MA Water Resources Research Center

Annual Report 2009-2010

March 1, 2009 – June 30, 2010

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Front cover photo: Wallum Lake, by MF Hatte

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http://www.umass.edu/tei/wrrc/WRRC2004/WRRCpublications.html

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Introduction

This report covers the period March 1, 2009 to June 30, 2010[1], the 44th 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 Director of Education and Outreach of the Engineering Research Center for Collaborative Adaptive Sensing of the Atmosphere at the University of Massachusetts Amherst.

Several research projects were conducted at the University of Massachusetts Amherst. Dr. David Boutt of the UMass Department of Geosciences evaluated the sustainability of fractured bedrock as a groundwater resource in his project *Characterizing and Quantifying Recharge at the Bedrock Interface.*

Dr. Baoshan Xing of the UMass Plant, Soil, and Insect Science Department extended work on a two-year project on the *Environmental Behaviors of Engineered Nanoparticles in Water*. His project was granted a no-cost extension until May 31, 2010.

Dr. Chul Park of the Department of Civil and Environmental Engineering worked a second year on his project entitled *Characterization of Wastewater Effluent from Western Massachusetts Publicly Owned Treatment Works using Metaproteomic Analysis*.

Three $5,000 projects to support graduate student projects were granted to study:

- *Characterization of Flow and Water Quality of Stormwater Runoff from a Green Roof* by Suzanne LePage and Dr. Paul Mathisen, Dept. of Civil and Environmental Engineering, Worcester Polytechnic Institute.
- *Bacterial Toxicity of Oxide Nanoparticles and Their Adhesion* by Wei Jiang and Dr. Baoshan Xing, Dept. of Plant, Soil, Insect Sciences, University of Massachusetts Amherst.
- *Impact of Nanoparticles on the Activated Sludge Process: Effects on Microbial Community Structure and Function* by Deepankar Goyal and Dr. Juliette Rooney-Varga, Dept. of Biological Sciences, University of Massachusetts Lowell.

The *Acid Rain Monitoring Project*, led by WRRC Associate Director Marie-Françoise Hatte, was continued for another year in order to document trends in surface water acidification.

Other projects conducted at WRRC include the *Tri-State Connecticut River Targeted Watershed Initiative*, and the continued collaboration with UMass Extension on the *Stream Continuity Project*. The Center is also working on a stormwater clearinghouse project that enables users to search the web for stormwater Best Management Practices and to find innovative technologies available to treat stormwater. The *Blackstone River Water Quality Modeling* project continued. Three new projects were the Massachusetts Department of Environmental Protection *Probabilistic Monitoring*

[1] The USGS reporting year covers March 1 to February 28, while the University of Massachusetts and the Commonwealth of Massachusetts fiscal years run from July 1 to June 30. Projects funded by the State are reported for the period July 1 2009 - June 30, 2010.

project, the Town of Winchendon *Growing a Green Community through Neighborhood Collaboration*, and an Army Corps of Engineers funded study of climate change impacts on the Great Lakes.

WRRC was involved in three projects incorporating modern information technology into environmental research, teaching at the middle school and University levels, and public outreach in the Connecticut River watershed. All three use location-aware hardware and software technologies and handheld computers to enhance understanding of complex, place-based environmental issues.

The seventh annual water resources research conference, *Monitoring and Responding to Water Resource Challenges*, was held at UMass on April 8, 2010.

Progress results for each project are summarized for the reporting year in the following sections.

Research Program

Nine research projects were conducted this fiscal year. One research project was funded through the USGS 104G program, and one research project received a no-cost extension for funds received through the previous USGS 104B program. Three new projects and one project continuation were funded through the 104B program and were completed this year. Progress results for the Acid Rain Monitoring Project, the Tri-State Connecticut River Targeted Watershed Initiative, the Blackstone River Water Quality Modeling study, the Probabilistic Monitoring project, the Town of Winchendon project, and the Great Lakes study are also reported here.

1. Characterizing and quantifying recharge at the bedrock interface (USGS 2009MA213G)

Primary Principal Investigator: Dr. David Boutt, UMass Amherst
Other PIs: Dr. Stephen B. Mabee
Start Date: 9/1/2009
End Date: 8/31/2012
Reporting Period: September 1, 2009 – February 28, 2010
Funding Source: USGS (104G)
Research Category: Groundwater Flow and Transport
Focus Categories: Groundwater; Water Supply; Water Quantity

Problem and Research Objectives

Evaluating the sustainability of fractured bedrock as a groundwater resource and understanding the environmental impacts of water withdrawals from the bedrock on nearby streams, wetlands, ecosystems and unconsolidated aquifer systems requires an estimate of the recharge and an understanding of the advective flux across the bedrock –overburden boundary. Few published studies address this issue with direct measurement (Rodhe and Bockgard, 2006, White and Burbey, 2007) while others use tracers (e.g. Rugh and Burbey, 2008) and numerical models to study the distribution of groundwater flow in the soil and bedrock (eg., Harte and Winter, 1995; Tiedeman et al., 1998). However, quantifying the flux of water between the overburden and bedrock remains one of the major sources of uncertainty in numerical models (Lyford et al., 2003). The only long term monitoring well that is screened in bedrock in Massachusetts (Figure 1) shows an interesting downward trend in hydraulic head over a period of almost 20 years while the hydraulic head from a nested piezometer in the surficial material above the bedrock piezometer does not show a similar trend. Understanding the dynamics of how systems like these interact is fundamental to improving our ability to manage and regulate these important resources.

The objectives of this project are to evaluate water flux across the overburden-bedrock interface under ambient and stressed conditions and to estimate its hydraulic conductivity in three typical hydrogeologic settings in the glaciated terrain of eastern Massachusetts. The hydrogeological conditions that will be examined include thick till overburden, thin till-shallow bedrock and coarse-grained stratified deposits. The work will be conducted in the Assabet River watershed because this watershed has previously been modeled by the USGS (DeSimone, 2004). The project complements past and ongoing work by the USGS in the New England region that evaluates water availability and the impacts of pumping on shallow aquifers and riparian systems (e.g.., DeSimone et al., 2002, DeSimone, 2004; Carlson et al., 2008). The proposed project is also designed to complement a project underway by the USGS Water Science Center in Northborough, Mass. that is assessing the factors affecting bedrock well yields in the Nashoba terrane. Many of these projects benefited from several years of cooperation between the Office of the Massachusetts State Geologist, University of Massachusetts, USGS and the Mass. Department of Environmental Protection.

The expected outcome of this work is a clearer understanding of the groundwater flux across the overburden-bedrock boundary and how the coupled systems respond to seasonal changes, individual recharge events and potential stresses due to pumping. Acquisition of these data will provide a basis for calibrating numerical models that investigate the effects of groundwater withdrawals (both surficial and bedrock) on stream baseflows and ecosystems.

Methodology

Site Selection

Well sites will be chosen in the context of the existing groundwater flow model by the USGS that meet the following characteristics: 1) lie in areas where the Nashoba formation outcrops or subcrops, 2) are covered by till or in an area of exposed bedrock, 3) are relatively close to outcrop data collection stations and bedrock wells studied previously, and 4) are in a model predicted recharge area.

At each location we will use (where applicable) 2D seismic refraction and resistivity surveys to determine the depth to bedrock along a number of cross sections. General topographic surveys will be performed and maps created for each well site.

Site Instrumentation

Each well site will be instrumented with the following: 1) a precipitation gage including air temperature, 2) soil moisture probes at 0.1, 0.2, 0.3 m depth, 3) a multilevel well screened at 2 locations in the surficial materials and 2 screened locations in the bedrock, 4) pressure transducers and thermocouples at each of the borehole screened locations. Precipitation will be measured with Texas Electronics Rain Gage (TE525-L) with air temperature being measured with a Campbell Scientific 107-L Temperature Sensor. The precipitation gage has a 0.254 mm tip resolution and a 15 cm orifice. Soil moisture will be measured at specified depths using the CS616-L water content reflectometer by Campbell Scientific. The probe uses time-domain measurement methods to measure the volumetric water content from 0% to saturation at a resolution of 0.1% volumetric water content. Rods having lengths of 30 cm will be buried to the specified depths.

Six-inch boreholes will be drilled through the overburden and at least 10 m into the bedrock. Split spoon samples will be taken at 2 m intervals in the surficial materials and the bedrock will be cored using a NX size core barrel. Wells will be furnished with the Solinst CMT multi-level sampling system that allows a maximum of 7 discrete measurement locations within a single 6 cm pipe. The exact depth of the borehole-screened area (we envision 0.25 m screened regions) will be determined based on site characteristics, such as depth to water table and thickness of till. The Solinst system requires the isolation of individual screened regions using bentonite clay. Care will be taken to make sure that regions are hydraulically isolated. Hydraulic head and water temperature will be measured at each screened region with a 35/D Druck pressure transducer (designed to fit in the 3/8" diameter port of the Solinst CMT) and a Campbell Scientific 107-L Temperature Sensor, respectively.

Data Collection

Data collection will take place over at least an 18 month time period starting in the late summer of 2010 and ending in the summer of 2011. At each site 13 separate pieces of data (precipitation, air temperature, 3 soil moisture contents, 4 hydraulic heads, and 4 water temperatures) will be recorded at 15-minute intervals. At each site all thirteen channels will be connected to a Campbell Scientific CR-1000 data logger equipped with an additional compact flash storage card with a capacity of 1GB. At 15 minute intervals this consists of 1248 measurements over the period of 1 day at each site. Bi-weekly visits to the field sites will be made to ensure proper functioning of the data collection efforts and to retrieve data. The hydraulic response of both the surficial and bedrock system to recharge events will be measured using the data specified above. Historically water levels in these materials reach their maximum during the late spring and minimum during early fall periods. In summary, field data collected during spring and fall hydrologic regimes will consist of time-synced hydraulic head measurements at multiple vertical locations at each of the study sites.

Data Reduction, Interpretation, Modeling

Data collected from the deployed instruments will be time-synced to ensure proper data analysis. Self-consistency in the data sets will be determined based on an assumed relationship between precipitation and soil moisture. Precipitation and air temperature data will be compared with climate data from the nearby Bedford and West Medway, Mass., weather stations (about 5 and 15 mi, respectively, from the basin). These stations were found to be representative of conditions in the study area by DeSimone (2004). Ground water level fluctuation and soil moisture will be analyzed to examine relationships and to determine the significance of vertical versus horizontal movement of water at the chosen sites. Hydraulic head distributions in the till and the bedrock will be examined for evidence of vertical transmission of water. Time series analysis (Eltahir and Yeh, 1999) will examine corresponding lag times between precipitation, soil moisture, and ground water level at various depths. Summary data sets will be developed for each site.

The hydraulic data together with the temperature data will be used to build 1-dimensional coupled saturated-unsaturated water flow and temperature models using the general finite-element method solver COMSOL multiphysics (Fleming, 2009). Hydraulic and heat boundary conditions will be provided by the field measurements. The integration of both head and temperature data into a model such as this reduces the degrees of freedom and will allow an estimation of the vertical flux across various boundaries (water table, till-bedrock interface) present in the model (Anderson, 2005) that is constrained by observations of head and temperature. A split data approach will be used to calibrate the model reserving the other half of the data to predict water flux under different hydraulic conditions throughout the data set. The hydraulic properties of the bedrock-till interface will be the main calibration parameter. For each site, a detailed quantitative model will be developed to understand the movement of water from the surface through to the bedrock. Recharge rates to the till (where present) will be estimated and the amount of leakage (recharge) to the bedrock will also be determined using the data collected. Results from this analysis will yield a detailed set of water fluxes for the hydrologic periods during data collection. The hydraulic properties of the bedrock-till interface will be an important calibration and model result.

Synthesis and Modeling

Observations of water and energy transport (i.e. temperature) will be summarized and compared to site characteristics such as till thickness, till composition, topographic setting, hydraulic heads of till and bedrock, bedrock hydraulic properties, distance to mapped structural features, and characteristics of fracture networks mapped in nearby outcrops. Recharge rates will be calculated and summarized for each site at monthly intervals. Relationships between the hydraulic conductivities determined at the bedrock-till interface and field observations will be made. Using the calibrated 1-dimensional models, we will perform some preliminary estimates of the impact of bedrock water withdrawals on the flux of water across the boundaries at the different sites. Fluid withdrawal will be simulated by modeling a pumping well placed into the bedrock at a specified depth. Results from the models will be used to infer the impact of further use of bedrock water supplies on surficial water supplies and recharge rates into the bedrock.

Principal Findings and Significance

Work on this project began on September 1, 2009. No findings have been developed yet as most of the effort to date has focused on site selection and preparing for field work in the summer of 2010. Here is an update on what has been completed to date:

1. A GIS based map was developed for the Assabet River watershed. The map includes spatial distribution of soil types, surficial geology, bedrock geology, land use types and existing bedrock monitoring well locations. This map was used to assess possible study site and data collection station locations, as well as for developing a soil-sampling program.
2. Study site selection criteria were developed and locations within the Assabet River catchment were evaluated. Based upon selection criteria, Gates Pond Reservoir, Berlin, Mass. was selected.
3. Access agreements between the Geosciences Department at the University of Massachusetts, Amherst and the Town of Hudson, Department of Public Works (the controlling entity of Gates Pond) were negotiated and approved.
4. Access agreements with the lessee of farmland located adjacent to Gates Pond Reservoir (231 Sawyer Hill Rd., Berlin, Mass.) are still under negotiation. Should negotiations prove fruitless, adequate contingency plans have been developed with the Town of Hudson, Mass. Department of Public Works.
5. Instrumentation and data collection methods for measuring aquifer response to precipitation inputs were researched and selected. Instrumentation is currently being ordered and will be installed in Summer 2010. The instrumentation will communicate with the Primary Investigators via cellular telemetry.

6. Preliminary soil samples were taken for a baseline grain size analysis. The analysis is currently in progress.
7. Geophysical methods for effectively evaluating the soil profile at Gates Pond Reservoir were evaluated and selected. Resistivity profiles will be taken using the University of Massachusetts, Amherst, Department of Geosciences' AGI Sting© R-1. Soil resistivity profiles will be performed in summer 2010.
8. A soil sampling regime and methods for characterizing the hydraulic properties of the site's soil were evaluated and selected. Soil sampling and hydraulic properties will be evaluated beginning summer 2010.
9. Statistical time-series analysis methods for establishing a hydraulic conductivity gradient across a surficial/bedrock interface were researched and tested for viability using MATLAB©. The data used for the statistical analysis was collected from a nested/bedrock piezometer located in Pelham, MA. The results of the statistical analysis helped determine the required sampling frequency of instrumentation that will be deployed in Summer 2010.
10. Bedrock wells at Gates Pond Reservoir were modified to accommodate down-hole instrumentation. Currently, two wells are equipped with Solinst LevelLoggers© and one BaroLogger© to gather baseline water level data.
11. Designs for down-hole fiber optic distributed temperature probes are currently being developed. The investigators are hopeful that all bedrock wells at the Gates Pond Reservoir will be equipped with fiber optic probes and will be functional by the end of Summer 2010.

Study area selection is complete and study design is on track and will continue through early Summer 2010. Liam B. Bevan, an M.S. student who will be performing the majority of the field and laboratory work for this project, began work in earnest during the fall of 2009. His initial efforts will be in characterizing the study area catchment using in-situ and laboratory techniques and installing and maintaining instrumentation.

Publications and Conference Presentations

Bevan, L.B., Boutt, D.F., Mabee, S.B. 2010. *Characterizing Groundwater Recharge Across the Surficial/Bedrock Interface*. Massachusetts Water Research Resource Center Annual Conference. April 8, 2010. (Poster session).

Student Support

Liam B. Bevan is fully supported by this project. He is pursuing an M.S. degree in geology in the Department of Geosciences at the University of Massachusetts, Amherst.

References

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Carlson, C.S., DeSimone, L.A., Weiskel, P.K., 2008, Simulated effects of year 2030 water-use and land-use changes on streamflow near the Interstate-495 corridor, Assabet and Upper Charles River Basins, eastern Massachusetts: U.S. Geological Survey Scientific Investigations Report 2008–5132, 108 p.

DeSimone, L.A., 2004, Simulation of ground-water flow and evaluation of water-management alternatives in the Assabet River Basin, eastern Massachusetts: U.S. Geological Survey Scientific Investigations Report 2004-5114, 133 p.

DeSimone, L.A., Walter, D.A., Eggleston, J.R., and Nimiroski, M.T., 2002, Simulation of ground-water flow and evaluation of water-management alternatives in the upper Charles River basin, eastern Massachusetts: U.S. Geological Survey Water-Resources Investigations Report 02-4234, 94 p.

Eltahir, E.A.B., and Yeh, P J.-F., 1999, On the Asymmetric response of aquifer water level to floods and droughts in Illinois, Water Resources Research, Vol. 35, No. 4, pp. 1199-1217.

Fleming, B.J., 2009, Ground water-surface water interactions in the Deerfield River watershed, Charlemont, MA. M.S. Thesis, University of Massachusetts-Amherst.

Harte, P.T. and Winter, T.C. 1995. Simulations of flow in crystalline rock and recharge from overlying glacial deposits in a hypothetical New England setting. Ground Water, v.33, no.6, pp.953-964.

