Water Resources Research Center Annual Technical Report FY 2008

Introduction

This report covers the period March 1, 2008 to February 28, 2009, the 43rd year of the Massachusetts Water Resources Research Center (WRRC). The Center is under the direction of Dr. Paula Rees, who holds a joint appointment as Director of the WRRC and as Education Co-Director of the Center for Collaborative Adaptive Sensing of the Atmosphere at the University of Massachusetts Amherst.

Dr. Stephen Mabee of the UMass Amherst Department of Geosciences finished work on a three-year 104G USGS grant to look at *A Regional Approach to Conceptualizing Fractured-Rock Aquifer Systems for Groundwater Management*, that was granted a no-cost extension to continue the research until December 2008.

At the University of Massachusetts Amherst, Dr. Baoshan Xing of the Plant, Soil, and Insect Sciences Department continued work on the second year of a two-year project on the *Environmental Behaviors of Engineered Nanoparticles in Water*. His project has been granted a no-cost extension until May 31, 2010.

This year we awarded four graduate student grants:

Lauren Luongo (PI Xiaoqi Zhang) at the university of Massachusetts Lowell studied the *Toxicity of Carbon Nanotubes to the Activated Sludge Process: Protective Ability of Extracellular Polymeric Substances*.

Steven F. Kichefski (PIs Ellen M. Douglas and Allen M. Gontz) at the University of Massachusetts Boston looked at *Quantifying Sediment Transport in Red Brook, Wareham, Massachusetts: Impacts of Dam Removal on Hydrogeomorphology and Aquatic Habitat*.

Pamela Westgate (PI Chul Park) of the University of Massachusetts Amherst worked on a project entitled *Characterization of Wastewater Effluent from Western Massachusetts Publicly Owned Treatment Works Using Metaproteomic Analysis*.

Yushiou Tasi (PI Richard Vogel), at Tufts University, worked on a project entitled *Estimation of Climatic and Anthropogenic Influences on Freshwater Availability*.

Other projects conducted at WRRC include the Acid Rain Monitoring Project, the Massachusetts Stormwater Technology Evaluation Project, and continued collaboration with UMass Extension on a stream continuity project. We also partly funded a project to train University of Massachusetts Chemistry Department graduate students to analyze water samples for inorganic constituents and work in a client-based laboratory.

The fifth annual water resources research conference, *Integrating Water Resources Management*, was held at UMass on April 8, 2008, and planning took place for the sixth annual conference, *Water Dependencies in New England: Systems, Stresses, and Responses*.

Research Program Introduction

The following six research projects were completed this year:

A Regional Approach to Conceptualizing Fractured-Rock Aquifer Systems for Groundwater Management

Basic Information

Title:	A Regional Approach to Conceptualizing Fractured-Rock Aquifer Systems for Groundwater Management
Project Number:	2003MA19G
Start Date:	9/30/2003
End Date:	12/27/2008
Funding Source:	104G
Congressional District:	1st District of MA
Research Category:	Ground-water Flow and Transport
Focus Category:	Water Supply, Groundwater, Water Quantity
Descriptors:	fracture characterization, domain analysis, well yield, fractured rock aquifers, groundwater availability, groundwater mapping, borehole geophysics
Principal Investigators:	Stephen B. Mabee, Michele Cooke

Publication

1. Manda, A.K; S.B Mabee, D.U. Wise, 2008, Influence of rock fabric on fracture attribute distribution and implications for groundwater flow in the Nashoba Terrane, Eastern Massachusetts, Journal of Structural Geology, (30) 464-477.
2. Manda, A.K, S.B. Mabee and D.F. Boutt, 2006. Characterizing fractured crystalline bedrock aquifers using hydrostructural domains in the Nashoba terrane, eastern Massachusetts. Geological Society of America Annual Meeting, Philadelphia, Abstracts with Programs, v.38, no.7, p.25.
3. Diggins, J.P., D.F. Boutt, A.K. Manda and S.B. Mabee, 2006. Estimating bulk permeability of fractured rock aquifers using detailed outcrop data and discrete fracture network modeling. Geological Society of America Annual Meeting, Philadelphia, Abstracts with Programs, v.38, no.7, p.223.
4. Boutt, D.F., A.K. Manda, S.B Mabee, J.P. Diggins, 2006, Characterizing fractured crystalline bedrock aquifers using discrete fracture networks in the Nashoba Terrane, Eastern Massachusetts, Eos Transactions, American Geophysical Union, v. 87, no. 52, Fall Meeting Supplement, Abstract H13D-1429.
5. Manda, A.K., S.B. Mabee and S.A. Hubb,. 2005. Field mapping and fracture characterization techniques predict groundwater preferential flow paths in fractured bedrock aquifers, Nashoba terrane, MA. EOS Transactions, American Geophysical Union, v.86, no. 52, Fall Meeting Supplement, Abstract H23E-1477.
6. Manda, Alex K., Stephen B. Mabee, 2008 (In prep) Contrasting various fracture sampling methods from layered rocks, Submitted to Hydrogeology Journal.
7. Manda, Alex K., Stephen B. Mabee, David F. Boutt, 2007, Discrete fracture network modeling of hydrostructural domains: an example from Eastern Massachusetts, in 2007 US EPA/NGWA Fractured rock Conference: State of the science and measuring success in remediation, September 24-26, 2007, Portland Maine: national Groundwater Association (CD-ROM).

Problem Statement and Research Objectives

The use of fractured-bedrock aquifers to meet private, public and commercial water supply needs is increasing in the New England region. Municipalities and water suppliers are finding it increasingly difficult to locate and develop water supplies in overburden aquifers because of contamination and a lack of suitable sites. In addition, recent droughts in the northeast have forced many communities and homeowners to drill new wells. As a result, water suppliers are going deeper into bedrock aquifers. Yet information on the factors that influence the availability and recharge characteristics of fractured bedrock aquifers in highly deformed crystalline metamorphic rocks is limited.

The availability of water in fractured rock aquifers is particularly critical in New England because growth and development along the coast, major transportation corridors and in rural communities adjacent to large metropolitan areas is rampant. For example, the I-495 corridor in Massachusetts, a circumferential highway 30 miles west of Boston, has become the focus of recent growth. Professional office buildings, research and development parks associated with the computer industry, warehouses and light industry are springing up along this corridor, as are housing and condominium developments. Municipalities and water suppliers are simply unprepared for the onslaught of development and need help in understanding the complex dynamics of the ground water system.

Sustaining and managing ground water resources in fractured bedrock requires an evaluation of 1) the availability of water, 2) the source and vulnerability of recharge to water supply wells and 3) the impact of water withdrawals from the bedrock on streams, wetlands and unconsolidated aquifer systems that overlie the bedrock. These evaluations all require basic information on the physical characteristics of the ground water system.

The objectives of this project are to gather regional bedrock characteristics that relate to the occurrence and movement of ground water in bedrock and use this information to begin constructing regional conceptual models of the fractured-rock aquifers in the Nashoba terrane in Massachusetts. The approach utilizes existing information augmented by the collection of low-cost field data to develop regional conceptual models of the ground water flow system. Water managers can then use these conceptual models as an initial framework for formulating an understanding of bedrock flow behavior and recharge characteristics.

Methodology

Specific tasks of this project involve: 1) Fracture Characterization and Domain Analysis - collection and synthesis of fracture characterization data over the region and mapping of the spatial distribution (domain analysis) of fracture sets and their characteristics, 2) Compilation and Analysis of Existing Well Data - compilation and statistical analysis, including variography, of available well data to link spatial continuity of well yields to characteristics of the fractured rock system, 3) Borehole Geophysics - collection of optical and acoustic televiewer data from selected boreholes to verify sheeting joints, 4) Compilation of Regional Litho-Group Map - development of a mapping classification system that uses the notion of “litho groups” to characterize bedrock units in terms of their fracture characteristics, physical properties and geologic setting (eg., overburden type and thickness) and 5) Conceptual Model - preparation of a qualitative conceptual model of ground water flow behavior in each litho group category.

Principal Findings and Significance

A new method has been developed to quantitatively assess the hydraulic properties of fractured rocks that is independent of geology. This approach uses easily obtained fracture data to prescribe hydraulic properties of discrete fracture networks (DFNs) to rocks with negligible matrix porosity. The properties that are required to provide a hydraulic property estimate are fracture intensity, size, intersection angle of fractures, and number of fracture sets in a fracture network. The ratio (R) of the permeability of a fracture network to the permeability of a single fracture within an identical model domain is used to quantify the hydraulic character of DFNs with fracture sets that comprise persistently parallel fractures. Results reveal that R is consistently most sensitive to the angle of intersection of fractures in a network and least sensitive to the fracture intensity. The analyses also show that there is a predictable relation between R and the above mentioned parameters. Thus, a methodology for developing type curves through numerical simulations is also provided. These type curves are a series of graphs, which provide R estimates that are based on unique combinations of fracture properties and configurations collected in the field. Estimates of R from the type curves can then be used to compute the first-order approximations of fracture network permeability or hydraulic aperture at a cost far less than that associated with performing aquifer tests.

Publications and Conference Presentations

a. Articles in Refereed Scientific Journals

Manda, Alex K., Stephen B. Mabee, Donald U. Wise. 2008. Influence of rock fabric on fracture attribute distribution and implications for groundwater flow in the Nashoba Terrane, eastern Massachusetts. Journal of Structural Geology, v.30, pp.464-477.

Manda, Alex K., Stephen B. Mabee, David F. Boutt. (In Review). Effects of fracture configurations and properties on the hydraulic properties of three-dimensional networks. Submitted to Water Resources Research.

Manda, Alex K., Stephen B. Mabee (In Review). Comparison of three fracture sampling methods in layered rocks. Submitted to International Journal of Rock Mechanics and Mining Science.

b. Dissertations

Manda, Alex K. 2009. Development and validation of conceptual models to characterize the fractured bedrock aquifer of the Nashoba Terrane, Massachusetts. Ph.D. Dissertation, Geosciences Department, University of Massachusetts, Amherst, Massachusetts, 159p.

c. Conference Proceedings

Manda, Alex K., Stephen B. Mabee, David F. Boutt. 2007. Discrete Fracture Network Modeling of Hydrostructural Domains: An Example from Eastern Massachusetts, *in* U.S. EPA/NGWA Fractured Rock Conference: State of the Science and Measuring Success in Remediation, September 24-26, 2007. Portland, Maine, pp.480-488.

d. Published Abstracts

Manda, Alex K, Stephen B. Mabee, David F. Boutt. 2006. Characterizing fractured crystalline bedrock aquifers using hydrostructural domains in the Nashoba terrane, eastern Massachusetts. Geological Society of America Annual Meeting, Philadelphia, Abstracts with Programs, v.38, no.7, p.25.

