of Bioretention Systems to Reduce Fecal Coliform Counts in Stormwater") − Articles in Refereed Scientific Journals − Rusciano, G.M. and C.C. Obropta. 2007. Biorention Column Study: Fecal Coliform and Total Suspended Solid Reductions. Transactions of the ASABE, 50(4): 1261−1269.
3. 2005NJ87B ("Lab−on−a−chip device for monitoring trace level arsenic") − Articles in Refereed Scientific Journals − Hylton, Kamilah; Somenath Mitra, 2008, A microfluidic hollow fiber membrane extractor for arsenic (V) detection, Analytica Chimica Acta, 607 (1), 45−49.
4. 2005NJ87B ("Lab−on−a−chip device for monitoring trace level arsenic") − Dissertations − Hylton, Kamilah, 2008, Micro−Scale Membrane Extraction For Monitoring Trace Water Pollutants, “Ph.D Dissertation,” Department of Chemistry and Environmental Science, College of Science and Liberal Arts, New Jersey Institute of Technology, Newark, NJ, 101 pages.
5. 2005NJ87B ("Lab−on−a−chip device for monitoring trace level arsenic") − Articles in Refereed Scientific Journals − Hylton, Kamilah; Somenath Mitra, 2007, Barrier film protected, and mixed solvent optimized micro−scale membrane extraction of methyl carbamate pesticides, Journal of Chromatography A, 1154(1−2), 60−65.
6. 2005NJ86B ("Microbial degradation of MTBE in anaerobic environments") − Conference Proceedings − Youngster, Laura; Piyapawn Somsamak; Max M Häggblom, 2008, Use of co−substrates and inhibitors to investigate anaerobic MTBE degradation, American Society of Microbiology 108th General Meeting, Boston, MA, June 1−5, 2008, abstract Q−198 (poster presentation)
7. 2004NJ71B ("Soil Moisture Regimes and Nitrate Leaching in Urban Wetlands") − Dissertations − Stander, Emilie, 2007, The effects of urban hydrology and elevated atmospheric deposition on nitrate retention and loss in urban wetlands, "Ph.D. Dissertation," Graduate Program in Ecology &Evolution, Graduate School − New Brunswick, Rutgers University, New Brunswick, NJ, 206 pp.
8. 2006NJ98B ("Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands") − Conference Proceedings − Wishart, D., Slater, L., Schnell, D. and Herman, G., 2008, Azimuthal self potential signatures associated with pneumatic fracturing, 21st Symposium on the Application of Geophysics to Environmental &Engineering Problems (SAGEEP), April 6−10, 2008, Phildelphia, PA, 4 pp.
9. 2006NJ98B ("Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands") − Conference Proceedings − Wishart, D., Slater, L. and Gates, A., 2007 Azimuthal self potential characterization of hydraulic anisotropy in fractured rock aquifers, 2007 U.S. EPA/ NGWA Fractured Rock Conference: State of the Science and Measuring Success in Remediation, September 24−26, 2007, Portland, ME, Abstract
10. 2006NJ98B ("Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands") − Dissertations − Wishart, D.N. 2008. Anisotropy Characterization of fracture−dominated media using azimuthal geoelectric methods. Ph.D. Dissertation. Department of Earth and Environmental Studies, Rutgers, The State University of New Jersey, Newark, NJ. 198 pp.
11. 2006NJ105B ("The Potential Impact of the Asian Isopod, Synidotea laevidorsalis (Miers 1881), on the Delaware Bay, USA") − Conference Proceedings − Boyd, S. and Bushek, D. 2007. Rapid

Ecological Assessment of a Non−Indigenous Isopod in Delaware Bay. Annual New Jersey Academy of Sciences Meeting, Kean University, Union, NJ. April 21, 2007. (Oral presentation)

12. 2006NJ105B ("The Potential Impact of the Asian Isopod, Synidotea laevidorsalis (Miers 1881), on the Delaware Bay, USA") − Conference Proceedings − Boyd, S. 2007. Biological Invasions with an Emphasis on two Delaware Bay Invaders. Bayshore Discovery Project seminar series, Haskin Shellfish Research Laboratory, Rutgers University, Bivalve, NJ. June 2007. (Oral presentation)