Lyford, F.P., Carlson, C.S. and Hansen, B.P., 2003, Delineation of Water Sources for Public-Supply Wells in Three Fractured-Bedrock Aquifer Systems in Massachusetts: U.S. Geological Survey Water-Resources Investigations Report 02-4290, 114 p.

Rodhe, A. and Bockgard, N. 2006. Groundwater recharge in a hard rock aquifer: A conceptual model including surface-loading effects. Journal of Hydrology, v.330, pp.389-401.

Rugh, D.F. and Burbey, T.J. 2008. Using saline tracers to evaluate preferential recharge in fractured rocks, Floyd County, Virginia, USA, Hydrogeology Journal, 16: 251-262.

Tiedeman, C.R., Goode, D.J. and P.A. Hsieh. 1998. Characterizing a ground water basin in a New England mountain and valley terrain. Ground Water, v.36, no.4, pp.611-620.

White, B.A. and Burbey, T.J. 2007. Evidence for structurally controlled recharge in the Blue Ridge Province, Virginia, USA. Hydrogeology Journal, v.15, pp.929-943.

2. Environmental behaviors of engineered nanoparticles in water (USGS 2007MA73B)

Principal Investigator: Dr. Baoshan Xing, UMass Amherst
Start Date: 3/1/2007
End Date: 5/31/2010
Reporting Period: March 1, 2009 – February 28, 2010
Funding Source: USGS (104B)
Research Category: Environmental and Water Chemistry
Focus Categories: Water Quality; Toxic Substances; Solute Transport
Descriptors: Nanoparticle; Sorption; Suspension; Phytotoxicity; Oxides; Natural Organic Matter; Environment

Problem and Research Objectives

Knowledge of engineered nanoparticles in water is critical for evaluating their environmental fate, exposure, risk and ecotoxicity. The research objectives for this project for FY09 were:

1) To characterize colloidal and aggregation behavior of nanoparticles as affected by pH and organic matter
2) To examine the adsorption and desorption of organic chemicals, and natural

organic matter by nanoparticles

Methodology

Batch sorption techniques, DSL, liquid scintillation counting, HPLC detection, TEM, AFM and SEM examinations.

Principal Findings and Significance

The colloidal stability of three structurally different humic acid (HA) coated Al_2O_3 nanoparticles (HAs-Al_2O_3 NPs) was studied in the presence of Ca^{2+}. HAs were obtained after sequential extractions of Amherst Peat Soil. Highly polar HA1-coated Al_2O_3 NPs exhibited strong aggregation in the presence of Ca^{2+}. HA3 and HA7-coated NPs showed weaker aggregation due to their increased aliphaticity and low polarity. HA7-Al_2O_3 NPs displayed the weakest aggregation behavior even at relatively high Ca^{2+} concentration. The inverse stability ratio ($\alpha=1/W$) was the lowest for HA7-Al_2O_3 NPs reflecting that strong steric stabilization enhanced colloidal stability. Atomic force microscopy (AFM) of pure Al_2O_3 NPs on Ca^{2+}-saturated mica clearly demonstrated significant aggregation following classical DLVO model for hard spheres. On the contrary, the weakly polar HA fraction produced an approximately 10 nm thick corona of adsorbed layer around each Al_2O_3 NP, thus stabilizing the coated nanoparticle suspension through a steric effect. Under alkaline conditions and at low ionic strength, adsorbed HA chains swelled, increasing their osmotic potential, which in turn resulted in stabilization of the colloids. Inherent structural variations of NOMs played a significant part in colloidal stability of the coated nanoparticles. Thus, development of sterically stabilized nanoparticles may have potential application for water remediation in marine and high salinity conditions.

Publications and Conference Presentations

Articles in Refereed Scientific Journals

Ghosh, S., Hamid Mashayekhi, P. Bhowmik and B. Xing. 2010. Colloidal stability of Al_2O_3 nanoparticles as affected by coating of structurally different humic acids. Langmuir, 26 (2): 873–879.

Yang, K. and B. Xing. 2009. Sorption of phenanthrene by humic acid-coated nanosized TiO_2 and ZnO. Environ. Sci. Technol. 43(6): 1845-1851.

Yang, K., D.H. Lin and B. Xing. 2009. Interactions of humic acid with nanosized inorganic oxides. Langmuir, 25(6): 3571-3576.

Lin, D.H., N. Liu, K.Yang, L.Z. Zhu, Y. Xu and B. Xing. 2009. The effect of ionic strength and pH on the stability of tannic acid-facilitated carbon nanotube suspensions. Carbon, 47: 2875-2882.

Yang, K. and B. Xing. 2009. Adsorption of fulvic acid by carbon nanotubes from water. Environ. Pollut. 157: 1095-1100.

Dissertations

Ghosh, Saikat 2010. "Influence of Natural Organic Matter and Synthetic Polyelectrolytes on Colloidal Behavior of Metal Oxide Nanoparticles" Ph.D. Dissertation. University of Massachusetts, May 2010.

Conference Proceedings

Jiang, Wei, H. Mashayekhi, and B. Xing. "Toxicity of Oxide Nanoparticles to Bacteria in Water." Poster presentation for the 6th Annual Water Resources Research Center, University of Massachusetts, Amherst, MA. April 7, 2009.

Mashayekhi, H. S. Ghosh and B. Xing. "Aggregation Behavior of C60 Fullerene Water Suspension in the Presence of Natural Organic Materials." International Conference on the Environmental Implications and Applications of Nanotechnology, Amherst (MA), June 9-11, 2009, p. 36.

Iorio, M., A. De Martino, R. Capasso and B. Xing. "Screening of nine different nanoparticles for the removal of MCPA from water." International Conference on the Environmental Implications and Applications of Nanotechnology, Amherst (MA), June 9-11, 2009, p. 49.

Zia, J., D. Amarasiriwardena and B. Xing. "Investigation of the adsorption characteristics of Sb, Cd, and pB by nano- and micro-particle titania." International Conference on the Environmental Implications and Applications of Nanotechnology, Amherst (MA), June 9-11, 2009, p. 51.

Jiang, Wei, and B. Xing. "Behavior of Nanoparticles at the Bacteria-Water Interface." Poster presentation for the 7th Annual Water Resources Research Center, University of Massachusetts, Amherst, MA. April 8, 2010.

Student Support, Department of Plant, Soil and Insect Sciences

- Mr. Hamid Mashayekhi, PhD Candidate
- Mr. Saikat Ghosh, PhD Candidate
- Ms. Wei Jiang, PhD Candidate

Notable Achievements and Awards

2009 Award Winning Poster presentation for the 6th Annual Water Resources Research Center. Jiang, Wei, H. Mashayekhi, and B. Xing. "Toxicity of Oxide Nanoparticles to Bacteria in Water." Poster presentation for the 6th Annual Water Resources Research Center, University of Massachusetts, Amherst, MA. April 7, 2009.

3. Characterization of wastewater effluent from Western Massachusetts publicly owned treatment works using metaproteomic analysis (USGS 2008MA155B)

Principal Investigator: Dr. Chul Park, UMass Amherst
Start Date: 6/1/2009
End Date: 5/31/2010
Funding Source: USGS (104B)
Reporting Period: March 1, 2009 – February 28, 2010
Research Category: Water Quality
Focus Categories: Ecology; Methods; Nutrients; Solute Transport; Wastewater; Water Quality
Descriptors: Connecticut River; Effluent; Protein; Proteomics; Wastewater

Problem and Research Objectives

Significant efforts have been made to reduce the nitrogen released from wastewater treatment plants (WWTPs) and this has been mainly achieved by upgrading the facility for enhanced nitrogen removal through nitrification and denitrification. Though these processes are effective for removing inorganic nitrogen (ammonia and nitrate) organic nitrogen remains little changed, presumably due to its recalcitrant nature, which leads to organic-N becoming a substantial fraction of the N in the final effluent. Thus, one major issue with effluent organic-N is whether it degrades and becomes bioavailable in receiving waters.

Our research group proposed a unique research plan based on proteomics analysis to characterize effluent proteins and to assess their fate in receiving waters. Better characterization of effluent proteins and better understanding of their fate in receiving waters are critical as proteins comprise a major fraction of effluent organic nitrogen. Furthermore, as proteins can be characterized at a molecular level, profiling of effluent proteins and tracking them in a well defined laboratory bioassay (that mimics receiving waters) will further enable us to determine the fate of proteins, and thus a significant fraction of organic-N, in receiving waters. The specific objectives of this project were as follows:

- Determine and characterize proteins in wastewater effluents from major dischargers to the Connecticut River, thus to Long Island Sound.
- Perform a laboratory bioassay and apply proteomics analysis before and after the bioassay to evaluate the bioavailability of effluent proteins in receiving waters.

Methodology

This research was conducted in two phases: 1) collecting effluents samples and characterizing effluent proteins from various wastewater treatment plants and 2) performing a laboratory bioassay to investigate the fate of effluent proteins and organic nitrogen in receiving waters.

Collection of samples

Primary and secondary effluents were collected from three wastewater treatment facilities that discharge to the Connecticut River in Western Massachusetts. The Northampton and Amherst facilities use conventional activated sludge while the Springfield Regional Wastewater Treatment Facility uses the Ludtzac Ettinger process to treat their wastewater. Samples were collected in plastic containers and kept on ice until processed later the same day. Total suspended solids (TSS), volatile suspended solids (VSS) and chemical oxygen demand (COD) measurements were taken the day of collection, while samples were frozen for later measurement of protein, total nitrogen, ammonium, nitrate and nitrite. The secondary effluent from each sample was also separated through a 0.45 μm filter.

Quantification of Proteins in Effluent

The Frølund adaptation of the Lowry method (1995) was mainly used to quantify proteins in wastewater effluents. This method can account for the interference of humic compounds in protein measurement. This method, however, often produces falsely negative protein concentrations for unconcentrated effluent samples. Thus, in this research the quantity of proteins in unconcentrated effluent was measured using the original Lowry method, while the protein concentration in ammonium sulfate concentrated samples was measured using the Frølund adaptation of the Lowry method. Light absorbance was measured with the Thermospectronic Genesys 10 UV Spectrophotometer (Thermo Spectronic, Madison, WI, USA) and concentrations were calculated from a standard curve created from 0, 10, 25, and 50 mg/L BSA standards.

Ammonium Sulfate Precipitation

In order to visualize proteins using sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE), secondary effluent and secondary filtered effluent were concentrated with 50% ammonium sulfate. The appropriate mass of ammonium sulfate was combined with 150 ml of primary effluent, 1.2 L of secondary effluent, and 2.2 L of 0.45 µm filtered secondary effluent, in 500 ml centrifuge bottles and one glass pyrex bottle (for 1 L of the 0.45 µm filtered secondary effluent). Precipitation procedures were conducted on ice for more than 12 hours, followed by centrifuging at 11,730 g for 45 minutes. The precipitate was re-suspended in a known volume of phosphate buffered saline (PBS: 10mM NaCl, 1.2mM KH_2PO_4, 6.0mM Na2HPO4), then dialyzed extensively in the same buffer with multiple changes at 4°C using a 6-8 kDa cellulose membrane.

Sodium Dodecyl Sulfate – Polyacrylamide Gel Electrophoresis

The SDS-PAGE was performed according to the method of Laemmli (1970). Ammonium sulfate concentrated samples were prepared for size separation on polyacrylamide gels by incubating at approximately 95°C for at least 10 minutes with a 3.3x sample buffer consisting of XT Mops sample buffer and a reducing agent (Bio-Rad, Hercules, CA, USA). Some samples were heat concentrated for up to one hour. Following heat concentration, samples were centrifuged at 12,000 rpm for 3 minutes and the supernatant was used for SDS-PAGE. Prepared samples were loaded onto pre-cast Criterion XT 4-12% gradient gels (Bio-Rad, Hercules, CA, USA) and separated on the gels by a current of 80V for 20 minutes, followed by 100V for two hours. After electrophoresis, gels were stained with silver nitrate or coomassie brilliant blue using Bio-Rad's Silver Stain Kit or Bio-Safe stain (Bio-Rad, Hercules, CA, USA). Gel images were digitally recorded using a CanoScan 8800F desktop scanner (Canon, Tokyo, Japan).

Zymogram analysis

Samples were subjected to zymogram analysis to determine if they contained active proteolytic enzymes. Enzyme activity was determined by separating proteins using electrophoresis in a casein-infused gel (Bio-Rad, Hercules, CA, USA). Before electrophoresis, the samples were combined with zymogram buffer (Bio-Rad, Hercules, CA, USA) and centrifuged at 12,000 rpm for 3 minutes; the supernatant was used for the zymogram analysis. Gel images were digitally recorded using a CanoScan desktop scanner (Canon, Tokyo, Japan).

Chemical Analysis

Total protein in each of the effluents, both raw and concentrated with ammonium sulfate, was measured using the Lowry method (1951) and determined with a calibration curve generated with bovine serum albumin (Fisherbrand Scientific, Pittsburg, PA, USA). On the day of sample collection, COD, TSS and VSS were measured for primary and secondary effluents according to Standard Methods (2005). COD was measured for secondary effluent filtered through a 0.45 µm filter, as well. Light absorbances for COD tests were determined using the Thermospectronic Genesys 10 UV Spectrophotometer (Thermo Spectronic, Madison, WI, USA) and concentrations calculated from a standard curve using 0, 10, 75, and 150 mg/L KHP standards.

Nitrogen species

Total nitrogen concentrations in primary and secondary effluent, and 0.45 µm filtered secondary effluent were determined using the persulfate method (Hach, Loveland, CO, USA) and confirmed using a Shimadzu TN analyzer (Shimadzu TOC-VCPH with TNM-1, Shimadzu North America, SSI Inc., Columbia, MD, USA). Ammonium, nitrate and nitrite ions in the solution phase (<0.45 µm) of primary and secondary effluents were measured using a Metrohm ion chromatograph (Metrohm, Herisau, Sz). Organic nitrogen was estimated by subtracting the sum of the nitrogen ions from the total nitrogen.

Laboratory bioassay

Several incubation conditions were tested in an effort to establish the final protocol of laboratory bioassay for this research. Some earlier incubation conditions included: 1) no mixing, 2) intermittent mixing, and 3) continuous mixing of the bioassay bottles. Each set of bioassay included a killed control set to make sure that changes in proteins and organic nitrogen during the bioassay were caused by biological activity. The earlier experiments also tested different dilution sets between effluents and the Connecticut River water at 1:9 and 5:5. For this laboratory bioassay, mainly effluents from Springfield Regional Wastewater Treatment Facility were used. The final bioassay protocol includes following conditions:

1) Filter river water using 100 μm filter.
2) Use 5:5 ratio for river water and secondary effluent for incubation.
3) Perform a separate bioassay on dissolved and whole fraction of secondary effluents.
4) Provide continuous mixing during the incubation.
5) Place the incubation bottles under natural sunlight conditions.

During this laboratory bioassay we also performed Tangential Flow Filtration (TFF) to effectively concentrate the sample before conducting all protein related analysis. Following the concentrating stage, proteins were separated by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). Some effluent concentrate samples were sent to another laboratory for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis to identify the proteins. In addition, various effluent parameters such as TSS, total organic carbon (TOC), cations, anions, and inorganic nitrogen species, as described earlier, were also measured.

Principal Findings and Significance

The current project has revealed several important and new findings regarding effluent organic nitrogen and effluent proteins. The most important finding of this research is that facilities with more advanced N removal processes contain a greater amount of organic nitrogen with a higher diversity of proteins and active enzymes in their final effluents. This indicates that effluent organic-N in advanced wastewater treatment plants differs significantly from that found in conventional wastewater treatment systems. The full effects of released enzymes and proteins in the receiving ecosystem are unknown, but are thought to increase the bioavailability of natural organic matter and to modulate nutrient cycling in the receiving water. As advanced removal of N becomes mandatory in wastewater treatment, it is imperative that this process and potential unintended consequences be fully understood.

The consistent differences between effluent protein profiles from each of the treatment plants investigated further suggest that effluent proteins and enzymes could serve as "fingerprints" of distinct wastewater treatment works and provide a means to track their fate in receiving waters. This fingerprinting concept was employed in the bioassay during the later part of this research and partially used to track the fate of preselected proteins during the incubation. Other major findings and significance of this research are further summarized below.

- The research revealed that proteins are significantly correlated with organic nitrogen in effluent from each of the wastewater treatment facilities, demonstrating the significance of protein molecules in effluent organic nitrogen. We believe that there has been no precedent study that has found this relationship or addressed the issue of proteins being an indication, or representative, of effluent organic nitrogen.
- We believe that this is also the first study showing changes in protein profiles, at a molecular level, across processes in a wastewater treatment plant. The results from this approach allowed direct evidence that some influent

wastewater proteins persist through the wastewater treatment process and some of these proteins are actually active proteolytic enzymes.