Diggins, John P., David F. Boutt, Alex K. Manda, Stephen B. Mabee. 2006. Estimating bulk permeability of fractured rock aquifers using detailed outcrop data and discrete fracture network modeling. Geological Society of America Annual Meeting, Philadelphia, Abstracts with Programs, v.38, no.7, p.223.

Manda, Alex K., Stephen B. Mabee, Steven A. Hubbs. 2005. Field mapping and fracture characterization techniques predict groundwater preferential flow paths in fractured bedrock aquifers, Nashoba terrane, MA. EOS Transactions, American Geophysical Union, v.86, no. 52, Fall Meeting Supplement, Abstract H23E-1477.

Manda, Alex K. 2005. Characterizing the fractured bedrock aquifer of the Nashoba Terrane, Massachusetts. Massachusetts Water Resources Research Center/UMass Extension 3rd Annual Conference, Research to Practice: Science for Sustainable Water Resources, Amherst (Poster).

Environmental Behaviors of Engineered Nanoparticles in Water

Basic Information

Title:	Environmental Behaviors of Engineered Nanoparticles in Water
Project Number:	2007MA73B
Start Date:	3/1/2007
End Date:	5/31/2010
Funding Source:	104B
Congressional District:	First
Research Category:	Water Quality
Focus Category:	Water Quality, Toxic Substances, Solute Transport
Descriptors:	
Principal Investigators:	Baoshan Xing, Baoshan Xing

Publication

Methodology:

Batch sorption techniques, DSL, liquid scintillation counting, HPLC detection, TEM and SEM examinations, and monitoring of plant growth in a greenhouse.

Principal Findings and Significance:

Our preliminary data show that ZnO nanoparticles were toxic to plants and present inside the root cells via uptake; the latter is significant in terms of possible accumulation along the food chain. Al_2O_3 nanoparticles in aqueous suspension could be stable in the presence of certain dissolved organic matter, and at pH being away from the zero point of charges. Natural Organic Matter (NOM)-facilitated suspension could promote the mobility and exposure of nanoparticles (oxides and carbon nanotubes). Coating of NOM on metal oxide nanoparticles greatly increased their sorption of polyaromatic hydrocarbons (PAH). Bisphenol A and 17α-ethinyl estradiol were strongly adsorbed carbon nanotubes (CNTs) with hysteresis. Therefore, CNTs, particularly single-walled CNTs, may be potentially used for water treatment. We also observed that π-π interaction is an important contribution for adsorption of aromatic-ring containing compounds by CNTs, such as bisphenol A and phenolic chemicals. These results are useful to understanding the interactions between CNTs and organic contaminants and environmental behavior of CNTs.

Publications and Conference Presentations:

Several Platform and poster presentations will be given at the International Conference of Environmental Application and Implication of Nanotechnology, June 9-11, 2009, Amherst, MA.

Articles in Refereed Scientific Journals

Ghosh, S., H. Mashayekhi, B. Pan, P. Bhowmik and B. Xing. 2008. Colloidal behavior of aluminum oxide nanoparticles as affected by pH and natural organic matter. Langmuir, 24(21): 12385-12391.

Wang, X.L., J.L. Lu, M. Xu and B. Xing. 2008. Sorption of pyrene by regular and nanoscaled metal oxide particles: Influence of adsorbed organic matter. Environ. Sci. Technol. 42(19); 7267-7272.

Pan, B., D.H. Lin, H. Mashayekhi and B. Xing. 2008. Adsorption and hysteresis of bisphenol A and 17α-ethinyl estradiol on carbon nanomaterials. Environ. Sci. Technol. 42(15): 5480-5485.

Lin, D.H. and B. Xing. 2008. Tannic acid adsorption and its role for stabilizing carbon nanotube suspensions. Environ. Sci. Technol. 42(15): 5917-5923.

Lin, D.H. and B. Xing. 2008. Root uptake and phytotoxicity of ZnO nanoparticles. Environ. Sci. Technol. 42(15): 5580-5585.

Lin, D.H. and B. Xing. 2008. Adsorption of phenolic compounds by carbon nanotubes: Role of aromaticity and substitution of hydroxyl groups. Environ. Sci. Technol. 42(19); 7254-7259.

Conference Proceedings

Ghosh, S. and B. Xing. “Influence of structurally different humic acids on the colloidal chemistry of aluminum oxide nanoparticles.” Humic Science & Technology Conference Twelve, Boston, MA, March 18-19, 2009. P. 51.

Pan, B. and B. Xing. “Competitive adsorption of endocrine disrupting chemicals on carbon nanotubes.” The 24th Annual International Conference on Soils, Sediments, and Water. Amherst, MA, October 20-23, 2008. p.90 in the abstract book.

Bai, Y.C., D.H. Lin and B. Xing. “Influence of sonochemical oxidation on the dispersion of multi-walled carbon nanotubes.” The 24th Annual International Conference on Soils, Sediments, and Water. Amherst, MA, October 20-23, 2008. p.92 in the abstract book.

Ghosh, S., B. Pan, H. Mashayekhi, P.C. Bhowmik and B. Xing. “Colloidal behavior of aluminum oxide nanoparticles as affected by pH and humic acid (HA).” The 24th Annual International Conference on Soils, Sediments, and Water. Amherst, MA, October 20-23, 2008. p.91 in the abstract book.

Pan, B. and B. Xing. “Adsorption of hydrophobic organic contaminants on carbon nanotubes in different organic solvents.” 2008 ASA-CSSA-SSSA International meetings, Houston, Oct. 5-9, 2008. Abstract #: 61-7.

Student Support

Mr. Hamid Mashayekhi and Miss Wei Jiang, Ph.D. students in the Department of Plant, Soil & Insect Sciences at the University of Massachusetts Amherst.

Notable Achievements and Awards

One of my graduate students, Wei Jiang, won a first place for her poster presentation at the "**Water Dependencies in New England**" 6th Annual Conference:
http://www.umass.edu/psis/news/ne_water_conf.html

Estimation of Climatic and Anthropogenic Influences on Freshwater Availability

Basic Information

Title:	Estimation of Climatic and Anthropogenic Influences on Freshwater Availability
Project Number:	2008MA125B
Start Date:	4/7/2008
End Date:	7/25/2008
Funding Source:	104B
Congressional District:	8th
Research Category:	Climate and Hydrologic Processes
Focus Category:	Water Supply, Water Use, Drought
Descriptors:	None
Principal Investigators:	Richard M. Vogel, Yushiou Tsai

Publication

Problem and Research Objectives

Of the previous research which attempt to evaluate sensitivity of streamflow to various factors, most of such studies have taken changes in climate into account, but fewer studies have considered both the changes in climate and land use. Generally it is agreed among researchers that land cover is a significant factor influencing watershed hydrology (Oudin et al., 2007; Andreassian 2004). In many watersheds around the globe, drastic landscape changes have occurred due to urbanization over decades. Numerous studies have found that impacts due to changes in land cover is important when considering their hydrologic impacts on urbanized watersheds (Beighley and Moglen, 2003; DeWalle et al., 2000, Zhang et al, 2001). Some of these urbanized watersheds, both in the U.S. (Canfield et al., 1999; Zarriello and Ries, 2000; Changnon 2002) and elsewhere (Schot and Vanderwal, 1992; Zarghami et al, 2008), have experienced surface and/or groundwater depletion due to increasing water demand that is largely driven by increases in human population density. Although many previous urban water demand studies have found that climate factors are important to urban water demand (Renwick and Green, 2000; Lyman, 1992; Foster et al., 1979; Billings and Day, 1989), few studies have addressed factors which impact both water supply and demand in a systematic fashion. One example is the study by Schulze (2000) which estimated precipitation elasticity of annual streamflow and precipitation elasticity of water demand by calibrating a water balance model across some watersheds in the South Africa. Thus a comprehensive analysis of all three essential influences: climate, land-use, and human water-withdrawal combined is needed to understand the relative importance of the interactions among those factors on water scarcity.

To achieve our objective, we proposed to evaluate the regional sensitivity of streamflow by first postulating

$$Q = f(P, T, L_a, L_g, L_f, L_u, W) \tag{1}$$

where Q, P, T, L_a, L_g, L_f, L_u, W represent streamflow, precipitation, temperature, agriculture land, grass land, forested land, urban land, and water withdrawals respectively. Then we proceeded on estimation of a specific measurement of sensitivity: elasticity based on equation (1).

Methodology

Estimation of Elasticity

Schaake (1990) borrowed the concept of elasticity from the field of economics and introduced the concept of elasticity of streamflow into the field of hydrology. In general, for variables Y and X_i which are associated by a continuous and differentiable function $y = f(x_1,..., x_i)$, the X_i elasticity of Y, which measures the proportional change in Y in response to proportional change in X_i, is defined as

$$\varepsilon_{y,x_i}(x_i) = \frac{\partial y}{\partial x_i}\frac{x_i}{y} \tag{2}$$

The point estimate of X_i elasticity of Y, which we term $\varepsilon_{y,x_i}(x_i)$, is a function of x_i and is critically dependent on the functional form $y = f(x_1,..., x_i)$ and its first order derivative $f'(x_1,..., x_i)$. The "factor" elasticity of streamflow denotes a proportional change in streamflow in response to a proportional change in a certain "factor", for example, the precipitation elasticity of streamflow represents a percentage change in streamflow in response to a percentage change in precipitation. Another commonly adopted measure of elasticity is defined about the mean values of the function so that the sensitivity of a variable Y to changes in variable X_i can be termed the X_i elasticity of Y about their mean values, which we denote as $\varepsilon_{\bar{y},\bar{x}_i}$, and define as:

$$\varepsilon_{\bar{y},\bar{x}_i} = \frac{\partial y}{\partial x_i}\frac{\bar{x}_i}{\bar{y}} \tag{3}$$

Standardized departures about mean-ordinary least squares (SDM-OLS) elasticity estimator:

According to equation (1), we suppose that the absolute change in Q is a linear combination of the absolute changes in P, T, L_a, L_g, L_f, L_u, and W:

$$dQ = \frac{\partial Q}{\partial P}dP + \frac{\partial Q}{\partial T}dT + \frac{\partial Q}{\partial L_a}dL_a + \frac{\partial Q}{\partial L_g}dL_g + \frac{\partial Q}{\partial L_f}dL_f + \frac{\partial Q}{\partial L_u}dL_u + \frac{\partial Q}{\partial W}dW \tag{4}$$

Substituting the absolute change in each term in (4) for the departure from the mean, we obtain:

$$Q - \overline{Q} = \frac{\partial Q}{\partial P}(P - \overline{P}) + \frac{\partial Q}{\partial T}(T - \overline{T}) + \frac{\partial Q}{\partial L_a}(L_a - \overline{L}_a) +$$

$$\frac{\partial Q}{\partial L_g}(L_g - \overline{L}_g) + \frac{\partial Q}{\partial L_f}(L_f - \overline{L}_f) + \frac{\partial Q}{\partial L_u}(L_u - \overline{L}_u) + \frac{\partial Q}{\partial W}(W - \overline{W}) \tag{5}$$

and equation (5) is equivalent to

$$\frac{Q - \overline{Q}}{\overline{Q}} = \frac{\partial Q}{\partial P}\frac{\overline{P}}{\overline{Q}}(\frac{P - \overline{P}}{\overline{P}}) + \frac{\partial Q}{\partial T}\frac{\overline{T}}{\overline{Q}}(\frac{T - \overline{T}}{\overline{T}}) + \frac{\partial Q}{\partial L_a}\frac{\overline{L}_a}{\overline{Q}}(\frac{L_a - \overline{L}_a}{\overline{L}_a}) +$$

$$\frac{\partial Q}{\partial L_g}\frac{\overline{L}_g}{\overline{Q}}(\frac{L_g - \overline{L}_g}{\overline{L}_g}) + \frac{\partial Q}{\partial L_f}\frac{\overline{L}_f}{\overline{Q}}(\frac{L_f - \overline{L}_f}{\overline{L}_f}) + \frac{\partial Q}{\partial L_u}\frac{\overline{L}_u}{\overline{Q}}(\frac{L_u - \overline{L}_u}{\overline{L}_u}) + \frac{\partial Q}{\partial W}\frac{\overline{W}}{\overline{Q}}(\frac{W - \overline{W}}{\overline{W}}) \tag{6}$$

According to equation (3), equation (6) can be expressed in terms of elasticities about the mean:

$$\frac{Q - \overline{Q}}{\overline{Q}} = \varepsilon_{\overline{Q},\overline{P}}(\frac{P - \overline{P}}{\overline{P}}) + \varepsilon_{\overline{Q},\overline{T}}(\frac{T - \overline{T}}{\overline{T}}) + \varepsilon_{\overline{Q},\overline{L}a}(\frac{L_a - \overline{L}_a}{\overline{L}_a}) +$$

$$\varepsilon_{\overline{Q},\overline{L}g}(\frac{L_g - \overline{L}_g}{\overline{L}_g}) + \varepsilon_{\overline{Q},\overline{L}f}(\frac{L_f - \overline{L}_f}{\overline{L}_f}) + \varepsilon_{\overline{Q},\overline{L}u}(\frac{L_u - \overline{L}_u}{\overline{L}_u}) + \varepsilon_{\overline{Q},\overline{W}}(\frac{W - \overline{W}}{\overline{W}}) \tag{7}$$

where $\varepsilon_{\overline{Q},\overline{P}}$, $\varepsilon_{\overline{Q},\overline{T}}$, $\varepsilon_{\overline{Q},\overline{L}a}$, $\varepsilon_{\overline{Q},\overline{L}g}$, $\varepsilon_{\overline{Q},\overline{L}f}$, $\varepsilon_{\overline{Q},\overline{L}u}$, $\varepsilon_{\overline{Q},\overline{W}}$ represent the precipitation, temperature, agriculture-land, grass-land, forested-land, urban-land, and water-withdrawal elasticities of streamflow, respectively. A natural estimator of the elasticities in equation (7) would be an ordinary least squares (OLS) regression estimator without fitting intercept if the residuals in (7) are approximated by a normal distribution. It will be necessary to check this assumption in practice.

Data

All watersheds across the eastern United States, consisted of water resources regions 01, 02, and 03 (Figure 1), are included in the analysis and they are delineated at the 8-digit hydrologic unit code (HUC) scale. For each HUC, we compiled a set of data which contains observations of streamflow, precipitation, temperature, size of forested land, size of agriculture land, size of grass land, size of urban land, and freshwater withdrawals for year 1995. All values in this set of data, except the land-use, freshwater withdrawals were smoothed temporally from water years 1993 to 1997 to represent the observations for 1995.

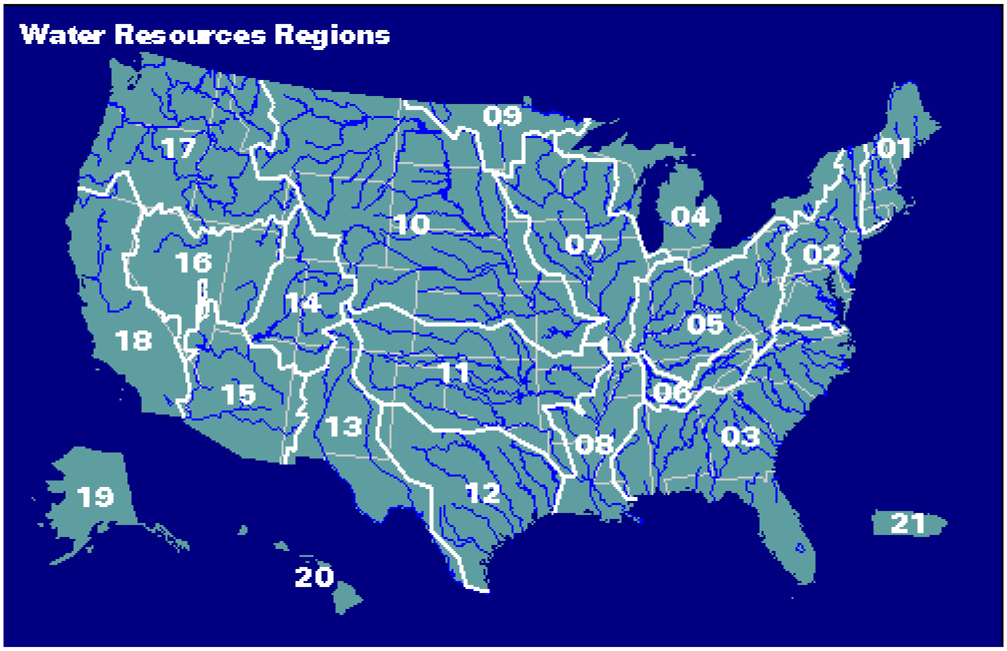


Figure 1. The map of the U.S. water resources regions.

***Streamflow Data*:** Monthly streamflow observations accounting for human water withdrowals and return flows for all watersheds were compiled by the U.S. Geological Survey (USGS). (Need to communicate with Wolock for details of concept or procedures of obtaining these flows) The annual mean streamflow (cubic kilometers) for water year 1995 was estimated by arithmetic mean. The annual minimum flow (cubic kilometers) for water year 1995 was represented by the minimum of the monthly flows from water years 1993 to 1997.
Climate Data: Monthly precipitation observations at water year 1995 are estimated from a spatial interpolation model: PRISM (parameter-elevation regressions on independent slopes model) for each watershed (Daly et al., 1994). PRISM is considered a better approach than other interpolation methods such as in verse distance or kriging for it employs spatial regression procedure that accounts for topography affecting precipitation or temperature. The annual mean precipitation (millimeters) was estimated by arithmetic mean. The annual mean temperature in $^{0}C\times10$ are used in this study.
***Land Use Data*:** The sizes of the forested, agriculture, grass and urban lands (in square kilometer) of all watersheds across the eastern U.S. at year 1997 were compiled by using Enhanced National Land-Coverage Datasets (NLCDE) that was developed based on the National Land Coverage Dataset (NLCD).
***Water Withdrawal Data*:** The total fresh water withdrawals (million gallons/day) of each watershed in 1995 were obtained from the water use data published by the USGS, in which estimates of withdrawals categorized by area, use, and source is compiled at a five-year interval. The total fresh water withdrawals which were the sum of the total fresh ground and surface water withdrawals are consisted of water use for public supply, commercial, domestic, industrial, thermoelectric power, mining, livestock, and irrigation.

Principal Findings and Significance

Results

The estimates of the elasticities of the annual mean streamflow (1) across the eastern United States were obtained for water resources regions 01, 02, and 03 and are given in Table 1 and Figure 2. The p-values associated with all estimates are fairly small, except these associated with temperature elasticity (p-value = 0.444), agriculture-land elasticity (p-value = 0.813), grass-land elasticity (p-value = 0.747), and water-withdrawal elasticity (p-value = 0.322) across region 01. Small p-values indicate model coefficients with a high degree of precision. In general, as long as the p-value is less than 0.05, the coefficients can be considered to be statistically significant. The estimates of temperature elasticity are negative as expected and indicate that the increase in temperature leads to decrease in streamflow. Generally, the water withdrawal elasticities had either high p-values (regions 1 and 2) or were positive (region 3) which makes little sense. We conclude that water withdrawal elasticity can only be computed at much smaller spatial and temporal scales than considered here.

A comparison of estimates of precipitation elasticity from this research, Vogel et al. (1999), and Limbrunner (1998) is shown in Table 2. There is fairly close agreement between the three studies.

The estimates of the elasticities of the annual minimum flow are given in Table 3 and Figure 3. A comparison of Tables 1 and 3, indicates that the relative sensitivity or elasticity corresponding to canges in urban land and human water are much greater for the low flows than for the annual mean streamflows. Further work is needed a much finer spatial and temporal scale to obtain more meaningful elasticities. Still, the results given here do quantify the impacts of changes in climate and land use on streamflows.

Table 1. The estimates of the elasticities of the annual mean streamflow and their p-values enclosed in brackets below the elasticity estimates.