- The research also showed that some bacterial proteins and enzymes that are generated during a biological treatment do indeed end up in the secondary effluent, as so-called soluble microbial products (SMP).
- The finding of active enzymes and proteins in filtered effluent samples is also important to note since the addition of a filtration process to a facility, such as microfiltration, is not likely to improve the capture of these potentially biological compounds.
- Because of these protein results, we gained new knowledge that different treatment works release different sets of proteins (thus, organic nitrogen) and proteolytic enzymes: this information could not be achieved by simple quantitative data or conventional size fractionation techniques. These results are important in that we do not know how these proteins and enzymes behave in the receiving water and what ecological and environmental impacts they may have. The study has provided us a chance to better characterize and identify effluent proteins and enzymes, which can be tracked thoroughly in well defined laboratory bioassays or even directly in the receiving water.
- The bioassay that was designed to mimic the reaction of wastewater effluents in natural receiving waters requires natural sunlight and continuous and uniform mixing during the incubation.
- Concentrations of both inorganic nitrogen (ammonia and nitrate) and organic nitrogen changed greatly during the bioassay, indicating a degradation of organic nitrogen and release of newly generated organic nitrogen.
- After incubation, new soluble protein bands were detected along with a substantial increase in algal biomass. This observation suggests that receiving waters utilized available effluent nitrogen, including organic nitrogen, and release of proteins from grown algal biomass contributed to a new set of dissolved organic nitrogen remaining in the bioassay.

Publications and Conference Presentations

Articles in Refereed Scientific Journals

Westgate, P. and Park, C. (In revision) Evaluation of proteins and organic nitrogen in wastewater treatment effluents. *Environmental Science and Technology.*

Dissertations

Westgate, Pamela 2009. MS Thesis: Characterization of Proteins in Effluents from Three Wastewater Treatment Plants that Discharge to the Connecticut River, MS Environmental Engineering, Aug 2009

Conference Proceedings

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

Westgate, Pamela and Park, C. 2010. Proteins and Nitrogen in Wastewater Effluent from Three Wastewater Treatment Plants that Discharge to the Connecticut River. Poster presentation for the 7th Annual Water Resources Research Center, University of Massachusetts, Amherst, MA. April 8, 2010.

Student Support
Primary funding was used to support Pamela Westgate for her MS research. Ms. Westgate defended her MS thesis in August 2009. Please see above.

Partial funding was also used to support the PI's PhD graduate students, Meng Wang and Dong-Hyun Chon, who participated in this project by operating laboratory scale activated sludge systems and provided wastewater effluent for proteomic characterization for this research.

Notable Achievements and Awards

As discussed above, the current research has revealed very important findings regarding the release of nitrogen from advanced wastewater treatment systems and its impact on the receiving water ecosystem. Nitrogen in domestic wastewater effluents is a hot topic, garnering a lot of attention these days from researchers and plant operators as regulators increase pressure to reduce nitrogen discharges from wastewater treatment plants. Due to the significance of the findings of this research, we submitted a full journal manuscript to *Environmental Science and Technology* (currently, in revision process). Furthermore, Springfield Water and Sewer Commission (SWSC), who provided the matching funds to this project, will likely continue the funding on this research topic. Dr. Douglas Borgatti from SWSC and the PI will also present the findings of this research at the annual New England Water and Environment Association Conference in January 2011 to discuss a regional nitrogen issue for wastewater treatment facilities.

4. Bacterial toxicity of oxide nanoparticles and their adhesion at bacteria-water interface (USGS 2009MA177B)

Principal Investigator: Dr. Baoshan Xing, UMass Amherst
Start Date: May 1, 2009
End Date: April 30, 2010
Reporting Period: March 1, 2009 – February 28, 2010
Funding Source: USGS (104B)
Research Category: Environmental and Water Chemistry
Focus Categories: Toxic Substances; Water Quality
Descriptors: Nanoparticles; Toxicity; Bacteria; Oxide; Water

Problem and Research Objectives

Oxide nanoparticles (NPs) are widely used, and they are potentially toxic. The goal of this work was to evaluate the toxicity of several engineered oxide nanoparticles to common bacteria species and the adhesion of nanoparticles to the bacteria surface.

Methodology

Batch experiments, FTIR, Characterization of Nanoparticles, Toxicity evaluation, AFM and TEM imaging.

Principal Findings and Significance

Toxicity of nano-scaled aluminum, silicon, titanium and zinc oxides to bacteria (*Bacillus subtilis*, *Escherichia coli* and *Pseudomonas fluorescens*) was examined and compared to that of their respective bulk (micro-scaled) counterparts. All nanoparticles but titanium oxide showed higher toxicity than their bulk counterparts. Toxicity of released metal ions was differentiated from that of the oxide particles.

ZnO was the most toxic among the three nanoparticles, causing 100% mortality to the three tested bacteria. Al_2O_3 nanoparticles had a mortality rate of 57% to *B. subtilis*, 36% to *E. coli*, and 70% to *P. fuorescens*. SiO_2 nanoparticles killed 40% of *B. subtilis*, 58% of *E. coli*, and 70% of *P. fluorescens*. TEM images showed attachment of nanoparticles to the bacteria, suggesting that the toxicity was affected by bacterial attachment. Bacterial responses to nanoparticles were different from their bulk counterparts; therefore nanoparticle toxicity mechanisms need to be studied thoroughly.

Publications and Conference Presentations

Articles in Refereed Scientific Journals

Jiang, W., H. Mashayekhi and B. Xing, 2009. Bacterial toxicity comparison between nano- and micro-scaled oxide particles. Environ. Pollut. 157:1619-1625.

Conference Proceedings

Jiang, W., H. Mashayekhi and B. Xing "Bacterial toxicity of oxide nanoparticles and their adhesion to bacteria cell walls". International Conference on the Environmental Implications and Applications of Nanotechnology, Amherst (MA), June 9-11, 2009, p. 27.

Wang, H., R. Wick and B. Xing . "Toxicity of nanoparticulate and bulk ZnO, Al_2O_3 and TiO_2 to the nematode *Caenorhabditis Elegans".* International Conference on the Environmental Implications and Applications of Nanotechnology, Amherst (MA), June 9-11, 2009, p. 31.

Jiang, W. and B. Xing. "Behavior of nanoparticles at the bacteria-water interface" The 7th Annual Massachusetts Water Resources Conference, Amherst, April 8, 2010. Abstract book, p. 25.

Student Support

Mr. Hamid Mashayekhi and Miss Wei Jiang, Ph.D. Department of Plant, Soil & Insect Sciences

Notable Achievements and Awards

2009, 1st Prize Award Winning Poster presentation for the 6th Annual Water Resources Research Center. Jiang, Wei, H. Mashayekhi, and B. Xing. "Toxicity of Oxide Nanoparticles to Bacteria in Water." Poster presentation for the 6th Annual Water Resources Research Center, University of Massachusetts, Amherst, MA. April 7, 2009.

Our papers were highlighted by the following online news networks:

Journal of Environmental Quality: "Fate and Transport of Engineered Nanomaterials in the Environment" by Daohui Lin, Xiaoli Tian, Fengchang Wu, and Baoshan Xing☐doi:10.2134/jeq2009.0423; Published online 18 Mar. 2010 https://www.soils.org/publications/jeq/new-articles

New Progress in the Study of Adsorption of Organic Chemical by Carbon Nanomaterials. June 13, 2010 Zhejiang University News http://www.ycpsoft.com/english/redir.php?catalog_id=279955&object_id=1453576

5. Impact of nanoparticles on the activated sludge process: effects on microbial community structure and function (USGS 2009MA178B)

Primary Principal Investigator: Dr. Juliette N. Rooney-Varga, UMass Lowell
Other PIs: Deepankar Goyal
Start Date: April 1, 2009
End Date: March 31, 2010
Reporting Period: March 1, 2009 – February 28, 2010
Funding Source: USGS (104B)
Research Category: Basic Research
Focus Categories: Toxic Substances; Wastewater
Descriptors: Activated Sludge; Carbon Nanotubes; Nanomaterials; Emerging Contaminants; Molecular Microbial Ecology; Microbial Community Analysis, ARISA

Problem and Research Objectives

Nanotechnology, or the ability to create and use materials at the scale of 1 to 100 nanometers, is a rapidly expanding sector that is generating materials with unique physical and chemical properties. In particular, carbon nanotubes (CNTs) are known for their unique mechanical, electronic, and biological properties and have far-reaching potential applications as components of personal care products, pharmaceuticals, electronic devices, energy storage devices, stains and coatings, and new environmental clean-up technologies (Masciangioli and Zhang, 2003; Boczkowski and Lanone, 2007; Chen, 2007; Erdem, 2007; Rivas et al., 2007; Kislyuk and Dimitriev, 2008; Prato et al., 2008; Theron et al., 2008). Massachusetts is poised to be a leader in nanotechnology research and development and this sector is expected to be a major component of the Commonwealth's economy for the foreseeable future. However, while the potential for nanotechnology is vast, relatively little is known about the health and environmental risks posed by nanomaterials (Colvin, 2003). Indeed, those watching the industry have commented that concern over unknown risks of nanomaterials is a major determinant of the future success of nanotechnology (Colvin, 2003).

Through nanomanufacturing and widespread use of nanomaterials, CNTs and other nanomaterials will inevitably be released into wastewater streams and enter wastewater treatment plants (Wiesne,r 2006). All publicly owned wastewater treatment facilities rely on the 'activated sludge process,' which relies on controlled microbial degradation of waste materials to remove chemical and biological contaminants (Wagner et al., 2002). However, little is known about how CNTs will affect the complex microbial communities that are responsible for the activated sludge process and whether microorganisms are capable of removing them. Effluent from wastewater treatment plants ultimately is released to the environment, where it can impact aquatic ecosystems and drinking water. Any toxicity to microorganisms exhibited by CNTs has the potential to dramatically reduce the efficacy of the activated sludge process, resulting in the release of untreated sewage, pathogenic microbes, and CNTs into the environment. Shock-loading of other contaminants has shown that treatment performance can be affected for weeks or months, resulting in a reduction in treatment efficiency, environmental release of toxic contaminants, and operation problems that may require months to recover (Boon et al., 2003; Henriques et al., 2007). In addition, the ability of CNTs to strongly adsorb organic matter can reduce the bioavailability and, therefore, microbial degradation of organic pollutants, which would then effectively bypass the treatment process.

The composition and function of activated sludge microbial communities have received considerable attention, although the function of many specific phylogenetic groups and the factors that control them are not yet well understood. In broad terms, activated sludge contains microbial eukaryotes ("microeukaryotes"), including protozoa, fungi, and metazoans, as well as a wide diversity of bacteria responsible for varied metabolic functions, including oxidation of organic compounds and removal of nitrogenous pollutants and phosphates (Weber et al., 2007). Within this microbial community, many complex ecological interactions are thought to be necessary for the effective functioning of activated sludge. For example, ciliated protozoa and fungi have been found to form tree-like and filamentous colonies, respectively, that form a back-bone for bacterial colonization, resulting in the production of flocs, which readily settle out of the liquid phase and are collected for effective removal from treated wastewater (Weber et al., 2007). Both bacteria and microeukaryotes are likely to contribute to the formation of extracellular polymeric substances (EPS), which are high molecular weight compounds with adhesive properties that are critical to the formation and integrity of flocs (and biofilms more generally) (Raska et al., 2006; Weber et al., 2007). In addition, specific taxonomic groups of bacteria are known to carry out key functions in activated sludge. For example, members of the *Planctomycetes* are responsible for anaerobic ammonium oxidation; several lineages within the kingdom *Euryarchaea* produce methane; members of the genus *Nitrospira* oxidize nitrite to nitrate (Juretschko et al., 2002); *Actinomycetes* may contribute to the production of foam and reduce the quality of effluent; and members of the *Chloroflexi* have been associated with bulking events (Kragelund et al., 2007). Thus, analysis of microbial community composition can provide meaningful insight into various activated sludge functions, as well as the factors that control them (Liu et al., 1997; Forney et al., 2001).

Relatively little is known about the potential toxicity of CNTs to activated sludge microorganisms and studies on pure cultures or defined mixed cultures have yielded conflicting results. There is strong evidence for CNT toxicity to pulmonary cells, as well as potential toxicity to epithelial, brain, and liver cells (Lam et al., 2006; Smart et al., 2006; Warheit 2006). Single-walled CNTs (SWCNTs) have been reported to be highly toxic to *Escherichia coli* str. K12 cells that come in direct contact with them (Kang et al., 2007). Ghafari et al. (2008) found a moderate impact of SWCNTs on *E. coli*-gfp viability, although they did not differentiate between planktonic cells and those in contact with SWCNT aggregates. Interestingly, they found that *Tetrahymena thermophila*, a ciliated protozoan that is an important member of wastewater treatment microbial communities, ingested CNTs. As a result, the protozoan's ability to ingest and digest bacterial cells was impeded, suggesting a negative impact on an important function of these protozoa, namely bacterivory (Ghafari et al., 2008). Conversely, the CNTs may also have a positive impact on activated sludge processes, as they caused an increase in the production of exudates by ciliates, which may benefit floc formation and, therefore, sludge settleability.

While pure culture studies have shown that nanomaterials can act as antimicrobial agents, the complexity of the activated sludge community make it unlikely to respond to CNTs in the same manner as simple pure culture systems. Our objective was to use state-of-the-art molecular techniques to determine the impact of CNTs on microbial community dynamics in batch reactors that model the activated sludge process.

Methodology

Experimental set-up

Fresh activated sludge was collected from an aeration basin at the Lowell Regional Wastewater Treatment Facility, Lowell. This facility is designed to treat primarily municipal wastewater through conventional primary and secondary treatment processes. Whole unscreened samples were transported to the laboratory and processed within 30 minutes of sample collection. Experimental conditions for batch-scale reactor studies were previously described by Yin et al. (2009). In order to distinguish between effects of CNTs and potential toxic effects of impurities associated with them (such as amorphous carbon and metal catalysts), triplicate CNT-exposed reactors were compared to triplicate reactors exposed to impurities alone. CNTs used in the current study consisted of >90% pure CNTs (Sigma-Aldrich, Inc., St. Louis MO) characterized by Raman spectroscopy (Table 1). Reactors were filled with 2 L of fresh activated sludge, with an initial soluble chemical oxygen demand (sCOD) of 20 mg L^{-1} from the aeration basin effluent (Yin et al., 2009). The sludge was fed with peptone and aerated prior to and during the experiment as described by Yin et al. (2009). Sub-samples for microbial community analysis were taken aseptically immediately after adding CNTs or impurities (T_0), at 1.25 hr (T_1) after initial exposure, and at 5 hr (T_4). The samples were placed in cryovials, and stored at -80°C until further processing.

DNA extraction and analysis

Genomic DNA was extracted and purified from 400 µL sub-samples of sludge using the FastDNA Spin kit for Soil (MP Biomedicals Inc., Solon, OH). ARISA-PCR was performed as previously described (Fisher and Triplett 1999), with minor modifications. Reaction mixtures contained 1× AmpliTaq PCR buffer (Applied Biosystems, Inc., Carlsbad, CA), 2.5 mM $MgCl_2$, 400 ng μL^{-1} bovine serum albumin (BSA), 200 µM each dNTP, 400 nM each primer, 2.5 U of *Taq* DNA polymerase, and 1, 5, 10, or 20 ng of genomic DNA in a final volume of 50 µL. The primers used were 1392F (5'-G [C/A] ACACACCGCCCGT-3') and 23SR (5'GGGTT[C/G/T] CCCCATTC[A/G]G-3'). The 5'end of primer 1392F was labeled with 6-carboxyfluorescein (6-FAM). The following thermal profile was used for PCR: denaturation at 94°C for 3 min, followed by 30 cycles of amplification at 94° C for 30 s, 56° C for 30 s, and 72° C for 45 s, followed by a final extension of 72° C for 7 min. PCR products were analyzed by electrophoresis in 1% agarose gels (Ausubel et al., 1997) and were purified using QiaQuick PCR Purification Kits (Qiagen, Inc., Valencia CA).

20 ng each purified PCR product were lyophilized and subjected to automated capillary electrophoresis (CE) analysis in conjunction with a 50 – 1200 bp size standard labeled with LIZ™ (Applied Biosystems, Inc.) at the Center for AIDS Research, UMass Medical School, Worcester MA. ARISA conditions were optimized by comparing profiles generated from multiple DNA template amounts (1, 5, 10, or 20 ng per 50 µL PCR) and PCR product amounts (5, 10, or 20 ng PCR product per well). Comparison of these conditions indicated that the highest diversity (species richness and evenness) and signal to noise ratios were achieved using 1 ng DNA template DNA for PCR and 20 ng PCR product for CE analyses, which were used in subsequent analyses.

ARISA profiles were analyzed using PeakScanner software (Applied Biosystems Inc.) and processed as described by Brown et al., (2005). The program's Interactive and Automatic Binner were used to bin peaks, with a window size (WS) of 3 bp and a shift value (Sh) of 0.1 (Ramette, 2009). Peak areas were normalized to total peak area per sample and peaks representing <1% total peak area for a given sample were considered indistinguishable from background and removed from the analysis. Data visualization and ordination analyses were conducted using the packages Ecodist (Goslee and Urban, 2007) and Vegan (http://vegan.r-forge.r-project.org/) in the R statistical programming environment (Goslee and Urban, 2007). Pairwise Bray-Curtis distances between samples were calculated using the Ecodist package and a hierarchical clustering algorithm with average linkage clustering were used to construct a dendrogram depicting relationships among the samples' ARISA profiles. Correspondence analysis (CA), which assumes a unimodal relationship between relative abundance (i.e., normalized peak area) and ordination axes, was used to analyze relationships between samples. The R package Vegan was used to determine whether CA ordination axes were correlated with environmental variables. The latter included the experiment from which samples were analyzed (E1 for the experiment comparing CNTs to CNT-associated impurities, conducted on June 28, 2007; E2 for the experiment comparing CNT-associated impurities to a control conducted on July 19, 2007); time elapsed from the initiation of the experiment to sampling (0, 1.25, or 5 hours); and treatment (CNTs, associated impurities, or feed alone). "Dummy" variables were assigned for categorical variables and set to 0 or 1 depending on the presence of a given variable. The "envfit" goodness of fit test with 1000 permutations was used to assess the fit of environmental variables to ordination axes.

In order to determine the phylogenetic identity of dominant community members, as detected by ARISA, phylogenetic analysis of 16S rRNA genes contiguous with fragments analyzed in ARISA was used (Brown et al., 2005). DNA amplicons containing partial 16S rRNA genes and associated intergenic spacer (IGS) regions were generated from selected activated sludge genomic DNA samples using primers 338F and 23SR (5'GGGTT[C/G/T] CCCCATTC[A/G]G-3') (Amann et al., 1990; Brown et al., 2005). The resulting amplicons were cloned using the TOPO TA Cloning Kit for Sequencing with One Shot® TOP10 Chemically Competent *E. coli*, as described by the manufacturer (Invitrogen Corp., Carlsbad, CA). 90 cloned inserts were analyzed using ARISA, as described above, except that the template DNA for PCR consisted of *E. coli* clone cell lysates (obtained by suspending individual colonies in 0.1 M Tris-Cl, pH 8.0, and incubating them at 99° C for 2 minutes). ARISA peaks from cloned inserts were considered to match OTUs from environmental community ARISA patterns if their peak size was placed within the same 3 bp bin as a given OTU from environmental samples.

At least one cloned insert representative of each ARISA OTU was sequenced in both directions by Beckman Coulter Genomics Inc. (Danvers MA, USA) with M13 primers. Vector and primer sequences were trimmed, trimmed sequences were aligned to the Silva database, and phylogenetic relationships among aligned sequences and their 40 nearest neighbors in the Silva database were analyzed using ARB (Ludwig et al., 2004; Pruesse et al., 2007). Trimmed sequences were deposited in GenBank under accession numbers HM205112 - HM205114.

Principal Findings and Significance

Results

Effects of CNTs and their associated impurities

Analysis of ARISA profiles revealed several differences between bacterial community structure in batch reactors exposed to CNTs for five hours when compared to those exposed to associated impurities alone. For example, the relative peak areas of dominant OTUs represented by peaks 419, 794, and 839 bp were significantly different in communities exposed to CNTs vs. those exposed to CNT-associated impurities (Fig. 1). Similarly, a Chi-square goodness-of-fit test of correspondence analysis (CA) axes revealed that the effect of CNTs on community structure was significant (p =0.043), while exposure to impurities alone was not (p= 0.604). In order to assess the effect of CNTs without interference from the strong effects of time and experiment, CA ordination was repeated with only the time T4 samples from the experiment comparing CNTs to impurities alone (E1). A statistically significant effect of CNTs was observed ($p<0.001$), while a similar analysis of the effects of impurities alone (CA with experiment E2, time T4 samples) revealed no effect ($p=0.316$), as was also evident from direct inspection of ARISA profiles (Fig. 1). Samples taken after only 1.25 hours exposure (time T1) revealed no clear differences in ARISA profiles between either CNT- and impurities-exposed reactors or between reactors exposed to impurities and control reactors), indicating that exposure for 1.25 hours was insufficient for CNT effects to be detected via the approach used here.

Both hierarchical clustering and correspondence analysis (CA) of all samples revealed strong effects of the amount of time elapsed prior to sampling (0, 1.25, or 5 hours) and the date of the experiment (Fig. 2). Baseline (T_0) communities for E1 and E2 were fairly similar. However, these communities diverged substantially over the short experimental time period of five hours, with the resulting communities sharing only 14/29 total OTUs and 4/9 total "dominant" (considered here to be those with average relative peak areas > 5%) OTUs.

Three of the OTUs found in environmental samples were identified among the 90 cloned inserts analyzed here. These included peaks corresponding to 419, 740, and 812 bp (Fig. 1). Phylogenetic analysis placed these OTUs within the families *Sphingomonadaceae* (419 bp) and *Cytophagaceae* (740 bp), and the genus *Zoogloea* (812 bp). Two representatives of OTU 812 were sequenced and found to be identical. The closest relatives of the sequences representing OTUs 419, 740, and 812 were: an uncultivated *Sphingomonadaceae* bacterium from snow (97.1% similarity); an uncultivated *Cytophagaceae* bacterium from activated sludge (89.5% similarity); and *Zoogloea resiniphila*, a denitrifier isolated from activated sludge (99.8% similarity).

Discussion

While CNTs have the potential to be highly toxic to microbial cells, their impact under the complex abiotic and biological conditions found in environmental microbial communities remains poorly understood. The current study revealed changes in microbial community structure in activated sludge batch reactors exposed to CNTs, while no effects of CNT-associated impurities were detected. Yin et al. (2009) analyzed bulk parameters and performance from the CNT-exposed batch reactors described here and similarly found that CNTs, but not their associated impurities, had several effects on sludge performance. These effects included: increased organic carbon removal primarily through organic carbon adsorption; less negative surface charges of activated sludge flocs; and improved sludge settleability (Yin et al., 2009). Other parameters such as pH, dissolved oxygen, specific resistance to filtration, and relative hydrophobicity were not significantly impacted (Yin et al., 2009). These findings suggest that CNTs impacted community structure through toxicity to some community members, by reducing organic carbon bioavailability, and/or by altering floc properties.

The fact that CNT effects on microbial community structure were detected was especially interesting given that, unlike some previous studies, the experimental conditions used did not maximize CNT-cell interactions. For example, an assay for cytotoxicity developed by Kang et al. (2007) relies on drawing planktonic cells onto a filter that is coated with nanoparticles and observing the resulting effects on cellular membrane integrity over time. Under these conditions, direct cell-nanoparticle contact is artificially induced and CNTs demonstrated high levels of toxicity to Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) and, to a lesser extent, Gram-positive (*Staphylococcus epidermis* and *Bacillus subtilis*) cells (Kang et al., 2009). In contrast, here, CNTs were added to activated sludge bioreactors in suspension, making CNT-cell contact much less likely. In addition, the presence of extracellular polymeric substances (EPS) and high concentrations of DOC in the batch reactors used here may have mitigated CNT toxicity to some extent, as CNTs are likely to become embedded in EPS and thereby prevented from coming in direct contact with cell membranes (Neal, 2008; Luongo and Zhang, 2010). Lastly, the exposure time was kept short in order to avoid confounding effects of starvation and/or accumulation of waste products in closed-system batch reactors. Despite the use of short incubation times, changes in community structure with both CNT exposure and time over the course of the experiment were found (Fig. 1 and 2). Previous studies have shown that cellular inactivation increased with time of exposure (Kang et al., 2009), indicating that use of longer incubation times in continuous reactors may increase effects of CNTs on community structure.

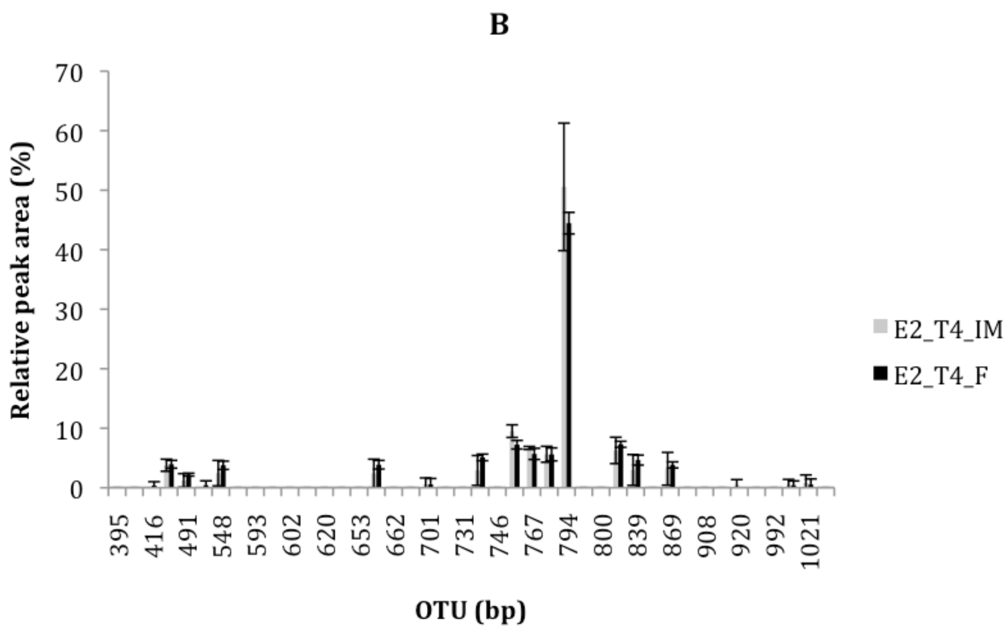
Phylogenetic analysis of cloned inserts that were matched to ARISA peaks revealed the presence of three phylogenetic groups that are responsible for important functions in activated sludge communities, including the members of the families *Sphingomonadaceae* (OTU 419) and *Cytophagaceae* (OTU 740) and the genus *Zoogloea* (OTU 812) (Manz et al., 1996; Neef et al., 1999; Juretschko et al., 2002; Wagner et al., 2002; Li et al., 2008). Of these, the sphingomonad (OTU 419) showed a trend of decreased relative peak intensity with exposure to CNTs (Fig. 1), indicating an adverse impact of CNTs on this group compared to other community members. Within wastewater treatment microbial communities, sphingomonads are thought to have wide metabolic diversity, are capable of degrading some xenobiotics, and contribute to the formation of flocs (Neef et al., 1999; Wagner et al., 2002). Although directly measuring these parameters was beyond the scope of the current study, the potential for negative impacts on CNTs on these microbial functions deserves further attention.

Table 1. Characteristics of CNTs used in the current study.

Purity	
Carbon nanotubes	>90%
Single-walled nanotubes	>50%
Impurities	
Amorphous carbon	<5%
Co	0.6%
Mg	1.2%
Mo	0.1%
Silicates	0.1%
Average outside diameter	1–2 nm
Density	1.7–2.1
Length	5–15 um
Specific surface area	>400 m2/g

Differences in the 'baseline' (T_0) community structure from one sampling date to another corroborate results obtained by Wittebolle et al. (2005), who observed that large community shifts occurred over a period as short as a few days in a given wastewater treatment plant and that community structure was related to performance of biological treatment. These findings underscore the need to analyze microbial community structure when assessing the effects of emerging contaminants on environmental systems, as differences in the starting community composition may alter the observed impacts on community performance.

In conclusion, our results indicate that the structure of activated sludge microbial communities is impacted by exposure to CNTs, even when such exposure is limited to a short time period, and that these effects were not due to impurities associated with CNTs. Community shifts found here indicated that CNTs differentially affect microbial species, as has been found under pure culture conditions (Kang et al., 2009). These results raise the concern of CNT impact on biological functions carried out by the activated sludge process.



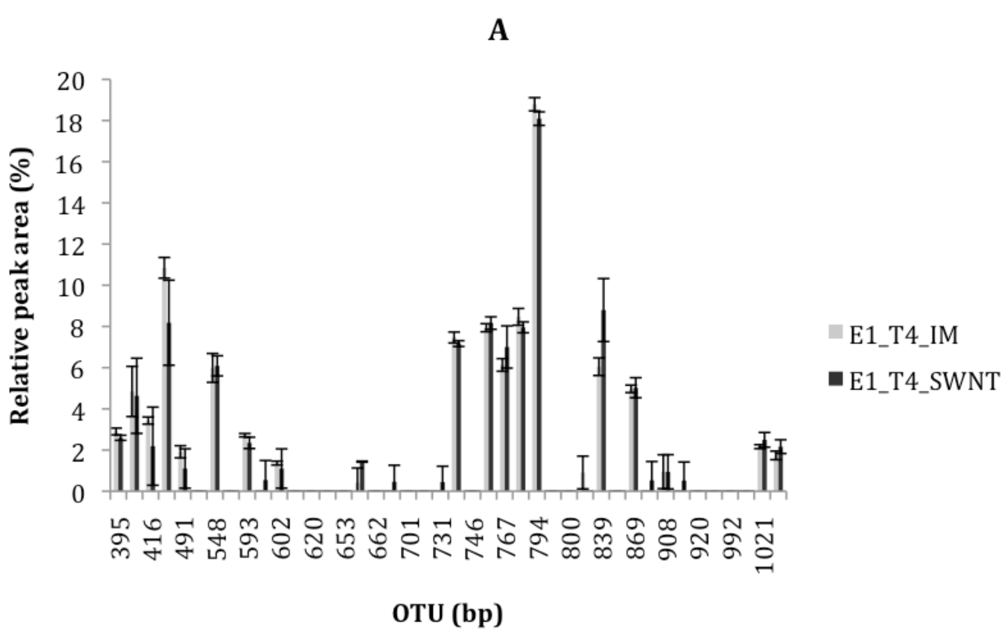


Figure 1. ARISA profiles of activated sludge bacterial communities exposed to CNTs, their associated impurities, or synthetic feed alone at the end of the experiments

(T4). Comparisons were made between CNT- and impurities-exposed (IM) reactors during one experiment (designated E1; panel A) and between impurities-exposed and control reactors receiving feed alone (F) in a second experiment (E2; panel B). Means and standard deviations of relative peak areas from triplicate batch reactors are shown.

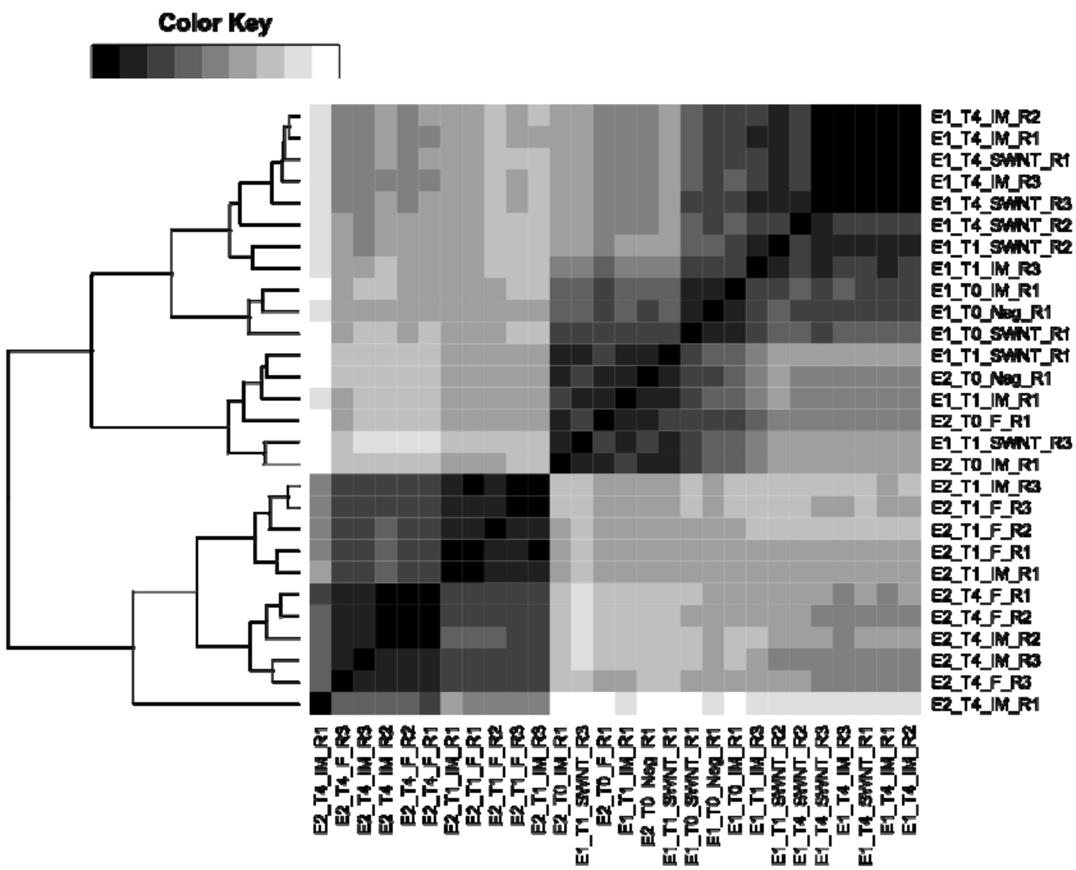


Figure 2. Hierarchical clustering analysis and heatmap of Bray-Curtis distances among samples taken from the first and second experiments (E1 and E2, respectively), at times 0, 1.25 hours, and 5 hours (T0, T1, and T4, respectively), and exposed to CNTs, impurities, or feed alone (SWNT, IM, or F, respectively).