Region(s)	**Elasticities of the Annual Mean Streamflow**						
	Precipi-tation $\varepsilon_{\overline{Q},\overline{P}}$	**Tempera-ture** $\varepsilon_{\overline{Q},\overline{T}}$	**Agricul-ture land** $\varepsilon_{\overline{Q},\overline{L}a}$	**Grass Land** $\varepsilon_{\overline{Q},\overline{L}g}$	**Forested Land** $\varepsilon_{\overline{Q},\overline{L}f}$	**Urban Land** $\varepsilon_{\overline{Q},\overline{L}u}$	**Water With-drawal** $\varepsilon_{\overline{Q},\overline{W}}$
01, 02, 03	1.443 (0.000)	-0.653 (0.000)	0.094 (0.000)	0.094 (0.000)	0.709 (0.000)	0.135 (0.000)	0.012 (0.071)
01	1.259 (0.00)	-0.065 (0.444)	0.006 (0.813)	0.007 (0.747)	0.883 (0.000)	0.160 (0.000)	-0.015 (0.322)
02	1.281 (0.001)	-0.450 (0.000)	0.186 (0.000)	0.115 (0.000)	0.609 (0.000)	0.140 (0.000)	-0.023 (0.094)
03	2.054 (0.000)	-0.710 (0.000)	0.136 (0.000)	0.128 (0.000)	0.609 (0.000)	0.147 (0.000)	0.024 (0.001)

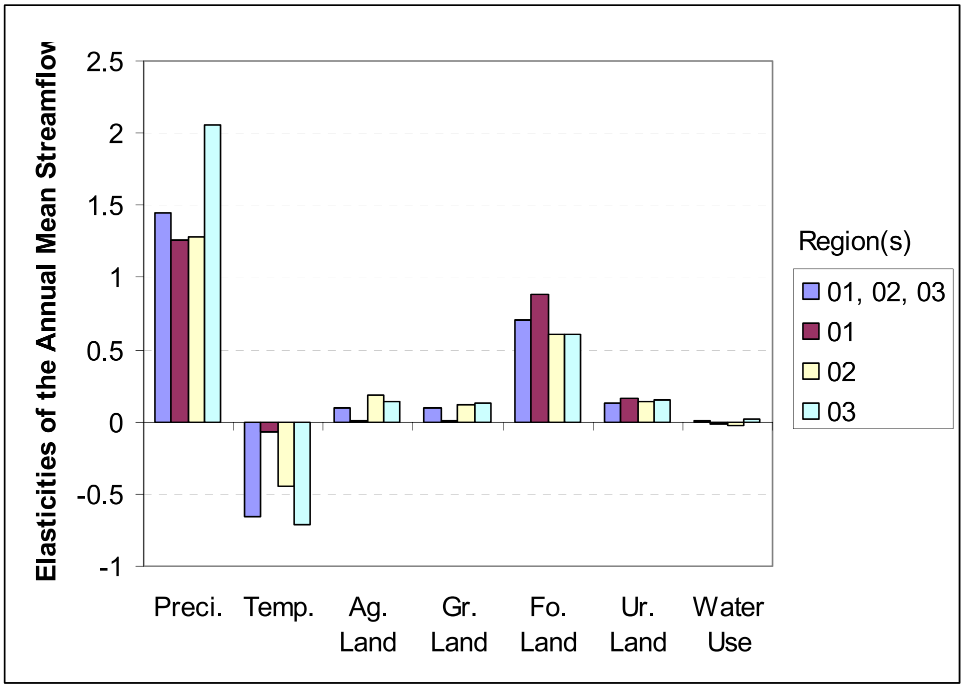


Figure 2. Estimates of all types of elasticities of the annual mean streamflow across (1) regions 01, 02, 03, (2) region 01, (3) region 02, and (4) region 03. The p-values associated with all estimates are fairly small, except these associated with temperature elasticity (p-value = 0.444), agriculture-land elasticity (p-value = 0.813), grass-land elasticity (p-value = 0.747), and water-withdrawal elasticity (p-value = 0.322) across region 01.

Table 2. Comparison of precipitation elasticity estimates obtained from this research, Vogel et al (1999), and Limbrunner (1998)

	Precipitation Elasticity		
Region	Elasticity obtained using SDM-OLS estimator (this research)	Mean at site elasticity (Limbrunner)	Elasticity by regional nonlinear regression (Vogel)
01	1.26	1.53	1.21
02	1.28	1.51	1.63
03	2.05	1.97	2.26

Table 3. The estimates of the elasticities of the annual low flow (the lowest monthly flows from water years 1993 to 1997) and their p-values enclosed in brackets below the elasticity estimates.

Region(s)	**Elasticities of the Annual Mean Streamflow**						
	Precipitation $\varepsilon_{\bar{Q},\bar{P}}$	**Temperature** $\varepsilon_{\bar{Q},\bar{T}}$	**Agriculture land** $\varepsilon_{\bar{Q},\bar{L}a}$	**Grass Land** $\varepsilon_{\bar{Q},\bar{L}g}$	**Forested Land** $\varepsilon_{\bar{Q},\bar{L}f}$	**Urban Land** $\varepsilon_{\bar{Q},\bar{L}u}$	**Water With-drawal** $\varepsilon_{\bar{Q},\bar{W}}$
01, 02, 03	2.656 (0.00)	-0.805 (0.00)	0.066 (0.237)	0.151 (0.020)	0.582 (0.000)	0.305 (0.000)	0.031 (0.250)

01	2.463 (0.213)	-1.445 (0.015)	-0.409 (0.020)	-0.196 (0.208)	0.868 (0.000)	0.226 (0.200)	0.214 (0.045)
02	2.367 (0.101)	-0.874 (0.019)	0.251 (0.004)	0.081 (0.430)	0.431 (0.016)	0.375 (0.000)	-0.094 (0.074)
03	2.409 (0.003)	-1.323 (0.162)	0.094 (0.341)	0.374 (0.007)	0.091 (0.677)	0.410 (0.000)	0.063 (0.065)

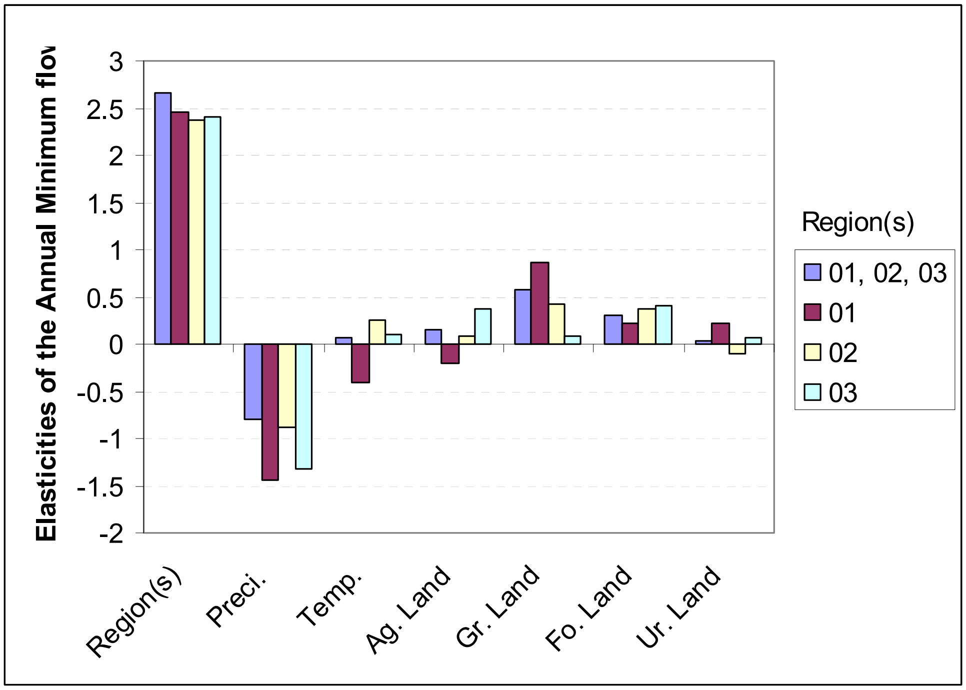


Figure 3. Estimates of all types of elasticities of the annual minimum flow across (1) regions 01, 02, 03, (2) region 01, (3) region 02, and (4) region 03.

Conclusions and Discussions

Our results indicate that across broad regions of the eastern United States the annual mean streamflow is most sensitive to the changes in annual mean precipitation, followed by changes in mean temperature, forested land, urban land and/or agriculture lands, grass land, and the human water withdrawals (p-value = 0.071 and 0.001 for regions 02 and 03 respectively). Over the spatial and temporal scales considered, changes in water use behavior do not seem to have a very large impact on streamflow levels. We expect that if the analysis was done at much finer spatial and temporal scales, that much greater water withdrawal elasticities would be seen. Generally, the impacts of changes in urban, agriculture, and grass lands to the annual mean streamflow are approximately the same throughout the eastern U.S. We also found similar precipitation elasticities of annual streamflow as did a recent national analysis by Limbrunner (1998) and Vogel et al. (1999).

Generally this initial research documents the impacts of changes in land use, climate and to some extent water withdrawals on annual average and annual minimum streamflows across broad regions of the eastern United States. The sensitivity of streamflows to changes in urban and forested land uses are quite dramatic and together, on par with the sensitivity of streamflows to changes in climate. Thus our work highlights the importance of land-use management for controlling future changes in streamflow.

Publications and Conference Presentations

a. Articles in Refereed Scientific Journals

Tsai, Y. and R.M. Vogel, 2009, Impact of Climatic and Human Influences on Freshwater Availability, *Advances in Water Resources*, manuscript in preparation.

c. Dissertations

Tsai, Y., 2009, The Sensitivity of Streamflow to Changes in Climate, Land Use and Water Infrastructure, Tufts University, dissertation in progress, expected completion, 2010.

Student Support

- List each student fully or partially supported with this project

  Yushiou Tasi
- The degree they were pursuing

  Ph.D.
- Their department

  Department of Civil and Environmental Engineering

References

Andréassian, V., 2004, Waters and Forests: From Historical Controversy to Scientific Debate, *Journal of Hydrology,* 291, 1-27.

Beighley, R.E., and G.E. Moglen, 2003, Adjusting measured peak discharges from an urbanizing watershed to reflect a stationary land use signal, *Water Resour. Res.*, 39(4), 1093, doi: 10.1029/2002WR001864.

Billings R.B. and W.M. Day, 1989, Demand management factors in residential water use: the southern Arizona experience, *Journal AWWA*, March, 58-64.