Publications and Conference Presentations

Goyal, D., J. X. Zhang, J. N. Rooney-Varga, 2010. Impacts of single-walled carbon nanotubes on microbial community structure in activated sludge. *Letters in applied microbiology 51(4):428-35,* October 2010.

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Student Support
Deepankar Goyal, M.S., Biological Sciences
Gregory Doyle, B.S., Biological Sciences

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6. Characterization of flow and water quality of stormwater runoff from a green roof (USGS 2009MA199B)

Principal Investigator: Dr. Paul Mathisen, Worcester Polytechnic Institute
Start Date: 4/1/09
End Date: 3/30/10 (initial end date); extended to 2/28/2011
Reporting Period: March 1, 2009 – February 28, 2010
Funding Source: USGS (104B)
Focus Categories: Hydrology; Water Quality; Water Quantity
Descriptors: Green Roof; Water Quality; Storm Water Runoff; NPDES Permit

Problem and Research Objectives

Low Impact Development (LID) techniques for site design are increasingly being utilized to mitigate the negative impacts associated with stormwater runoff, and green roofs are one such application. The ability of green roofs to reduce the total and peak volumes of stormwater runoff has been fairly well documented, but performance varies in different climate zones, and there is limited information available regarding green roof effectiveness in New England, a region whose weather patterns are notoriously variable from season to season and often even day-to-day. Additionally, there are questions regarding the impact that green roofs have on water quality. While there seems to be a general consensus that green roofs will leach phosphorus, and sometimes other contaminants, into stormwater runoff within the first few years after installation, it is assumed that this phenomenon will not continue after the green roof vegetation has been established. However, it is still unclear whether or not this assumption is valid, and very few research projects have attempted to provide the necessary insight into the hydrologic and chemical processes that are contributing to this question.

Accordingly, the goals of this research were to provide insight into the hydrologic and geochemical processes that contribute to green roof performance. The specific objectives included the following:

- Determine the effectiveness of a green roof in attenuating stormwater flow
- Document a green roof's impact on water quality, specifically regarding phosphorus
- Identify the key components of the processes that are likely leading to the highest variability in observed water quality parameters – hence, the highest potential that a change in design could lead to significant improvements.

In addition to providing insight into green roof performance, these objectives are intended to provide a foundation for future research efforts to explore the behavior of phosphorus in soil solutions and its implications for stormwater treatment.

Methodology

The methodology for achieving the project objectives combined field monitoring and laboratory testing and analyses to characterize the quality of runoff associated with the Nitsch/Magliozzi Green Roof, an extensive green roof located on top of a new residence hall at WPI. This roof, which was donated to enhance the sustainability of the building and foster continued research and education, provided the context for the project. The research tasks included field monitoring of the roof drainage, laboratory testing of green roof panels under simulated rainfall conditions, bench-scale testing of phosphorus desorption from the growing medium, and laboratory analyses of water quality, soil characteristics, and plant phosphorus content. The methodology provided a basis for gaining a better understanding of the relationship between rainfall and runoff volumes, phosphorus sorption/desorption in the growing medium, and plant uptake processes.

The field monitoring program focused on the seasonal variations of water quality throughout a complete growing season. Two flow meters and sampling ports have been installed within the storm drain system of the residence hall: one to measure drainage from the green roof; and the other to measure drainage from the "non-green" portion of the roof. Using these sampling ports, a total of 25 grab samples from each roof were collected and analyzed between June 2009 and April 2010.

The laboratory testing and analysis program was developed to characterize both the stormwater retention performance and water quality characteristics of the green roof. For this program, two of the green roof panels were brought into a greenhouse maintained at WPI by WPI's Biology Department. A stand was constructed which allowed for the application of simulated rainfall and collection and measurement of runoff for each panel. For water quality monitoring, runoff from each panel was detoured through a flow-through device attached to a water quality monitoring sonde (Hach MS5 Hydrolab unit), and grab samples were collected at key points during the simulated storms. The Hach MS5 Hydrolab units, one of which was acquired using support from this grant, were important components of this system. Soil and plant samples were also collected, and additional bench-scale tests were completed to characterize the nature of the phosphorus desorption from the media. All samples of water, plant, and soil were analyzed in the water quality laboratory in WPI's Department of Civil and Environmental Engineering.

Principal Findings and Significance

In regards to storm-water flow attenuation, results from the greenhouse experiments showed that green roof performance was more effective for smaller storms, and was influenced by the soil properties (including field capacity and moisture content). Overall, these results are consistent with the published literature. For example, the reduced retention capacity observed during higher flow conditions is a common trend that has been reported for extensive green roof performance. At high rainfall intensities, the field capacity of the green roof panels is quickly exceeded, and the thin layer of the extensive green roof design does not provide much storage capacity. However, while the growing medium did not provide much storage during the heavier simulated rain event, the green roof vegetation's ability to rapidly uptake water when it becomes available did provide a stormwater retention benefit. The improved performance during the lower flow conditions was found to be more heavily influenced by the soil than by the plants. The highest retention rates in the simulated rain events were observed when the antecedent moisture content was low (9-11%). In contrast, for a light rain event, the moisture content of the soil at the beginning was the highest of all tests (26%), and the green roof panels retained only 38% of the influent volume, despite the fact this simulated storm used the smallest volume of water of all simulated events. Clearly the growing medium's field capacity is a critical design factor that is indicative of green roof performance.

In regards to water quality, phosphorus concentrations observed in runoff during greenhouse tests, were similar in magnitude to the concentrations in samples collected from the green and white roofs, which were relatively high. These high concentrations were found to be primarily influenced by phosphorus in the growing medium, which quickly desorbs in response to flushing due to storm events. For all greenhouse tests, the phosphorus concentrations (and other constituents as well) showed up in the "first flush" runoff samples and continued to increase throughout the duration of the storm and after the simulated rainfall had stopped. This trend was consistently observed in all storms, regardless of their size or intensity. These results indicate that the desorption of phosphorus from the growing medium happens quickly, and the soil is not rapidly depleted of its phosphorus content. Also, the green roof panel whose soil was higher in phosphorus concentration (Stand B) also produced runoff with higher phosphorus concentrations than the other panel tested in the greenhouse (Stand A). Meanwhile, the growth of green roof plant material and its associated nutrient uptake processes did not appear to reduce the amount of phosphorus that ended up in the runoff. These results confirm that the growing medium is the source of phosphorus in runoff. However, while a bench-scale laboratory experiment indicated that phosphorus levels in runoff may decrease over time, the rate of desorption is not constant and cannot be easily predicted. Additional investigations will be needed in order to predict the long-term impact of a green roof on phosphorus loading.

With consideration to the design of green roofs, a number of key processes/factors were defined. First, this research showed that soil storage and soil moisture content are particularly important considerations with respect to green roof performance. Soil storage is heavily influenced by antecedent moisture content, and soil moisture content is a function of both weather, which cannot be controlled, and plant variety, which generally can be controlled. These results should help future designers determine whether the weather patterns in a particular location where a green roof is being considered will be hindrance to the effectiveness of a green roof. Areas experiencing significant amounts of rainfall that may keep the soil at field capacity would not be a good choice. However, selecting plant varieties that quickly uptake water, such as sedum and delosperma, will provide the ability to regenerate the holding capacity of the growing medium and will improve the performance of green roofs. Also, efforts should be taken to engineer new soil media that will maximize the field capacity of green roof designs. Second, the research showed that the leaching of phosphorus from the growing medium must be taken into consideration when designing a green roof. Previous studies have made assumptions that the leaching of phosphorus will decrease over time and many have predicted that the phenomenon will only occur for a few years after installation. However, the results of this study indicate that this assumption may not be valid. The long-term phosphorus loading resulting from a green roof may continue longer than previously assumed. Until additional investigations are conducted to develop a prediction model, the impacts of a green roof must be given careful consideration if being installed where phosphorus levels in stormwater are a concern. Further, it is recommended that phosphorus use be minimized in the growing medium. The typical green roof plant varieties, such as those studied here, do not appear to uptake very much of this nutrient, even in their first few establishment years.

In general, these results provide a basis for developing improved predictions of storm-water retention performance, gaining deeper insight into the transformations of phosphorus in the green roof panels, and developing a process by which continued, in-depth study could be performed under controlled laboratory and field conditions.

Publications and Conference Presentations

The results summarized in this summary report are also described in more detail in a Master of Science thesis prepared by Suzanne LePage in partial fulfillment of the requirements for her Master of Science degree at Worcester Polytechnic Institute. The results were also disseminated via a presentation at the EWRI Congress of the American Society of Civil Engineers (ASCE), and via a poster presentation at the Annual Water Resources Conference in Amherst, MA. The details of these items are included in the following listing:

<u>Dissertations/MS Theses</u>

LePage, Suzanne, 2010. An investigation of the hydrologic and geochemical processes contributing to green roof performance. MS Thesis, Worcester Polytechnic Institute, completed in May 2010

<u>Other Publications and presentations</u>

LePage, Suzanne and Paul Mathisen, 2010. *An investigation of the hydrologic and geochemical processes contributing to green roof performance.* Presentation at the American Society of Civil Engineers (ASCE) World Environmental and Water Resources Congress 2010. Providence, Rhode Island. May 20, 2010.

LePage, Suzanne, 2010. *An Investigation into the Water Quality Impacts of a Green Roof*. Poster presentation at WPI Graduate Achievement Day, Worcester Polytechnic Institute, Worcester, MA on March 31, 2010.

LePage, Suzanne,2010. *An Investigation into the Water Quality Impacts of a Green Roof*. Poster presentation at the 7th Annual Water Resources Research Conference, Amherst, MA on April 8, 2010. 2nd Place Award.

Student Support

This project provided equipment that assisted the research program of 1 graduate student, Suzanne LePage, at Worcester Polytechnic Institute. The matching funds designated in this grant included the student time and effort as part of an independent study project (ISP) completed in the fall of 2009.

Notable Achievements and Awards

2nd Place award for Poster entitled "*An Investigation into the Water Quality Impacts of a Green Roof*", which was presented at the Seventh Annual Water Resources Research Conference Poster Contest on April 8, 2010

7. Acid rain monitoring project (USGS-2009MA211B)

Principal Investigator: Marie-Françoise Hatte, MA Water Resources Research Center, UMass Amherst
Start Date: March 1, 2009
End Date: February 28, 2010
Reporting Period: March 1, 2009 – June 30, 2010
Funding Source: USGS (104B) and MassDEP
Descriptors: Acid Deposition; Surface Water Quality; Volunteer Monitoring

Problem and Research Objectives

The Acid Rain Monitoring project continued for the 8th consecutive year following an 8 year hiatus which was preceded by 10 years of consecutive sampling. Approximately 150 sites (mostly streams) were sampled by volunteer collectors and tested for pH and alkalinity by volunteer labs. Of those, 26 long-term sites were analyzed for color, SO_4, NO_3-N, Cl, Ca, Mg, K, Mn, Fe, Cu, Si, and Al. New data on lakes and streams collected over the past 8 years will aid in evaluating whether or not changes result from passage of state and federal Clean Air Act revisions. More than 43,000 records of water chemistry for Massachusetts' lakes and streams, covering 1983-2010, are posted on a web site in a searchable and downloadable form so that additional data analyses specific to the user may be conducted (http://umatei.tei.umass.edu/ColdFusionProjects/AcidRainMonitoring/).

Methodology

Methods were mostly unchanged from previous years: Volunteer collectors are contacted a month before the collection to confirm participation. Clean sample bottles are sent to them in the mail or via UPS, along with sampling directions, a field sheet/chain of custody form, and directions to the sampling sites if necessary. Collectors visit their site(s) twice a year, in April and October, when they collect a surface water sample from the bank or wading a short distance into the water body. They collect upstream of their body after rinsing their sample bottle 3 times with lake or stream water. If collecting by a bridge, they collect upstream of the bridge unless safety and access do not allow it. They fill in their field data sheet with date, time, and site code information, place their samples on ice in a cooler and deliver the samples to their local laboratory right away. They are instructed to collect their samples as close to the lab analysis time as possible. In a few cases, samples are collected the day prior to analysis because the lab is not open on traditional "ARM Sunday." Previous studies by our research team have established that pH does not change significantly when the samples are refrigerated and stored in the dark.

Volunteer labs are sent any needed supplies (sulfuric acid titrating cartridge, electrode, buffers), 2 quality control (QC) samples, aliquot containers for long-term site samples, and a lab sheet one week to ten days before the collection. They analyze the first QC sample in the week prior to the collection and call in their results to the Statewide Coordinator. If QC results are not acceptable, the volunteer analyst discusses possible reasons with the Statewide Coordinator and the Lab Director and makes modifications until acceptable results are obtained. On Collection day, volunteer labs analyze the second QC sample before and after the regular samples, and report the results on their lab sheet along with the regular samples. Analyses are done on their pH-meters with KCl-filled combination pH electrodes. Acid neutralizing capacity (ANC) is measured with a double end-point titration to pH 4.5 and 4.2. Most labs use a Hach digital titrator for the ANC determination, but some use traditional pipette titration equipment. Aliquots are taken from the 26 long-term site samples to fill one 60 mL bottle and one 50 mL tube for later analysis of ions and color. These aliquots are kept refrigerated until pick-up from UMass staff. Within two days after the collection, ARM staff collects aliquots, empty bottles, and results. The Cape Cod lab mails those in, with aliquot samples refrigerated in a cooler with dry ice.

UMass Chemistry Department's Dr. Julian Tyson and his laboratory team of graduate students run the Environmental Analysis Lab (EAL) and provide the QC samples for pH and ANC to all of the volunteer labs. EAL also provides analysis for pH and ANC for selected sampling sites, as well as color and ion analysis for the long-term sites. Anion aliquots are kept refrigerated, and cation aliquots are acidified to a pH of 2 for preservation.

Aliquots for the 26 long-term sites are analyzed for color on a spectrophotometer within one day; anions within one month on an Ion Chromatograph; and cations within 6 months (but usually 2 months) on an ICP at the Environmental Analysis Lab (EAL) on the UMass Amherst campus. The data is sent via MS Excel spreadsheet to the Statewide Coordinator who uploads it into the web-based database.

The Statewide Coordinator reviews the QC results for all labs and flags data for any lab results that do not pass Data Quality Objectives (within 0.3 units for pH and within 3 mg/L for ANC). pH and ANC data are entered by one ARM staff and proofed by another. Data are uploaded into the web-based database at http://umatei.tei.umass.edu/ColdFusionProjects/AcidRainMonitoring/ and posted on the ARM web page at http://www.umass.edu/tei/wrrc/arm/.

Principal Findings and Significance

Data Analysis Results

Bivariate analysis for pH and ANC

Table 2 displays the number of sites out of 151 that show a significant change over time for pH or ANC. If the difference was not statistically significant ($p>0.05$), the sites are tabulated in the 'No Change' (not significantly different) category.

Table 3 displays the results of the t-test analysis, showing how many sites have a significant change in the current period compared to historical data.

Those results are also graphed in figures 1 and 2.

Table 2: Bivariate analysis results for pH and ANC

	All seasons		April		October	
	pH	**ANC**	**pH**	**ANC**	**pH**	**ANC**
No Change	96	120	92	105	116	123
Increased	48	22	58	44	18	15
Decreased	7	9	1	2	17	13

Table 3: Standard t-test results for pH and ANC

	All Seasons		April		October	
	pH	**ANC**	**pH**	**ANC**	**pH**	**ANC**
No Change	101	113	105	107	124	125
Increased	42	21	44	44	15	15
Decreased	8	17	2	0	12	11

Figure 1. Changes in pH and ANC, from bivariate analysis

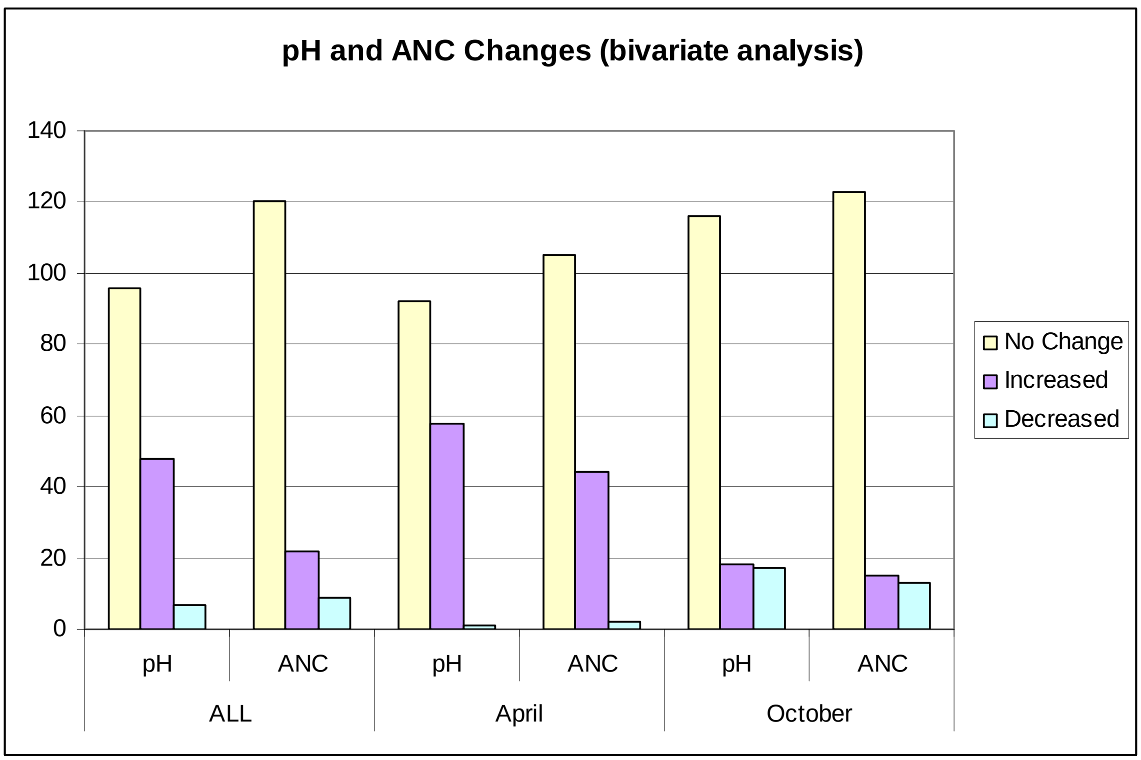
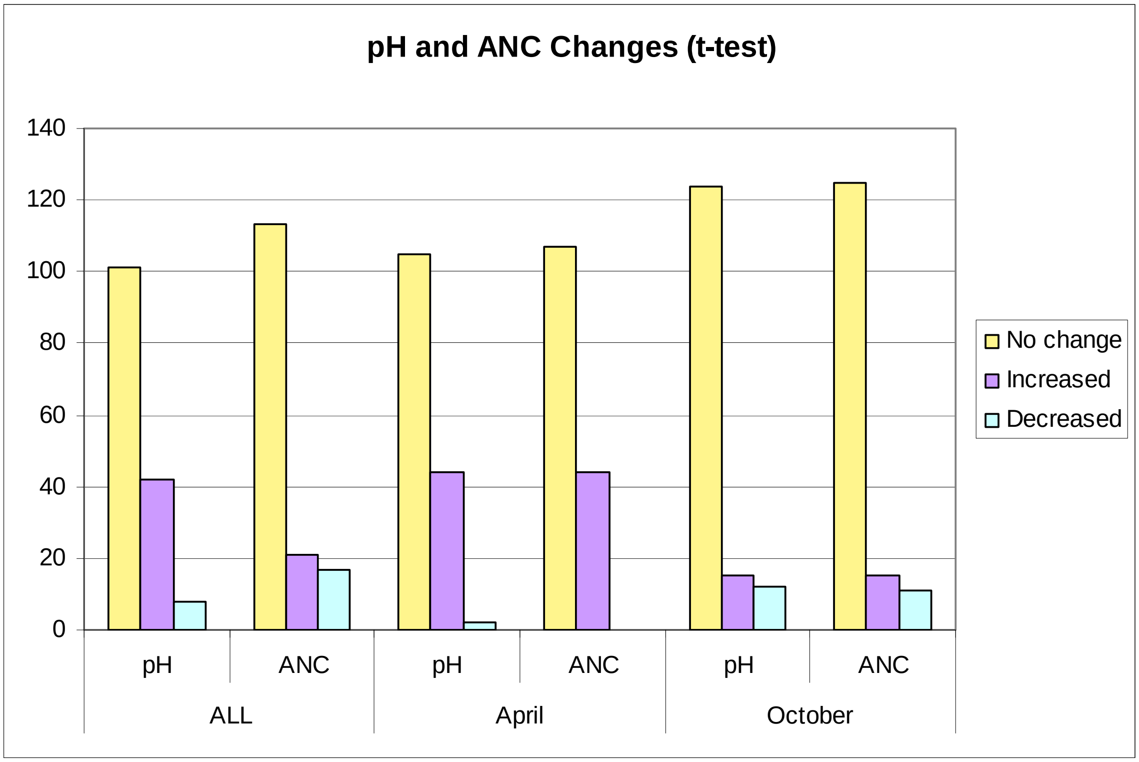


Figure 2. Changes in pH and ANC, from t-test analysis



While the two types of statistical analyses give somewhat different results, they both suggest that neither pH nor ANC has changed significantly over time at most sites. However, for those sites that show a significant change, more show an increase than a decrease in value. That is especially true for pH, with almost one third of the sites that *have* changed, showing a statistically significant increase. ANC shows a less clear trend, except when spring and fall seasons are analyzed separately. In that case, many more sites show an increase in ANC in April than in October.

Ions and Color

Bivariate and standard t-test analyses were run on the 26 long-term sites that are analyzed for 10 ions and color. (In Phase V we analyze 11 ions, but Cu was not part of the cation suite in Phases I through III so no comparison can be made for that ion).

Table 4 and figure 3 show the results of the bivariate analysis for ions and color, while table 5 and figure 4 show the results of the standard t-test analysis.

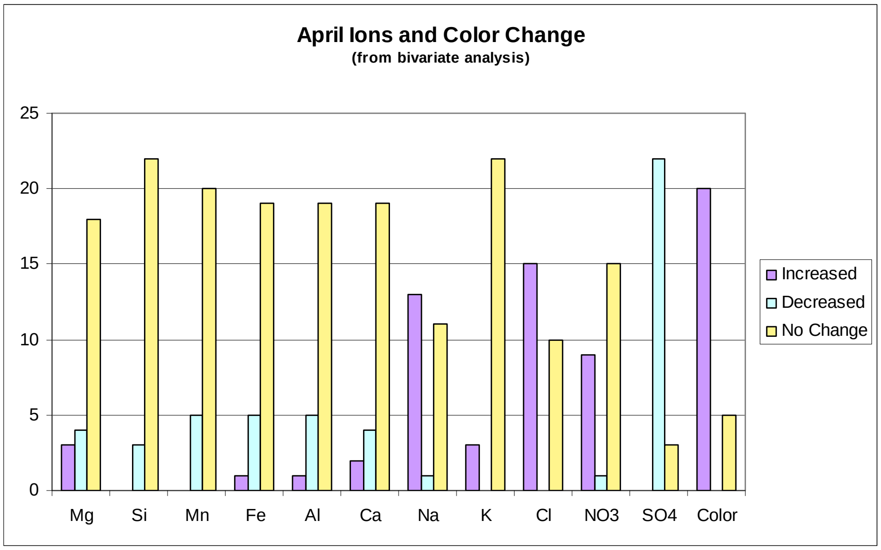
Table 4: Bivariate analysis results for ions and color

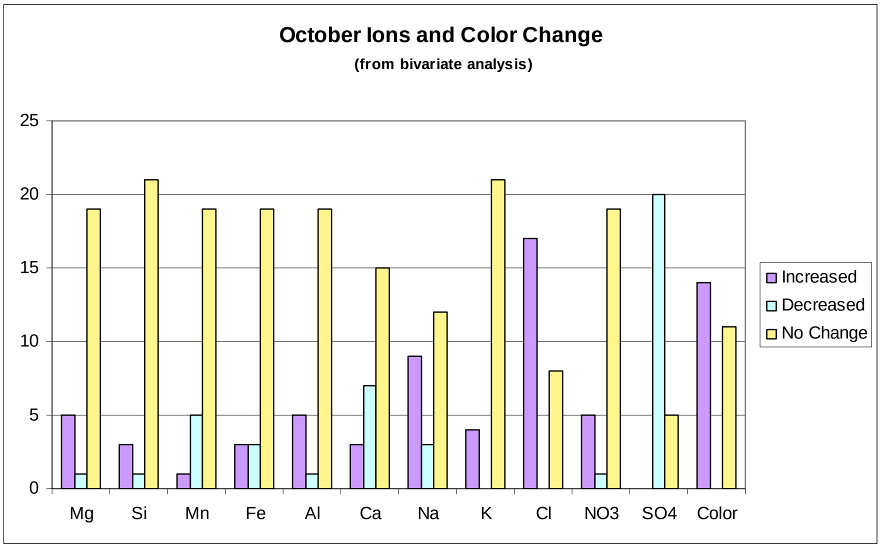
	April			October			All Seasons		
	No Change	Increased	Decreased	No Change	Increased	Decreased	No Change	Increased	Decreased
Mg	18	3	4	19	5	1	19	3	3
Si	22	0	3	21	3	1	23	1	1
Mn	20	0	5	19	1	5	19	1	5
Fe	19	1	5	19	3	3	18	4	3
Al	19	1	5	19	5	1	19	4	2
Ca	19	2	4	15	3	7	14	4	7
Na	11	13	1	12	9	3	12	12	1
K	22	3	0	21	4	0	22	3	0
Cl	10	15	0	8	17	0	6	19	0
NO3	15	9	1	19	5	1	14	10	1
SO4	3	0	22	5	0	20	8	0	17
Color	5	20	0	11	14	0	8	17	0

Table 5: T-test analysis results for ions and color

	April			October			All		
	No change	Increased	Decreased	No change	Increased	Decreased	No change	Increased	Decreased
Mg	19	4	2	20	2	3	18	3	4
Si	21	2	2	21	3	1	22	2	1
Mn	18	1	6	18	1	6	19	1	5
Fe	19	3	3	22	2	1	21	2	2
Al	23	1	1	21	1	3	20	2	3
Ca	15	5	5	18	3	4	16	3	6
Na	12	11	2	11	13	1	10	14	1
K	23	2	0	21	4	0	7	18	0
NO3	22	2	1	13	9	3	14	1	10
SO4	6	2	17	3	2	20	6	0	19
Color	14	10	1	6	19	0	8	17	0

Figure 3: Results of bivariate analysis for ions and color, all seasons, April, and October.





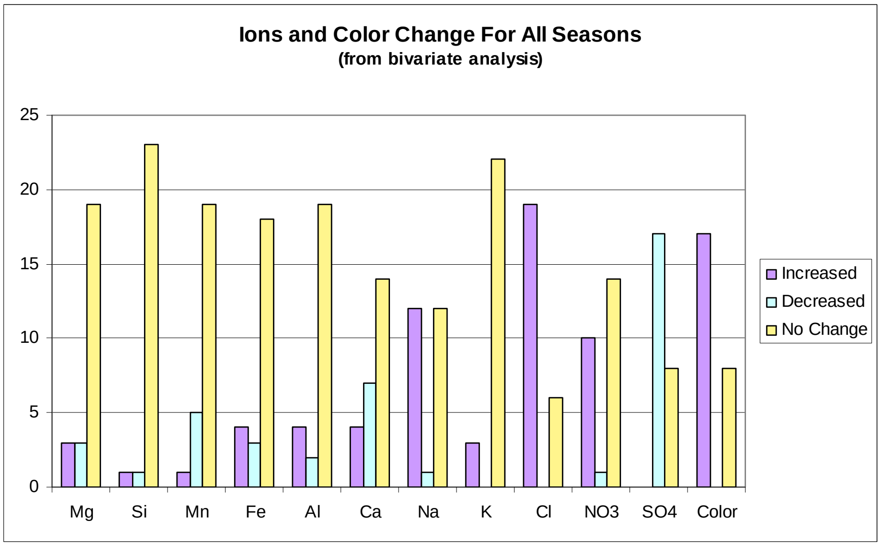
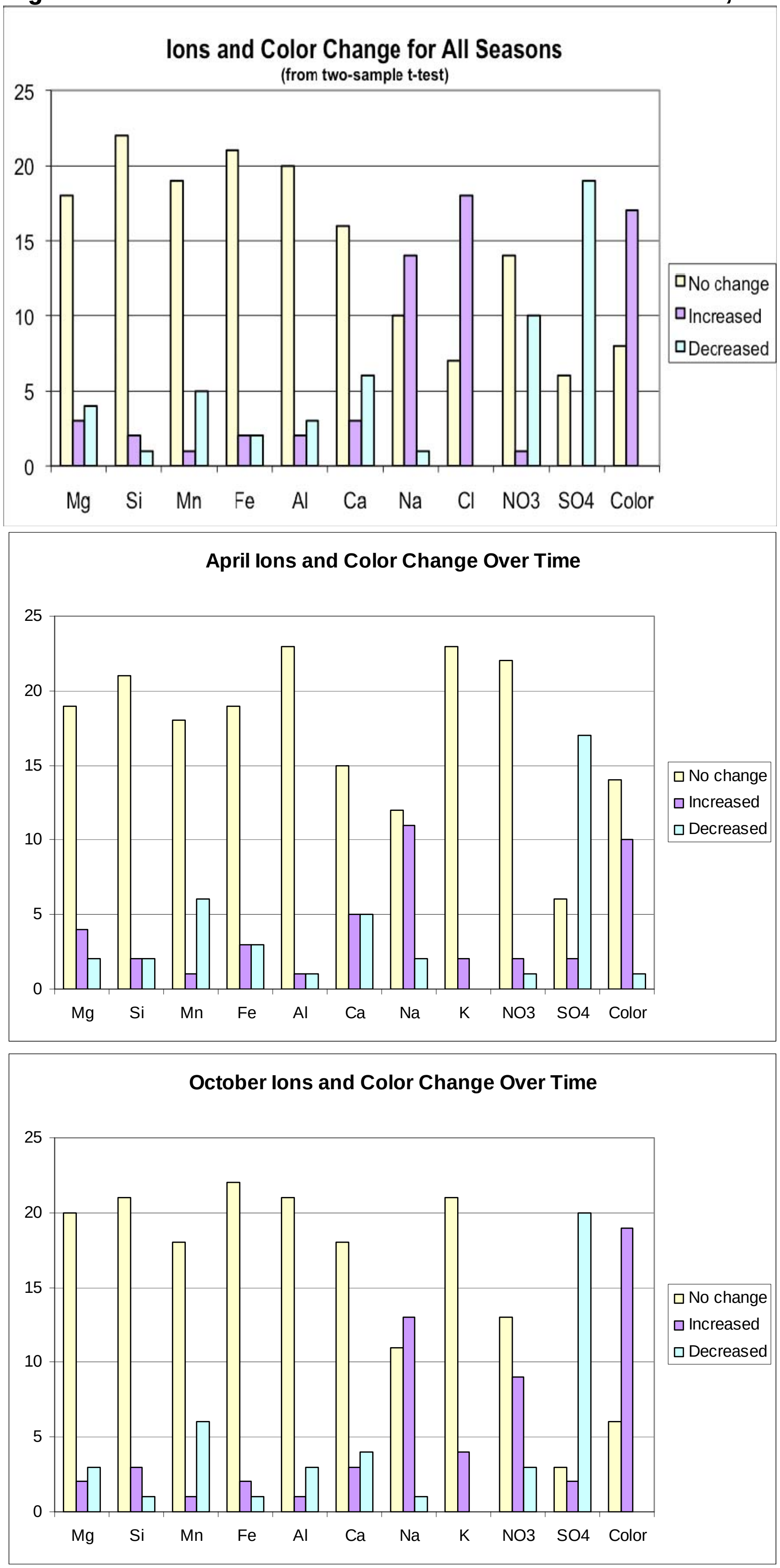


Figure 4: Results of standard t-test for ions and color, all seasons



Ion and color results may be summarized as follows:
Most cations show *no significant* change over time for the 26 sites we are following. Base cations calcium and magnesium still show no sign of recovery, if anything calcium actually seems to be still declining. At this time we cannot confidently assess an increase or a decline in aluminum. A notable difference, however, can be seen for sodium and with chloride, which increased for almost half of the sites no matter what season and with both types of statistics used. All anions show *significant* change. This change is seen more clearly with the bivariate analysis, which tracks concentrations continuously over time, while the t-test compares only the set of data from the first 10 years with the last 10 years of the project. Chloride never decreases with time, and increases for two-thirds of the sites. Nitrate's change is less definite, but it clearly increases for about a third of the sites and decreases on average for a couple of sites. Sulfate shows the most dramatic change, a strong decrease for over two-thirds of the sites. Color shows a consistent increase over time, for over two-thirds of the sites in all seasons.

Discussion

These results are mostly consistent with what we found for an earlier analysis we performed on lakes in Phase IV of this project, and are also consistent with results from other research studies in the northeast. The main difference is that more sites (up to 30%) now show an increase in pH, and we are seeing a clearer increase in nitrate in Phase V.

It is interesting to note that more sites show an increase in both pH and ANC in the April samples than in the October samples, and this trend holds with both statistical tests performed. April is the time of year when we typically see the lowest pH and ANC values, most probably due to snowmelt waters that carry an important amount of nitrates into surface waters. We would therefore expect to see a corresponding decrease in nitrate in April. However, the bivariate analysis shows no change, and the t-test actually shows more sites increasing than decreasing in nitrate in the April samples. An explanation might be that the reason for the increase in pH is not so much due to the reduction in nitrate, but rather reflects the reduction in sulfates. Further research or literature review should be done in order to draw a confident conclusion.

Indeed sulfate continues to show a strong and significant decline, in line with decreases in emissions of sulfur dioxide that followed the 1990 Clean Air Amendment. The increase in nitrate is also not surprising, despite a similar decrease in NOx emissions from power plants, because nitrogen emissions from vehicle sources have increased over time. Since roads in Massachusetts are often located along streams, and because roads are designed to channel water off and away from their surface, increased NOx emissions have a direct path into surface waters. Correspondingly, we continue to document a significant increase in sodium and especially chloride. This results very likely from road salting practices in the northeast.