Canfield, S., L. Claessens, C. Hopkinson, Jr, E. Rastetter, and J. Vallino, 1999. Long-Term Effect of Municipal Water Use on the Water Budget of the Ipswich River Basin. *Biol. Bull*. 197: 295-297.

Foster, H.S. Jr. and B.R. Beattie, 1979, Urban residential demand for water in the United States, Land Economics, 55(1), 43-58.

DeWalle, D.R., B.R. Swistock, T.E. Johnson, and K.J. McGuire, 2000, Potential effects of climate change and urbanization on mean annual streamflow in the United States, *Water Resources Research*, 36(9), 2655-2664.

Farmer, D., M. Sivapalan, and C. Jothityangkoon, 2003, Climate, soil, and vegetation controls upon the variability of water balance in temperate and semiarid landscapes: Downward approach to water balance analysis, *Water Resources Research*, 39(2), 1035, doi: 10.1029/2001WR000328.

Limbrunner, J.F., 1998, Climatic elasticity of streamflow in the United States, M.S. thesis, 39pp, Tufts Univ. Medford, Mass.

Lyman, R.A., 1992, Peak and off-peak residential water demand, *Water Resources Research*, 28(9), 2159-2167.
Oudin, L., V. Andréassian, J. Lerat, C. Michel, 2008, Has Land Cover A Significant Impact on Mean Annual Streamflow? An International Assessment Using 1508 Catchments, *Journal of Hydrology,* 357, 303-316.
Renwick, M. E. and R. D. Green, 2000. Do Residential Water Demand Side management Policies Measure Up? An Analysis of Eight California Water Agencies. *Journal of Environmental Economics and Management* 40: 37-55.
Schaake, J.C., 1990, From climate to flow, in Climate Change and U.S. Water Resources, edited by P. E. Waggoner, chap. 8, pp. 177-206, John Wiley, New York.
Schot, P.P, J. Vanderwal, 1992, Human impact on regional groundwater composition through intervention in natural flow patterns and changes in land-use, *Journal of hydrology*, Vol 134, Issue 1-4, 297-313.
Vogel, R.M., I. Wilson, C. Daly, 1999, Regional Regression Models of Annual Streamflow for the United States, *Journal of Irrigation and Drainage Engineering*, 125 (3), 148-157.
Zhang, L., W.R. Dawes, and G.R. Walker, 2001, Response of mean annual evapotranspiration to vegetation changes at catchment scale, *Water Resources Research*, 37(3), 701-708.
Zarghami, M., A. Abrishamchi, and R. Ardakanian, 2008, Multi-criteria decision making for integrated urban water management, *Water Resources management*, Vol. 22, Issue 8, 1017-1029.
Zarriello, P.J. and K.G. Ries, III, 2000. A precipitation-runoff model for the analysis of the effects of water withdrawals on streamflow, Ipswich River Basin, Massachusetts, U.S. Geological Survey Water-Resources Investigation Report 00-4029. 107 pp.

Quantifying Sediment Transport in Red Brook, Wareham, Massachusetts: Impacts of Dam Removal

Basic Information

Title:	Quantifying Sediment Transport in Red Brook, Wareham, Massachusetts: Impacts of Dam Removal
Project Number:	2008MA133B
Start Date:	6/1/2008
End Date:	5/31/2009
Funding Source:	104B
Congressional District:	9
Research Category:	Climate and Hydrologic Processes
Focus Category:	Geomorphological Processes, Sediments, Management and Planning
Descriptors:	None
Principal Investigators:	Ellen Marie Douglas, Allen Gontz, Steven Kichefski

Publication

Problem and Research Objectives

The U.S. Environmental Protection Agency identified sediment as the most widespread pollutant in the Nation's rivers and streams, affecting aquatic habitat, drinking water treatment processes, and recreational uses of rivers, lakes, and estuaries (Bent et al., 2001). Confounding these impacts is the fact that dams, dikes and water control structures impound sediment and impede the natural flow and transport processes within a river. In addition, the effects of the removal of such flow impoundments on sediment processes are largely unknown. Since 2000, the Massachusetts Riverways Program and partners have overseen the removal of six dams and have seven more priority projects in various stages of the dam removal process[1]. Despite the importance of sediment concentrations On water quality, little has been done in Massachusetts to document the long term impacts of dam removal on sediment transport and its ultimate impact on the local watershed. With this in mind, our research has quantified the pre- and post- dam removal sediment dynamics within the Red Brook, a 4.5 mile small, spring-fed, coastal stream near the town of Wareham in southeastern Massachusetts. Red Brook is currently on the priority projects list of the Massachusetts Riverways Program[2]. The long-term goal of the Red Brook Restoration project is to naturalize the stream and restore its function by removing man-made structures, eliminating sources of unnatural sedimentation, and enhancing habitat for anadromous fishes, specifically Salter brook trout[3]. This sea-run brook trout is found in very few places in Massachusetts, making this a critical habitat for restoration. The Red Brook Restoration project is innovative in that the sediment mitigation plan will not include dredging, but rather, will rely on the natural re-suspension and transport of accumulated sediment (Tim Purinton, Massachusetts Riverways Program, personal communication, Nov 14, 2006). Critical needs for this project include understanding sediment dynamics, determining sediment sources and developing a sediment management plan. In support of these critical needs, the objectives of our research are to:

- Characterize the hydrogeomorphic characteristics of the lower Red Brook;
- Quantify cross-section geometry and sediment transport before and after removal of the Upper Flume, which occurred in September 2008..
- Test and compare methods outlined in the newly published guidelines for stream barrier removal.

Methodology

[1] http://www.mass.gov/dfwele/river/programs/stream/index.htm
[2] http://www.mass.gov/dfwele/river/programs/priorityprojects/redbrook.htm
[3]http://www.americanrivers.org/site/News2?JServSessionIdr006=fo8tyzfmr1.app6b&page=NewsArticle&id=9111&news_iv_ctrl=-1

Monitoring began in April 2008 with a combination of in-situ measurements (for channel geometry and bedload sampling), geophysical techniques (ground penetrating radar) and a remotely-accessed environmental sensor network to monitor flow in the Brook before and after the flume removal. We have based our monitoring approach on four methodologies recommended in the *Stream Barrier Removal Monitoring Guide* (Collins *et al*., 2007). These include detailed cross-section surveys, grain-size analysis, longitudinal profiles and photostations. Prior to Upper Flume removal in September 2008, we established 14 permanent cross-sections throughout the study area with two of these several hundred feet upstream of the Upper Flume as reference cross-sections. When surveying each cross-section we also probed the channel bottom to refusal to determine the depth of unconsolidated sand deposits overlaying the natural gravel bed. The natural gravel bed is the preferred habitat for salter trout. In June 2008, we conducted a Ground Penetrating Radar survey of the project reach. This provided another means of defining the longitudinal profile of the reach and to estimate the depth of sand deposits. Also in June 2008, thanks to the funds made available through this WRRC grant, we installed a remotely monitored acoustic depth sensor for continuous monitoring of changes in the water surface elevation of the Brook (see Figure 1). Distance to the water surface is measured continuously; data is telemetrically transmitted to a websit: https://www.hobolink.com/p/0c1219967f03a7a652064389eeb98356. A rating curve for this cross-section is being established using periodic streamflow measurements. An electromagnetic current sensor will be added to this station in early summer 2009. This will enable us to continuously measure changes in both depth and velocity, and thereby remotely monitor streamflow. In July 2008, we surveyed a longitudinal profile and valley-wide cross-sections using a Real Time Kinetic GPS system. We are periodically collecting bedload transport and streamflow measurements from the upstream and downstream ends of the study reach in order to estimate sediment flux through the system. All 14 cross-sections were resurveyed in Winter 2009 to establish sub-annual, post-flume removal changes in channel geometry. Another round of cross-section surveys is scheduled for Summer 2009.

Figure 1: Remotely accessed water depth sensor installed at Red Brook with funding from this grant.

Principal Findings and Significance

Continuous WSE data collected from the sensor indicate a significant tidal influence, which needs to be accounted for in our rating curve (see Figure 2). Data reduction and analysis is currently underway.

Statistical analysis of the difference between Winter 2009 and Summer 2008 geometry at the 14 cross-sections indicated significant changes only in the cross-sections closest to the former Upper Flume site (see Figure 3a and 3b). This is one of the major challenges of this project. A streamflow hydrograph estimated from the sensor data combined with the established rating curve is being used to calibrate a HEC-RAS model of the Brook. This model will be used to estimate the time for transport of sand deposits within the reach and project the possible effects of future restoration activities at the Brook.

References

Bent, G. C., J. R. Gray, K. P. Smith and G. D. Glysson, 2001. A synopsis of technical issues for monitoring sediment in highway and urban runoff, U. S. Geological Survey Open File Report 00-497, Northborough, Massachusetts.

Collins, M, K. Lucey, B. Lambert, J. Kachmar, J. Turek, E. Hutchins, T. Purinton and D. Neils. 2007. Stream Barrier Removal Monitoring Guide, Gulf of Maine Council on the Marine Environment. Available on-line at www.gulfofmaine.org /streambarrierremoval.

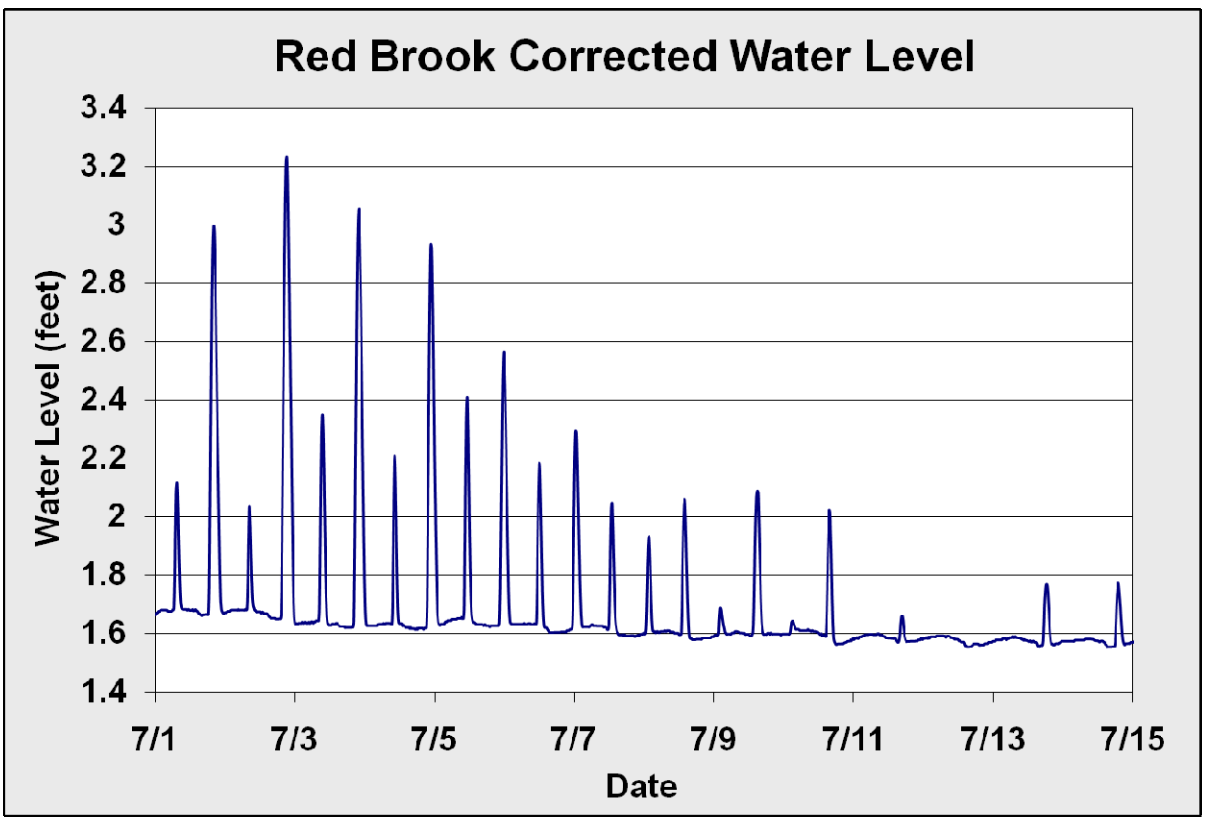
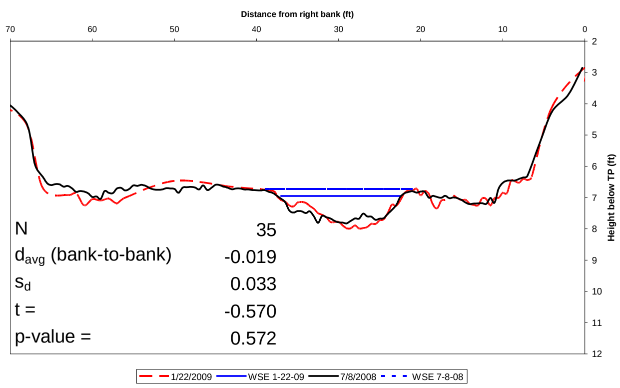


Figure 2: Segment of continuously monitored water levels from acoustic sensor installed with funding from this grant.

Reference Reach



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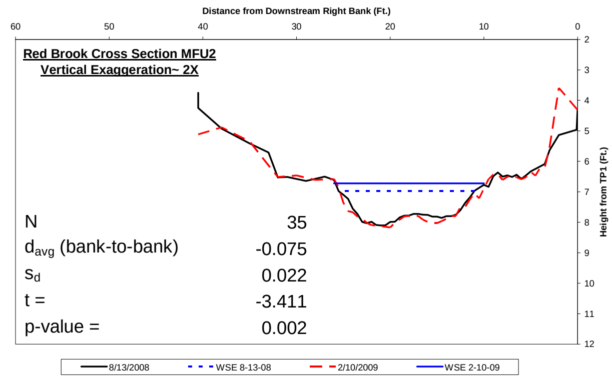

Figure 3a: Difference between Summer 2008 (black) and Winter 2009 (red) channel elevations at the reference reach. Average difference is not statistically significant at 95%.

Figure 3b: Difference between Summer 2008 (black) and Winter 2009 (red) channel elevations at cross-section just downstream of former Upper Flume location. Average difference is statistically significant at 95%.

Publications and Conference Presentations

Articles in Refereed Scientific Journals

Kichefski, S. and E. M. Douglas, Monitoring changes in flow and sediment transport in Red Brook, a small coastal stream in southeastern, Massachusetts, in preparation.

Fradkin, B. and E. M. Douglas, Modeling the impacts of river restoration on fluvial hydrology in Red Brook, in preparation.

Conference Presentations

Monitoring and Modeling the Hydrological Impacts of Stream Restoration in Red Brook, a small coastal stream in southeastern Massachusetts, Water Resources Research Conference, April 2009, Amherst, MA.

Monitoring the restoration of Red Brook, a small coastal stream in southeastern Massachusetta, Geological Society of America, Northeast Chapter, March 2009, Portland ME.

Modeling the Hydrological Impacts of Stream Restoration in Red Brook, a small coastal stream in southeastern Massachusetts, Geological Society of America, Northeast Chapter, March 2009, Portland ME.

Monitoring the restoration of Red Brook, a small coastal stream in southeastern Massachusetts, AGU Fall 2008, San Francisco, CA.

Graduate Theses

Kichefski, Steven, Monitoring changes in flow and sediment transport in Red Brook, a small coastal stream in southeastern, Massachusetts, MS thesis, Environmental Science, University of Massachusetts Boston, August 2009.

Fradkin, Barry, Modeling the impacts of river restoration on fluvial hydrology in Red Brook, MS thesis, Environmental Science, University of Massachusetts Boston, August 2009.

<u>Graduate Student Support</u>

Matching funds for this project supported Steven F. Kichefski during the 2008-2009 academic year towards completion of an MS in Envirnomental Sciences at the University of Massachusetts, Boston.

Toxicity of carbon nanotubes to the activated sludge process: protective ability of extracellular polymeric substances

Basic Information

Title:	Toxicity of carbon nanotubes to the activated sludge process: protective ability of extracellular polymeric substances
Project Number:	2008MA135B
Start Date:	4/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	5th
Research Category:	Biological Sciences
Focus Category:	Toxic Substances, Wastewater, None
Descriptors:	None
Principal Investigators:	Xiaoqi (Jackie) Zhang, Lauren Ann Luongo

Publication

Problem and Research Objectives: The discharge of carbon nanotubes (CNTs) from industrial waste or disposal of such materials from commercial and/or domestic use will inevitably occur with increasing production and enter into wastewater treatment facilities with unknown consequences. The objective of this study was to evaluate the possible toxicity that multi-walled carbon nanotubes (MWCNTs) incur on the microbial communities present in the activated sludge by using a respiration inhibition test and the role of EPS when the activated sludge is exposed to MWCNTs.

Methodology:

(1) MWCNTs

MWCNTs with purity greater than 90% (Sigma-Aldrich) were used. The outer diameter, inner diameter, and length were reported by the manufacturer to be 10-15 nm, 2-6 nm, and 0.1-10 μm. The impurities include 2.3% Al and 1.9% Fe trace metal with no amorphous carbon present.

Four concentrations of MWCNTs in distilled water were prepared, 0.64, 1.44, 2.16, and 3.24 g/L. Selection of these concentrations was based on preliminary tests performed in the laboratory in order to achieve a dose-response of the impact of MWCNTs on the respiratory inhibition to the microbial communities in the activated sludge. The MWCNTs were sonicated to achieve better dispersion by using an ultrasonic cup horn (Sonicator 3000 Ultrasonic Liquid Processor, Misonix Incorporated).

(2) Field sampling and sample preparation

Fresh activated sludge was obtained from the aeration tank of the Lowell Wastewater Treatment Facility (Lowell, MA) every morning before each experiment and transported immediately to the laboratory. In the laboratory, the mixed liquor was mixed, aerated and its mixed liquor suspended solids (MLSS) was measured according to standard methods (American Public Health Association, 1998). As part of the requirements for the respiration inhibition test conducted later, the mixed liquor was concentrated to a MLSS of 2000 mg/L based on the initial MLSS information (EPA, 1996). Half of the concentrated mixed liquor was sheared to release the EPS from the activated sludge flocs and the other half was left as unsheared. A commercial Waring blender (model 5011) was used to successfully shear the mixed liquor for 5 minutes on high (22,000 rpm) (Henriques and Love, 2007). The blender was wrapped with ice packs to prevent temperature increases during the shearing process.

(3) EPS content quantification

Both the sheared and unsheared samples were filtered through a 1.0 μm glass fiber filter by using a 25 mL syringe (and stored at -20°C if not analyzed immediately). The EPS content was quantified through soluble protein and carbohydrate analyses to determine the release of EPS as a result of mechanical shearing. A Total Protein Kit (Micro-Lowry Peterson's Modification) was obtained from Sigma-Aldrich (Lowry et al., 1951), BSA was used as standard. The Dubois method was used for carbohydrate analysis (Dubois et al., 1956), dextrose was used as standard. A UV-visible spectrophotometer (Agilent 8453) was used to measure the absorbance. DNA concentrations were also measured using a fluorometer (Hoefer DyNA Quant 200, Amersham Biosciences) and calf thymus as a standard solution of known DNA concentration (Labarca et al., 1980). DNA concentrations were measured to test for any disruption in cell viability during the shearing process.

(4) Respiration inhibition test

A respiration inhibition test was used to measure biological activity. It was performed on both sheared mixed liquor and unsheared mixed liquor to demonstrate the potential toxicity posed by MWCNTs and to better understand the extent of EPS in protecting the microorganisms from the toxicity of CNTs.

Principal Findings and Significance:

The main conclusions that can be drawn from this study are summarized as the following:

- Shearing didn't affect respiration rates.
- Greater respiration inhibition was seen in the sheared activated sludge (Figure 1), suggesting the importance of EPS
    - By binding MWCNTs
    - Reduce their toxicity
- Mechanical shearing of mixed liquor (and the subsequent release of EPS into the bulk liquid) allowed the microbial communities to be more readily exposed to the MWCNTs, which subsequently resulted in more respiration inhibition for the sheared mixed liquor compared to the unsheared mixed liquor.

This work illustrates that MWCNTs could pose toxicity in a biological wastewater treatment process. Further research is needed to exam the mechanisms of the toxicity induced by MWCNTs and the factors that have contributed to the toxicity seen.