The consistent increase in color over time suggests that there is a greater release of organic acids from the New England forested landscape than in the past. These weak acids may be diluting the stronger mineral acids, resulting in the observed stable to slightly increasing pH values across the region.

In conclusion, to answer our question whether the 1990 Clean Air Act Amendment has resulted in improved water quality in Massachusetts surface waters, the answer is a cautious "somewhat." More water bodies seem to have improved than worsened.

However, increased concentrations of nitrogen in receiving waters suggest that the forests may have reached their N absorption capacity. This indicates that continued NOx emission controls are necessary, particularly from vehicle sources. Reductions in sulfate in receiving waters seems to be correlated mainly with decreased inputs, as no clear trends in Ca or Mg, which would buffer the sulfate, were observed.

Students Supported

1 BS student in Economics at UMass Amherst
1 BS student in Mathematics at UMass Amherst
1 BS student in Chemical Engineering at UMass Amherst
1 PhD student in Chemistry at UMass Amherst.

8. Tri-State Connecticut River targeted watershed initiative

Principal Investigator: Jerry Schoen, MA Water Resources Research Center, UMass Amherst
Start Date: December 1, 2007
End Date: December 31, 2010
Reporting Period: July 1, 2009 – June 30, 2010
Funding Source: USEPA
Descriptors: Connecticut River; Water Quality; Volunteer Monitoring; Information Technology

Problem and Research Objectives

The Connecticut River has been described as "the Pioneer Valley's Boston Harbor" because the river still has significant water quality problems. In New Hampshire and Vermont, water quality is impaired due to erosion, sedimentation, and combined sewer overflows, and mercury and PCBs render fish consumption unsafe. From the Holyoke Dam south to Connecticut, water quality standards are not supported (Class B fishable/swimmable) due to pathogens and suspended solids, primarily from urban runoff and combined sewer overflows. According to the USGS, bacteria levels in the lower Connecticut River, which can measure as high as 10,000 fc/100ml, are among the highest found in southern New England rivers. In addition, the Connecticut Department of Environmental Protection concluded that nitrogen loads from the Connecticut River to Long Island Sound must be reduced by 58% in order to reverse eutrophication. Similar to Boston Harbor, clean-up costs are very high, estimated at $325 million for CSOs in Springfield, Chicopee, and Holyoke alone. This is an environmental justice issue, as many low-income residents in the Holyoke-Springfield reach use the river for fishing and swimming. The benefits of cleaner water will also be enormous due to the popularity of the river for recreation and riverfront economic development.

The Tri-State Connecticut River Targeted Watershed Initiative addresses the most significant water quality problems of the Connecticut River watershed: major bacterial pollution from combined sewer overflows and urban stormwater; extensive streambank erosion; threats to public water supplies; and nutrient loading from agricultural runoff. It is funded under a $953,000 Targeted Watershed Initiative grant from the U.S. Environmental Protection Agency, matched by $458,000 in local funding commitments.

WRRC involvement in this project, carried out in collaboration with the UMass Center for Educational Software Development (CESD), is aimed at improving main stem water quality and public use, and conducting innovative public outreach and participation. University activities include "rapid response" water quality monitoring and an innovative IT-based public outreach campaign that includes a web-based virtual watershed tour highlighting water quality problems and project sites, and mobile story tours for each task in the EPA grant.

Water Quality Monitoring

Until now only limited water quality information has been available for the Connecticut River. This information has indicated that in many urbanized areas the river's bacterial contamination is so high during wet weather events—due to combined sewer overflow discharges and to urban stormwater flows—that it does not meet standards for recreational uses.

This bacteria monitoring project examined bacteria at 16 sites (drawn from a list of 26 sites) twice a week in two urbanized reaches of the river in Massachusetts, Chicopee to Holyoke and Turners Falls to Greenfield; and one mixed urban/suburban/rural reach in New Hampshire and Vermont, from Lebanon and Wilder to Cornish NH and Weathersfield VT, during the high-use summer recreation months of 2008 and 2009. All sites sampled are considered to receive a high degree of use for swimming, boating, fishing and other river recreation. Samples were analyzed at four local wastewater treatment plants and a private laboratory.

During the second year of the two year project, there were 40 sampling days in which a total of 419 bacteria samples were collected.

Major findings that are relative to *E. coli* bacteria are:

- Water quality appears to be worse on wet days than on dry days.
- Vermont and New Hampshire sites generally support contact recreation in both wet and dry weather conditions.
- With the exception of the Barton Cove site (MAG4), the northern Massachusetts sites were supportive of contact recreation during dry weather, and partially supportive during wet weather. Site MAG4 exhibited high bacteria levels on several occasions, during both wet and dry weather in 2009. Further study of this site is warranted, to determine the cause of the high bacteria levels.
- The more urbanized southern Massachusetts reach frequently exceeded primary contact recreation limits during wet weather and occasionally did so in dry weather at some sites. The North End/Bassett Marina site (MAC1) is of particular concern, as this site usually exceeded the contact limit, regardless of weather conditions.

The nutrient monitoring project involves demonstration best management practices (BMPs) undertaken at the UMass Hadley farm to fence livestock out of a stream running through the farm and install native plantings to restore riparian corridors. The samples are collected in wet weather as well as in dry weather events.

In addition to samples taken in 2008, one dry-weather and two wet-weather samples were collected in 2009 for the nutrient monitoring. Additional samples will be taken when the installation of BMPs is complete.

Information Technology

Project Website with Virtual Watershed Tour

WRRC and CESD continued to work on and improve the project web site: http://www.cesd.umass.edu/twi/. The web site includes a multimedia *virtual tour* of the watershed. Maps, photographs, graphs, audio and text illustrate valuable recreational, economic, and public health resources provided by the river along its length from source to sea. Site users will be able to virtually fly over the watershed and zoom in to selected locations to learn of popular boating, fishing, swimming areas, water supply, agricultural lands, etc. The site contains links to other sites about natural and cultural history of the Connecticut River.

Mobile Story Tours

WRRC and CESD are continuing to develop mobile tours for each of the project components. Users will be able to learn of events and activities occurring at project site areas by playing back information about the project on mobile devices, while walking through the sites.

Electronic Field Guide

WRRC is continuing this project using software adapted from UMass Boston's Electronic Field Guide (EFG) project http://efg.cs.umb.edu/efg/ to produce an electronic field guide to observational water quality indicators (e.g. pictures and narrative description of pollution or sediment plumes, degraded stream banks, when foam is or is not likely to be a sign of pollution). This is being created for the web site and for handheld versions. The guide will advise users how to document suspected pollution problems with photos, description and location information, how to submit observations to project staff. Project staff will follow up to validate observations and contact local authorities as appropriate.

Notable Achievements and Awards

Results from this project were used in a successful application by the Pioneer Valley Planning Commission (with the WRRC as a subcontractor) to the federal 604(b) program for continued monitoring of nine Connecticut River Mainstem sites and of numerous tributary sites in Massachusetts, to locate sources of bacterial pollution.

The information technology practices used in this project were cited in a successful proposal by UMass Amherst and Boston campuses to the National Science Foundation's Course, Curriculum and Laboratory Improvement Program. WRRC will collaborate with the UMA Center for Educational Software Development, the Landscape Architecture Program, and the Biology Department of both campuses on this two-year project, beginning in July 2010.

Publications and Conference Presentations

Jerry Schoen, 2010. Rapid Response Water Quality Monitoring and Public Awareness Final Report. Water Resources Research Center, University of Massachusetts, Amherst MA 01003.

9. Connecticut River water quality monitoring and source tracking project / Connecticut River Watershed

Principal Investigator: Jerry Schoen, MA Water Resources Research Center, UMass Amherst
Start Date: August 1, 2009
End Date: August 30, 2011
Reporting Period: July 1, 2009 – June 30, 2010
Funding Source: MassDEP
Descriptors: Connecticut River; Bacteria Monitoring

Problem and Research Objectives

The project continues an on-going volunteer based bacteria monitoring program in the Connecticut River watershed in Franklin, Hampshire and Hampden Counties. The project involves the collection of bacteria samples along the main stem of the river, new collection of baseline bacteria data on tributaries suspected to be sources of bacteria but where little or no data exists to document the problem, and to perform new monitoring and field reconnaissance at specific locations for bacteria source tracking. Data collected will be shared with the public, DEP, municipal officials, and other stakeholders through posting the data to an established web site targeting recreational river users as well as outreach through local media and forum outlets.

Limited water quality sampling undertaken in 2006 by consultants for the Connecticut River Clean-up Committee in the Holyoke-Springfield, MA reach of the river showed average *E. coli* bacteria levels during wet weather events of 7,480 colonies/100ml in Holyoke, 1,800 colonies/100ml in Chicopee and 1,267 colonies/100ml in Springfield, well above the water quality upper limit of 126 colonies/100ml indicating impaired river water and failure to meet water quality standards for recreational uses. More recent bacteria monitoring performed in 2008 and 2009 under the U.S. EPA funded Tri-State Connecticut River Targeted Watershed Initiative Grant further confirmed these findings. The EPA-funded monitoring project examined water temperature and bacteria at 26 sites along the main stem of the Connecticut River on three river stretches between White River Junction, New Hampshire and Hartford, Vermont, Turners Falls and Greenfield, Massachusetts, and between Holyoke and Agawam, Massachusetts.

Combined sewer overflow abatement projects (CSOs) have been underway since the 1980s and continue as funding is made available. However, public officials are constantly debating sources of pollution and bacteria and whether their community is responsible for it. In addition to CSOs, urban runoff is a suspected source of the documented impairment. Underground streams in urban areas are usually high in bacteria even without CSO discharges to them. DEP's bacteria source tracking team is focusing on Integrated List streams that are impaired for bacteria. However, there are numerous small tributaries to the Connecticut River that are not on the Integrated List for bacteria impairment and therefore are not being monitored by DEP, but are likely sources of bacteria loading. The project complements DEP's monitoring and source tracking program by focusing on waters not monitored by DEP but suspected to be contributing sources to the impairment due to their urbanized watersheds or by identifying parcels with highly threatening land uses.

Methods

The Pioneer Valley Planning Commission (PVPC) partnered with the Connecticut River Watershed Council (CRWC) and the Water Resources Research Center at UMass Amherst to perform the scope of work as described below.

QAPP

WRRC, in coordination with PVPC and CRWC, coordinated a single DEP/EPA approved QAPP for assuring a quality sampling program based on amendments to the current EPA approved Quality Assurance Project Plan (QAPP) for the Tri-State Connecticut River Targeted Watershed Initiative Volunteer Monitoring Program. This process involved inclusion of sampling, analytical and quality control procedures for new monitoring sites and parameters for the source tracking component of the project. Standard Operating Procedures (SOP) for laboratory analysis for CRWC's new lab at their office in Greenfield, MA will also be included. CRWC's lab became operational in May of 2010.

Volunteer Coordination and Training

PVPC coordinated volunteers in Hampshire and Hampden Counties and CRWC coordinated volunteers in Franklin County. Volunteers collected water quality samples during the high-use summer recreation months (May-October). PVPC and

CRWC staff served as Regional Coordinators to oversee sample event preparation, activities of volunteer field samplers, sample transport to laboratories, and communication with labs relative to volunteer field samplers.

WRRC performed two volunteer-monitor training sessions (one in the upper reach and one in the lower reach) in May 2010. WRRC will also facilitate two end of the season summary and wrap up sessions (in 2010 and 2011) to discuss the results of the monitoring season and thank the volunteers to garner support for the next season's monitoring. Sampling sites were broken out into three tiers: Tier 1, Tier 2, and Tier 3 sites.

Tier 1 sites include 15 sites along the main stem of the Connecticut River in Franklin, Hampshire and Hampden Counties, essentially the border with Vermont to the border with Connecticut. These are the same 15 sites involved in the EPA Targeted Watershed Initiative monitoring program. Samples were and will continue to be collected at these sites one day per week for bacteria analysis.

Tier 2 monitoring sites are on Connecticut River tributaries that are suspected to be contributing bacteria loading to the main stem based on the land uses within the watershed and /or documented water quality impairments. Tier 2 tributaries were identified based on the bacteria levels at the main stem sites, guidance from the Advisory Committee, and DEP's bacteria source tracking team. Up to 30 Tier 2 sites on tributaries along the entire main stem of the Connecticut River in Massachusetts will be monitored two times per month for 6 months (total) for bacteria "screening level" sampling.

Tier 3 monitoring sites will be identified specifically for bacteria source tracking along those Tier 2 tributaries where bacteria screening results indicate bacteria levels in excess of secondary contact standards for *E. coli*. Tier 3 monitoring sites may include pipe discharges or in-stream grab samples. Up to 20 Tier 3 monitoring sites will be sampled once per month for six months.

<u>Sample Collection and Source Tracking</u>

WRRC serves as Sampling Coordinator and communicates with labs including establishing a sampling schedule, receiving data reports from lab for posting data to the website and sharing with Regional Coordinators to inform the source tracking program. Volunteers, with assistance from the Regional Coordinators (PVPC, CRWC), collect samples at designated locations and drop off at labs. In addition to collecting samples from either stream flows or piped outfalls, source tracking may involve field reconnaissance to gather information about the surrounding area, identify "suspect" pipes, stains, odors, and poor land use practices. Dry weather flows at piped outfalls may be field screened for optical brighteners. Local DPWs will also be notified of source tracking activities within their communities to coordinate resources (e.g. infrastructure mapping), testing (e.g. dye testing) and data collection that is available through the municipality.

<u>Lab Analysis</u>

PVPC and CRWC coordinate sample analysis for *E. coli* bacteria levels at the municipal wastewater treatment plant lab in Holyoke (operated by Suez/United Water) and, CRWC's lab in Greenfield. CRWC's lab will analyze up to 500 samples for *E. coli* using the Colilert system. Holyoke's lab will analyze up to 700 samples for *E. coli* utilizing EPA SOP 1603 for membrane filtration. Holyoke's lab, Suez/United Water, is donating $18,500 worth of lab services to the project.

Outreach and Education / Technology Transfer

WRRC continues to maintain and post data to the Connecticut River website established for the Tri-State Connecticut River Targeted Watershed Initiative (http://www.umass.edu/tei/mwwp/ctrivermonitoring.html). This site is currently hosted and maintained by the Water Resources Research Center at UMass Amherst. Data continues to be posted to the website within 24 hours of completed laboratory analysis to alert recreational users to water quality conditions. At the outset of monitoring in May 2010, this website will have been operational for the 2008 and 2009 seasons. Thus, its use and availability to river recreationalists will have been established. Under this project, project partners will continue to promote awareness of the website.

Other Publications and presentations

Newspaper Coverage

The Republican
"Connecticut River water quality monitoring project will keep river users informed of E. coli levels". Published: Sunday, June 06, 2010, 1:00 AM Updated: Monday, June 07, 2010, 7:29 AM. John Appleton, The Republican.

http://blog.masslive.com/breakingnews/print.html?entry=/2010/06/connecticut_river_water_qualit.html

Television Coverage

Channel 22 News
"Monitoring the quality of the CT River: Monitors water quality at a number of sites" Published: Friday, 04 Jun 2010, 5:17 PM EDT
http://www.wwlp.com/dpp/news/local/monitoring-the-quality-of-the-ct-river

Channel 22 News
"Water quality monitored on Conn. River: Volunteers will collect water samples this summer" Published: Sunday, 06 Jun 2010, 10:52 AM EDT
http://www.wwlp.com/dpp/news/massachusetts/water-quality-monitored-on-conn-river

10. Blackstone River water quality modeling study

Principal Investigator: Dr. Paula Rees, MA Water Resources Research Center, UMass Amherst
Start Date: 2/26/2004
End Date: On-going
Reporting Period: July 1, 2009 – June 30, 2010
Funding Source: Upper Blackstone Water Pollution Abatement District
Descriptors: Blackstone River; Water Quality Monitoring; Water Quality Modeling; Watershed Management
Focus Categories: Nonpoint Pollution; Hydrology; Water Quality; Management & Planning

Problem and Research Objectives

The purpose of this study is to assess existing water quality conditions, identify sources and quantify pollutant loads to the river, develop modeling tools for determining the fate and transport of nutrients along the river, and utilize these tools to evaluate the effectiveness of various management strategies (both point- and nonpoint source controls) for improving water quality and ecosystem health along the Blackstone River. The questions to be answered include:

- Based on existing data, particularly including data collected since completion of the Blackstone River Initiative, what is the current status of the Blackstone in terms of water quality conditions and ecosystem health during both dry and wet conditions along its various reaches?
- How have water quality and ecosystem health changed over time and how may they be expected to change in the future?
- How does water quality compare to that of other watersheds, both developed and non-developed, and thus what concentrations are feasible to attain along the Blackstone for a variety of water quality parameters?
- What are the sources of pollutants most negatively affecting Blackstone River water quality and ecosystem health?
- What are the relative contributions of pollutants from these sources?
- What strategies to improve water quality have been successfully implemented in similar watersheds?
- What are the most effective methods (feasible, reasonable, equitable, and economic) for improving water quality and ecosystem health of the Blackstone River?
- How are improvements in water quality and ecosystem health along various reaches of the Blackstone River anticipated to affect downstream receiving waters?
- What critical gaps are there in our understanding of loading and important processes impacting nutrient concentrations along the Blackstone River?
- What critical gaps are there in our understanding of the effects of point and nonpoint source pollution on ecological health within the Blackstone.