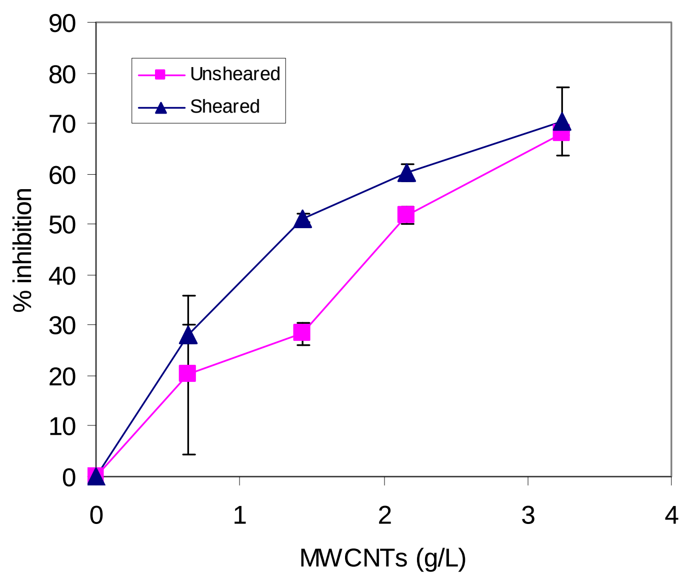

Figure 1. Respiration inhibition for both sheared and unsheared activated sludge.

Publications and Conference Presentations

Dissertation

Luongo, Lauren, 2008, Toxicity of carbon nanotubes to the activated sludge process: Protective ability of extracellular polymeric substances, MS thesis, Department of Civil & Environmental Engineering, University of Massachusetts Lowell, Lowell, MA, ~180 pages.

Conference Proceedings

Luongo, Lauren and Xiaoqi Zhang, 2009, Toxicity of carbon nanotubes to the activated sludge process: Protective ability of extracellular polymeric substances. *International Conference on the Environmental Implications and Applications of Nanotechnology*. June, 2009, Amherst, MA. (Accepted)

Student Support

Lauren Luongo, (2008) MS in Environmental Studies, Department of Civil & Environmental Engineering, UML

References:

American Public Health Association, American Water Works Association, Water Environment Federation, 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. Washington, DC.

EPA (1996). Modified Activated Sludge, Respiration Inhibition Test for Sparingly Soluble Chemicals. Ecological Effects Test Guidelines OPPTS 850.6800, Environmental Protection Agency (EPA).

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., (1956). Colorimetric method for determination of sugars and related substances. Analytical Chemistry 28, 350-357.

Henriques, I. D. S., Love, N.G. (2007). The role of extracellular polymeric substances in the toxicity response of activated sludge bacteria to chemical toxins. Water Research 41(18): 4177-4185.

Labarca, C., and Paigen, K. (1980). A simple, rapid, and sensitive DNA assay procedure. Analytical Biochemistry 102, 344-52.

Lowry, O. H., Rosebrough, N.J., Farr, L., Randall, R. (1951). Protein measurement with the folin phenol reagent. Journal of Biological Chemistry 193, 265-275.

Characterization of wastewater effluent from Western Massachusetts publicly owned treatment works using metaproteomic analysis

Basic Information

Title:	Characterization of wastewater effluent from Western Massachusetts publicly owned treatment works using metaproteomic analysis
Project Number:	2008MA155B
Start Date:	5/18/2008
End Date:	5/17/2009
Funding Source:	104B
Congressional District:	MA-001
Research Category:	Water Quality
Focus Category:	Water Quality, Ecology, Wastewater
Descriptors:	None
Principal Investigators:	Chul Park

Publication

Problem and Research Objectives

Current effluent standards for publicly owned treatment works (POTWs) require 5-day biological oxygen demand (BOD_5) and total suspended solids (TSS) to be less than 30 mg/L on a monthly average basis. While the implementation of these regulatory standards has contributed to significant improvements in the health of receiving waters in the United States, they still allow a considerable amount of organic matter to enter into natural waters via the discharge of treated wastewater. For example, it was reported by the EPA (2000) that POTW effluents account for 42% of the total BOD_5 load into the Connecticut River, which is greater than that from urban and rural run offs and other types of point-source discharges into the same water body.

While pathogenic organisms and trace organics in the wastewater effluent have been extensively studied, organic matter contributing to the allowable limit of 30 mg/L BOD_5 and TSS remains largely uncharacterized. It is expected that POTW effluent would contain any form of organic matter, from unprocessed or partially degraded influent sewage organics to the constituents of biological sludges that escape settling or membrane processes due to ineffective solid/liquid separation. Given the wide array of inputs into a wastewater treatment plant and the biological processes that occur in wastewater treatment facilities, there are many possible sources of organic pollutants that could be commonly released from POTWs under current environmental regulations.

It was previously reported that wastewater effluent organic matter mainly consists of proteins, polysaccharides, and humic substances, with proteins being the most quantitative organic constituent (Confer et al., 1998; Park, 2002). Although proteins constitute a significant portion of POTW effluent organic matter, their identity and nature remain largely unrevealed (Holbrook *et al*., 2005; Jarusutthirak *et al.*, 2002). Consequently, their ecological and environmental impact on receiving waters has been rarely characterized.

The objective of this research was to apply molecular biological techniques in protein research (proteomics) to wastewater effluents to characterize proteins present in effluents that are continuously discharged to the Connecticut River.

Methodology

The proposed research work was composed of two main research tasks: 1) development of methodology, especially a protein concentrating procedure and 2) characterization of effluent proteins from two local wastewater treatment plants that discharge effluents to the Connecticut River. The treatment plants included in this study were the Amherst and Northampton, MA wastewater treatment plants.

The development of an efficient concentrating method is necessary to apply proteomics to wastewater effluent analysis. Various sample preparation processes including ammonium sulfate precipitation, freeze drying, and ultrafiltration have been conducted to find the best method for concentrating proteins in effluents. We determined that ammonium sulfate method was the most suitable for concentrating the proteins and preparing the samples for downstream proteomic analysis: some of these results are shown in the following section. Following the concentrating stage, proteins were separated by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). We have tried several gel staining methods including Coomassie blue staining, silver staining, and zinc staining and we have chosen the first two staining procedures for our routine analysis. We have also conducted zymogramic electrophoresis to detect and isolate active proteolytic enzymes from various effluent samples. Some effluent concentrate samples were sent to another laboratory for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis to identify isolated proteins. In addition, various effluent parameters such as TSS, chemical oxygen demand (COD), cations, anions, and inorganic nitrogen species were measured.

Principal Findings and Significance

The SDS-PAGE results first showed that the protein profiles between primary effluent (partially treated raw sewage) and secondary effluent (final effluent) are consistently different. Figure 1 shows the protein profile in primary and secondary effluents from the Northampton wastewater treatment plant (WWTP). As the figure shows, some heavier proteins appear only in the secondary effluent but not in the primary effluent, indicating that they are soluble microbial products produced during the biological process in wastewater treatment. On the other hand, some protein bands show in both primary and secondary effluents, signifying that these influent proteins persist in the treatment system. Figure 1 also shows that samples that were freeze dried were not as well resolved on the gel as the ammonium sulfate concentrated samples. This is also important information obtained in this study because selecting a right concentration method is critical in performing gel electrophoresis and subsequent mass spectrometry. Most interestingly, 0.45μm filtered secondary effluent (Lane 3) shares high similarity with the crude effluent (Lane 2), indicating that the cell/particle-free fraction of effluent still contains a significant number of protein molecules. This data implies that although some additional filtration steps such as microfiltration will be implemented in the facility, these materials will still be continuously lost to the receiving water. That is, different types of unit operation need to be considered if these protein materials are to be removed from the final discharge.

Figure 2 shows that effluent proteins in Amherst WWTP are substantially different from those from the Northampton wastewater treatment facility (Figure 1), strongly suggesting that two facilities result in different microbial products. This data further suggest that our proteomic approach on effluent could also be used for studying upstream processes.

Figure 3 demonstrates that all effluent samples revealed distinct proteolytic activity against casein proteins. The detection of proteolytic enzymes from the secondary effluent (even from 0.45μm filtered sample) itself is meaningful, but more importantly the data implies that effluent-derived enzymes can degrade aquatic organic matter and, therefore, possibly modulate nutrient cycling in receiving waters.

The current research has allowed us to establish the proteomics method that will be used for future research. The research will be expanded to obtain protein profiles from different facilities including the facilities with biological nutrient removal processes. In the long term, protein bands will be analyzed using tandem mass spectrometry (MALDI-TOF/TOF and LC-MS/MS) until a mass map of proteins from a given facility is constructed. We expect that the established proteomic datasets will permit monitoring the fate of proteins directly in the receiving water or modified laboratory bioassays to evaluate the bioavailability of effluent proteins in receiving waters.

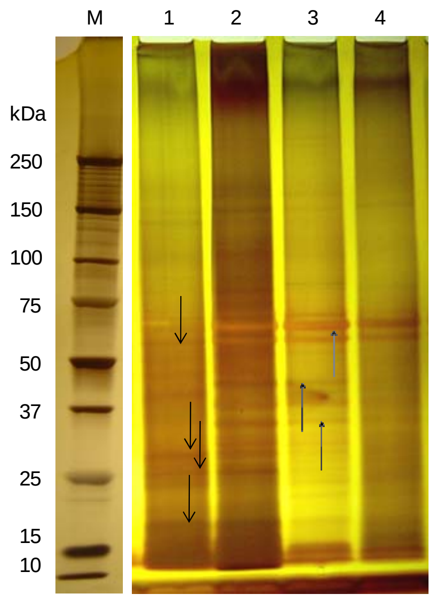

Figure 1. SDS-PAGE of primary effluent (Lane 1), secondary crude effluent (Lane 2), secondary 0.45µm filtered effluent (Lane 3) following ammonium sulfate precipitation, and secondary 0.45µm filtered effluent following freeze drying (Lane 4) from activated sludge facility in Northampton, MA. Up arrows are examples of protein bands that are only found in secondary effluent but not in primary effluent, i.e., soluble microbial products. Down arrows are examples of proteins that are found both in primary and secondary effluents, indicating their persistence in the treatment process. Lane M: molecular weight markers.

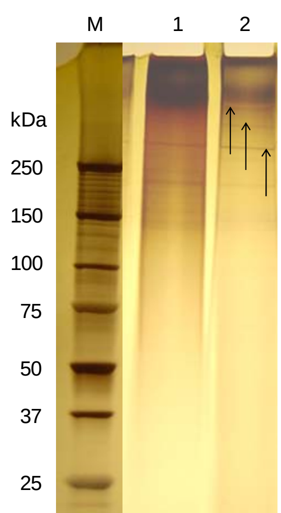

Figure 2. SDS-PAGE of secondary crude effluent (Lane 1) and secondary 0.45μm filtered effluent (Lane 2) following ammonium sulfate precipitation from activated sludge facility in Amherst, MA. Arrows are examples of proteins that are found in the current facility but not in Northampton facility. Lane M: molecular weight markers.

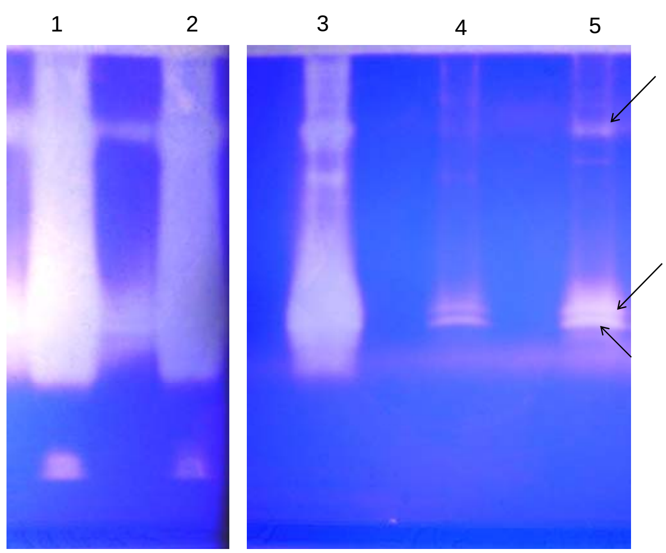

Figure 3. Zymmogramic electrophoresis of Northampton WWTP's primary effluent (Lane 1), Amherst WWTP's primary effluent (Lane 2), Northampton WWTP's secondary crude effluent (Lane 3), secondary 0.45μm filtered effluent (Lane 4), and Amherst WWTP's secondary crude effluent (Lane 5). Proteolytic activity is evidenced by clear streaks and bands where the enzymes have digested the casein protein. Areas of undigested casein are blue. Enzyme bands indicated with arrows are presumably the same proteolytic enzymes found from two different facilities' effluents.

Publications and Conference Presentations

Conference Platform Presentation:

Pamela Westgate and Chul Park (2009) Characterizing the proteins in domestic wastewater effluent discharged to the Connecticut River using proteomic analysis, MAWRRC Conference, University of Massachusetts Amherst.

Poster Presentation and Conference Proceeding

Pamela Westgate and Chul Park (2009) Evaluation of Effluent Proteins: Towards Characterization of Effluent Organic Nitrogen, Water Environment Federation 82nd Annual Technical Exhibition and Conference (WEFTEC 2009), Orlando, FL.

Student Support

Pamela Westgate, Master Candidate, Department of Civil & Environmental Engineering, UMass Amherst

Notable Achievements and Awards

Provide a brief description of any especially notable achievements and awards resulting from work supported by section 104 and required matching funds and by supplemental grants during the reporting period.

The PI's startup funds at UMass Amherst were also used to conduct the current research and to support Ms. Westgate. The data from this research was very useful for preparing a new proposal to MAWRRC funds in 2009. Our proposal "Assessing the Transport and Fate of Effluent Organic Nitrogen in the Connecticut River and Long Island Sound Using Mass Mapping Proteomics Technology" was selected for funding ($30,000) in 2009. This project also brought up the matching funds ($30,000) from Springfield Water and Sewer Commission.

References

Confer, D.R., Logan, B.E. (1998). Location of Protein and Polysaccharide Hydrolytic Activity in Suspended and Biolfilm Wastewater Cultures. *Wat. Res.* 32 (1): 31-38.

Holbrook, R. D., Breidenich, J., Derose, P.C. (2005) Impact of Reclaimed Water on Select Organic Matter Properties of a Receiving Stream-Fluorescence and Perylene Sorption Behavior. *Environmental Science and Technology*, 39, 6453-6460.

Jarusutthirak, C., Amy, G., Croué, J.-C. (2002) Fouling Characteristics of Wastewater Effluent Organic Matter (EfOM) isolates on NF and UF Membranes.

US EPA (2000) Progress in Water Quality-An Evaluation of the National Investment in Municipal Wastewater Treatment. EPA-832-R-00-008, June, 2000.

Environmental Analyses Support

Basic Information

Title:	Environmental Analyses Support
Project Number:	2008MA170B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	1st
Research Category:	Water Quality
Focus Category:	Water Quality, Acid Deposition, Methods
Descriptors:	
Principal Investigators:	Paula Sturdevant Rees, Marie-Francoise Walk

Publication

Problem and Research Objectives

Water quality analyses are in high demand on the University of Massachusetts Amherst campus from a variety of sources: faculty and their graduate students need analytical work done for their research projects; volunteer monitoring groups need a reliable source for quality assurance/quality control audit samples as well as low detection level analyses for nutrients; special projects such as the Acid Rain Monitoring project also need QA/QC samples and the success of these project relies on accurate, low detection limit ion analyses.

Methodology

The research Lab group of Professor Julian Tyson started training on inorganic water analyses at the Environmental Analyses Laboratory in the spring of 2008. The team consisted of five PhD students in the Chemistry Department. They were joined by a sixth member in January 2009. They were all trained in the analysis of pH and alkalinity using a pH-meter and a two-end point titration method. They were also trained in analyzing water samples for total phosphorus and chlorophyll on a UV-visible Spectrophotometer (Shimadzu dual beam, 10 cm path length). Additionally, the students were trained to analyze Acid Rain Monitoring Project samples for SO_4, NO_3, and Cl on an Ion Chromatograph. Finally they learned how to determine the concentrations of Fe, Mg, Si, Mn, Al, Ca, K, Cu, and Na on an Inductively Coupled Plasma Spectrophotometer.

The group organized a new space for the EAL, and provided services for several projects:
They manufactured pH/ANC and dissolved oxygen quality control samples for six Volunteer Monitoring Projects throughout Massachusetts, and pH/ANC quality control samples for the Acid Rain Monitoring Project.

They provided Total Phosphorus and chlorophyll analyses for three Volunteer groups in Massachusetts, a research group in Colorado, and a research project at the University of Massachusetts.

They also performed miscellaneous ion analyses for researchers on campus.

Principal Findings and Significance

This project was successful in training six graduate students in the workings of a service laboratory. They learned new analysis methods and generated data for several research and community projects. They also learned the importance of chain of custody, the maintenance of records, the importance of quality control in performing analyses, and what is involved in dealing with laboratory “clients.”

This setup also allowed for the training of undergraduate students in the Chemistry Department and from nearby high schools, under the supervision of the senior Doctoral Candidate in the Tyson Group.

A significant finding is that such a lab cannot be run exclusively by a group of graduate students. While the students can handle sample analyses, they lack the time and long-term commitment to handle of the details of a service laboratory, such as communications with clients and billing. We conclude that some support staff is necessary in the model to provide high-quality and timely analyses for on and off campus clients.

Publications and Conference Presentations

None at this time

Student Support

- Chengbei Li, PhD student in University of Massachusetts Amherst Chemistry Department was supported with these USGS funds.

Information Transfer Program Introduction

One Information Transfer Project was funded this year:

Water Conference 2008

Basic Information

Title:	Water Conference 2008
Project Number:	2008MA174B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	1st District of Massachusetts
Research Category:	Not Applicable
Focus Category:	Water Quality, Hydrology, Non Point Pollution
Descriptors:	
Principal Investigators:	Paula Sturdevant Rees, Marie-Francoise Walk

Publication

The Water Resources Research Center organized the fifth annual Water Resources Research Conference: *Integrating Water Resources Management.*

The Cooperative State Research, Education, and Extension Service New England Regional Program again cooperated in planning the conference. Six co-sponsors helped underwrite the cost of the conference. Attendance increased from last year to 144. Thanks to an increased sponsorship from the Massachusetts Department of Environmental Protection, attendance and presentations by DEP personnel were greatly increased this year. The Steering Committee was expanded to include many non-UMass professionals.

Thirty posters were presented and a Best Student Poster Award was introduced this year thanks to a private sponsorship of $,1000. The winning poster was "Modeling the effect of leachate transport on regional groundwater chemistry" by Nicholas Newcomb, an undergraduate student in the Natural Science department of Hampshire College.

There were 36 paper platform presentations in three concurrent sessions. The presentations were grouped into four tracks subdivided into three sessions each:

<u>Water Resources Management and Planning</u>
- Water Quality and Enforcement
- Effective Water Management Regulations
- Water Resources Planning

<u>Water Issues in the Field, Lab, and Classroom</u>
- Fish: Water Resources Management Indicator
- Water Research and Climate Change
- Case Studies in Water Resources Education

<u>Stormwater Challenges</u>
- Low Impact Development
- Stormwater Best Management Practices
- Stormwater Monitoring and Management

<u>Identification, Assessment, and Remediation</u>
- Surface / Ground Water Interactions
- Contaminants in Water
- Wastewater Issues

The Keynote Address was given by Ira Leighton, Deputy Regional Administrator for USEAPA New England on *New Developments in Stormwater Policy and Remediation.* Follow-up communications with Mr. Leighton have led to the draft of stormwater modeling proposals at the WRRC.

Students Supported:
1 BS student in Economics at UMass Amherst.

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	1	0	0	0	1
Masters	3	0	0	0	3
Ph.D.	4	0	0	0	4
Post-Doc.	0	0	0	0	0
Total	8	0	0	0	8

Notable Awards and Achievements

Wei Jiang, PhD student in Plant, Soil, and Insect Sciences at the University of Massachusetts, and supported by a 104B grant through the Massachusetts Water Resources Research Center, won first place for her poster presentation at the "Water Dependencies in New England", Massachusetts 6th Annual Water Resources Conference: http://www.umass.edu/psis/news/ne_water_conf.html

104B startup funds for Pamela Westgate and Chul Park at UMass Amherst were used to conduct research that led to a successful full proposal to MAWRRC in 2009 and also brought a 30,000 matching fund from the Springfield Water and Sewer Commission.

Research projects supported by the MA WRRC in 2008 contributed to seven refereed journal publications and five additional publications either currently in preparation or under review.

Research projects supported by the MA WRRC in 2008 contributed to 17 conference presentations.

Research projects supported by the MA WRRC contributed to eight dissertations in 2008.

Publications from Prior Years