Background

The Blackstone River (Figure 1) originates at the confluence of Middle River and Mill Brook in Worcester, Massachusetts. It flows southeast for 46 miles into Rhode Island where it joins the Seekonk and Providence Rivers, which discharge to Narragansett Bay. The Blackstone River watershed, shown in Figure 1, has an area of approximately 480 square miles. The mainstem of the Blackstone River is joined by six major tributaries: Quinsigamond River, Mumford River, West River, Mill River, Peters River, and Branch River, as well as many smaller tributaries. The watershed consists of over 1,300 acres of lakes and ponds including the largest, Lake

Quinsigamond. Several reservoirs in the northwest portion of the basin are used in conjunction with out-of-basin sources for the City of Worcester water supply.

The Blackstone is known as the "Birthplace of the American Industrial Revolution." During its 46 mile run toward Narragansett Bay, the river drops 438 ft (Shanahan, 1994; BRNHC, 2006), a steeper gradient than the Colorado River (Arizona Humanities Council, 2006). Recognizing the hydraulic potential of the river, Samuel Slater built the first mill in America at the outlet of the Blackstone in 1793. Others followed suit, and at one point the river had almost one dam for every mile of river along its run. The active and remnant dams along the river strongly influence water quality along the river, in part through their impacts on sediment and associated contaminant transport as well as travel time.

The historical significance of the Blackstone River has been widely recognized. In 1986, by an Act of Congress, the John H. Chafee Blackstone River Valley National Heritage Corridor (BRNHC) was established. This designation provides the region an organizational framework with the ability to preserve the unique and significant value of the Blackstone Valley and to celebrate the role it played in the development of the nation (BRNHC, 2006). In 1998, the Blackstone received American Heritage River status, opening up the potential for making more efficient and effective use of existing federal

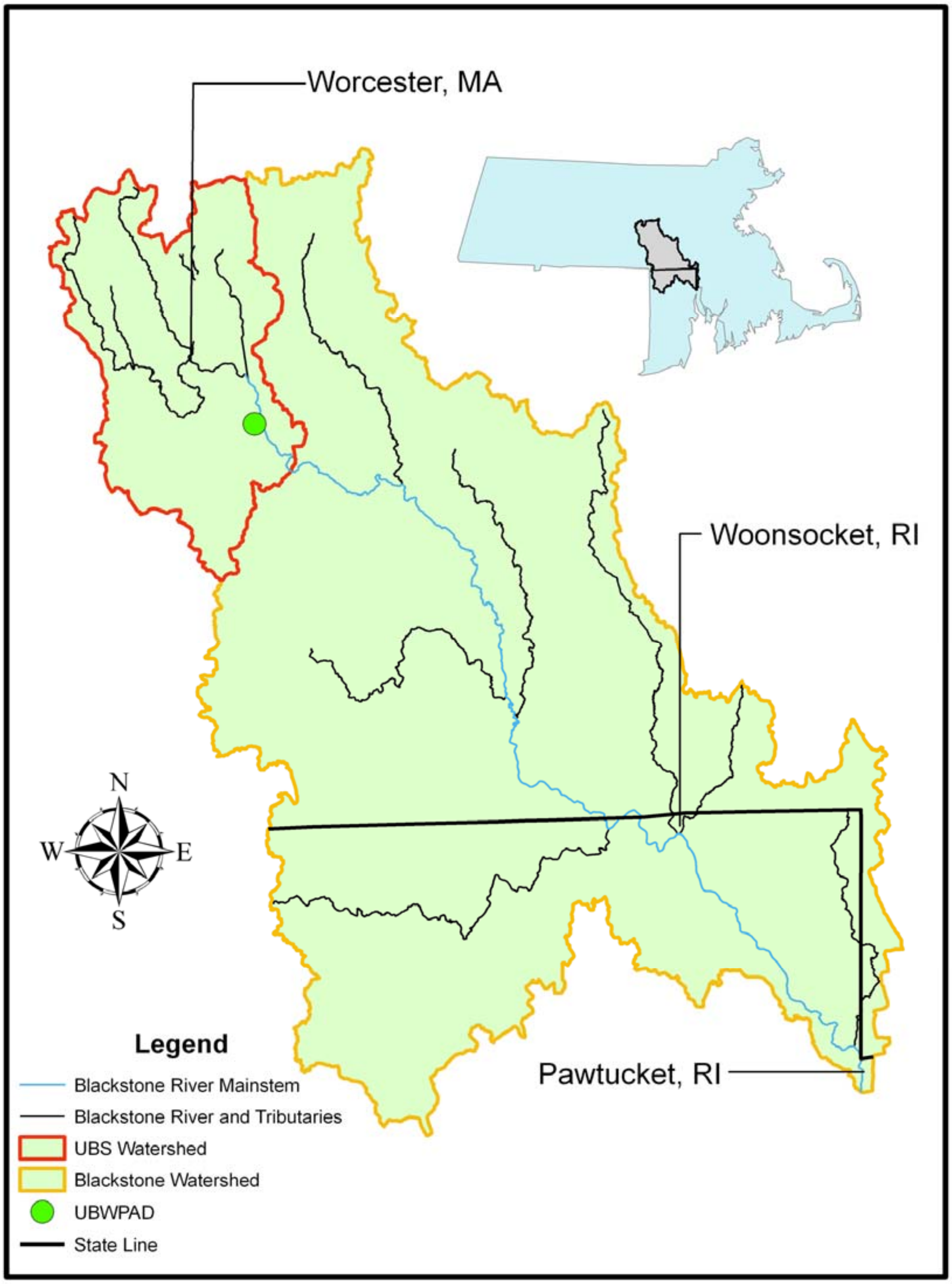


Figure 1. Blackstone Watershed

resources and cutting red-tape, without any new regulations on private property owners or state and local governments (USEPA, 2006).

In 2002, the Blackstone was one of eight rivers named to the Urban Rivers Restoration Pilot Study conducted by the United States Environmental Protection Agency (USEPA) and the United States Army Corps of Engineers (ACOE). The Urban Rivers Restoration Pilot Study is aimed at promoting collaboration among the EPA, ACOE, local businesses and the non-profit community within the watershed in order to advance pollution prevention, water quality improvements and restoration of wildlife habitat within the watershed (USEPA and ACOE, 2006).

Methodology

In 2004, the Upper Blackstone Water Pollution Abatement District (UBWPAD) initiated the Blackstone River Water Quality Study in order to develop a watershed management tool for the Blackstone River basin that could be used to evaluate the impacts of the plant effluent, the effectiveness of point source control versus non-point source management, and the effectiveness of alternative management strategies on downstream river quality. The study was initiated to enhance the overall understanding of flow and water quality characteristics of the river. Specifically, the study was designed to:

- Conduct a field-sampling program to provide wet and dry weather water quality data in headwater and mainstem locations in the Blackstone River watershed (see Mangarillo, 2006 and 2009; Patterson, 2007).
- Evaluate and model dynamic water quality conditions incorporating daily, monthly, seasonal and inter-annual variability.
- Incorporate explicitly into the modeling analysis point source (e.g. waste water treatment facilities) and non-point source (stormwater runoff) loads to the river.

To support this effort, the Blackstone River HSPF Water Quality Model was developed by the Massachusetts Water Resources Research Center in collaboration with CDM. This model is based on an existing water quantity model of the Blackstone River watershed, which was developed by the United States Geological Survey (USGS) (Barbaro and Zariello, 2006). The University of Massachusetts Amherst (UMass Amherst) and CDM extended the simulation period of the model through 2007 and employed HSPF modules for simulating water quality in addition to water quantity. The water quality model was officially released to the public for comment and review in June 2008. Model calibration to field measurements collected from 1997 through 2007 by a number of different agencies was documented in the *Blackstone River HSPF Water Quality Model Calibration Report* (CDM and UMass, 2008). This version of the model was utilized in the development of the *Blackstone River HSPF Model Scenario Report* (MAWRRC, 2008).

<u>Work under this reporting period</u>

During the spring and summer of 2009, hourly dissolved oxygen (DO) observations collected at several locations along the Blackstone mainstem during 2006 were utilized to refine the model calibration, with focus on the model mainstem slope, DO and temperature parameters. No observable differences in simulated nutrient concentrations based on the 2008 and the 2009 calibrations were detected. As a result, no changes to the nutrient model parameters were made. The net result was improved simulation of diurnal DO dynamics and minimal changes in simulated nutrient and chlorophyll-*a* concentrations.

Subsequent to refinement of the model for enhanced DO calibration, a revised scenario study was conducted. Ten scenarios (Table 1) were developed to assess the effectiveness of three alternative management strategies on downstream water quality under actual flow conditions, including: (1) point source reductions at UBWPAD, (2) nonpoint source (NPS) pollution reduction, and (3) dam management to reduce or eliminate the additional travel time created by the impoundments behind the dams. In the model, dam management was simulated by the removal of the dams, but there may be other ways to achieve the same objectives. An eleventh scenario examined nutrient and chlorophyll conditions in the watershed preanthropogenic influence. In these scenarios, nutrient effluent limits for small WWTFs along the river were left at their historical values based on the best available data for each facility. Nutrient effluent limits for the two largest WWTFs, UBWPAD and Woonsocket, RI, were adjusted. The historical values for Woonsocket were adjusted to approximate attainment of the 2008 National Pollution Discharge Elimination System (NPDES) limit for that facility. Depending on the scenario, loads from UBWPAD were based on either historical observed values, values adjusted to approximate attainment of the 2001 NPDES plant design, or values adjusted to approximate attainment of the 2008 NPDES plant permit. In addition to utilization of the refined model and an expanded list of scenarios, a revised set of scenario comparison metrics (Table 2) was developed for this study. These metrics were derived from the draft *Total Maximum Daily Load For Nutrients in the Upper/Middle Charles River, Massachusetts* (CRWA and Numeric Environmental Services, 2009). While these metrics offer a useful point of reference, natural variability in base-line conditions warrants the development, in coordination with regional regulatory agencies, of metrics specific to the unique characteristics of the Blackstone.

Graphs and tables of simulated summer low flow (7Q10 conditions) instream concentrations were utilized to summarize the scenario comparison in terms of the selected metrics. Hydrologic conditions for 2002 were found to be representative of summer low flow (7Q10) conditions and were the basis for presentation of the results. However, because the model was run dynamically from 1997 to 2007, the results presented for 2002 represent river response to the full range of hydrologic and loading conditions that occurred during the recreational season, including but not limited to summer low flow.

Table 1: Summary of model scenarios

Scenario	**UBWPAD**	**Woonsocket**	**NPS Reduction**	**Dam Conditions**
Historical	Historical	Historical	0	Existing
UP1	2001 Design	2008 Permit	0	Existing
UP2	2008 Permit	2008 Permit	0	Existing
ZeroUB	No Load (Flow Only)	2008 Permit	0	Existing
UP1_NPS20	2001 Design	2008 Permit	20%	Existing
UP1_NPS60	2001 Design	2008 Permit	60%	Existing
UP1_FERC	2001 Design	2008 Permit	0	FERC Dams Only
UP1_NoDams	2001 Design	2008 Permit	0	No Dams
UP1_NPS60_FERC	2001 Design	2008 Permit	60%	FERC Dams Only
UP2_NPS60_FERC	2008 Permit	2008 Permit	60%	FERC Dams Only
Pristine	No Load	No Load	Forest	Existing

Table 2: Metrics utilized in study

Parameter	Summary Statistic	Target Concentration
Chlorophyll-*a*	Summer Mean	≤ 10 mg/L
	Summer Peak (90th Percentile)	≤ 20 mg/L
Total Phosphorus	Summer Peak (90th Percentile)	≤ 0.1 mg/L
	Summer Mean	≤ 0.1 mg/L
Dissolved Oxygen	Minimum Instantaneous (10th Percentile)	≥5 mg/L
	7-day Minimum	≥5 mg/L
	Maximum Instantaneous (90^{tt}Percentile)	≤ 125% saturation
Total Nitrogen	Summer Mean	≤ 0.94 mg/L
	Summer Peak (90th Percentile)	≤ 0.94 mg/L

In spring 2010, the model was extended to include 2008 (modeling period 1996 - 2008). Post-processing routines were developed to utilize hourly model output to calculate bi-weekly baseflow and stormflow simulated concentrations for 2007 and 2008. For model validation, the bi-weekly model results were compared against bi-weekly base- and stormflow composite water quality monitoring data collected by the U.S. Geological for the same period. Hourly model data were also compared against new data available from the Massachusetts Department of Environmental Protection for 2008, including hourly DO and temperature data at several locations along the mainstem of the river.

Principal Findings and Significance

Model simulations were performed to evaluate the effectiveness of point source load reductions at UBWPAD, nonpoint source pollution reduction, and impoundment or dam management on downstream water quality conditions. For the purpose of this study, dam management was simulated through dam removal and subsequent evaluation of how changes in the hydrodynamics of the system impact water quality, in particular instream Chlorophyll-*a* and TP concentrations. The impacts of the dam removal scenarios provide a reference "maximum benefit or drawback" associated with dam management options. The results thus offer an indication of whether the study of additional dam management scenarios is warranted.

The 2009 scenario results indicate that several factors limit or influence instream responses to nutrient reduction including phosphorus abundance, travel and residence time, and sedimentation processes. Limiting factors and their inter-linkages are discussed further below.

Simulation results indicate that travel time, or more specifically the increased residence time of phosphorus in impoundments, is one of the important factors controlling algal growth along the river. When impoundments are present to retard the downstream transport of phosphorus, even slightly elevated levels of phosphorus can result in higher Chlorophyll-*a* concentrations along the river. However, if no impoundments are present, there is insufficient time for algae to take advantage of increased phosphorus levels. For example, dam management combined with the 2001 NPDES design at UBWPAD may be sufficient to manage Chlorophyll-*a* concentrations along the Massachusetts portions of the river. However, reduced opportunities for algal uptake and sedimentation of phosphorus in Massachusetts segments of the river result in higher phosphorus availability along the Rhode Island segments of the river in comparison to UP1 load reductions only (e.g., UP1 vs. UP1_FERC and UP1_NoDams). This results in higher Chlorophyll-*a* concentrations, but only in the presence of impoundments (e.g., FERC versus no dam scenarios).

Simulated Chlorophyll-*a* concentrations in Rhode Island are fairly insensitive to changes in phosphorus load alone. This is likely due to the high availability of phosphorus in comparison to ambient background conditions for forested land use where phosphorus concentrations are low enough that algal growth is limited independent of travel time. However, while load reductions paired with dam management have the combined potential to result in Chlorophyll-*a* values below the target values, the resulting TP concentrations along the river remain above the target values. If phosphorus levels in the river are only of concern due to their influence on algal growth, higher target values may be acceptable if the hydrodynamics of the river are also managed.

Based on model simulation results for the river management scenarios described in this report, no single strategy (point source load control, non-point source load reduction, impoundment management) meets the Chlorophyll-*a* metrics identified for the study throughout the river, with the exception of removing all the dams in the river. None of the scenarios that were simulated achieved the total phosphorous metrics for the study throughout the river.

Students Supported

Over the course of the project, 1 PhD (Jim Mangarillo) and 2 M.S. (Jim Mangarillo and Megan Patterson) students have been supported as well as numerous hourly students and two undergraduate summer researchers (Ryan Leblanc, Noam Perlmutter).

During this reporting period, the project supported one Postdoctoral Fellow who was assisted by undergraduate students.

Publications and Conference Presentations

James T. Mangarillo, Jr., 2008. Watershed Scale Modeling of the Blackstone River Watershed using HSPF. NEWEA CSO Conference, Boston, MA January 29, 2008.

Mangarillo James T., Jr., 2005. Basin-Scale Methodology for Evaluating Relative Impacts of Pollution Source Abatement, ERWI Conference, Presented July 21, 2005, Williamsburg, Virginia.

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James T. Mangarillo, Jr. ,Dr. Paula L. Sturdevant-Rees, 2008. Watershed Scale Modeling of Pollution Reduction Scenarios in the Blackstone River watershed using HSPF. Poster Presentation, WRRC, April 2008.

James T. Mangarillo, Jr. 2008. Blackstone River Assessment and Modeling Study. June 5, 2008.

Jeffrey D. Walker, Paula Rees, Tom Walsh, 2010. Adaptive Management in the Blackstone River Basin using a Dynamic Water Quality Model. Presentation, January 27, 2010 NEWEA 2010

James T. Mangarillo, Jr. 2009. Utilization of a Dynamic Model to Assess the Impact of Management Strategies on Water Quality in the Blackstone River. 6thAnnual WRRC Conference UMass Amherst, April 7, 2009.

Jeffrey D. Walker, Paula Sturdevant Rees and Thomas K. Walsh, 2009. The Importance of In-stream Hydraulics in River Water Quality Models: Lessons from the Blackstone River. EWRI 2009.

Sarah M. Dorner, Kerri A. Alderisio, Jianyong Wu,Sharon C. Long, Paula L. Sturdevant Rees, 2006. Integrating Microbial Source Tracking and Hydrology to Better Anticipate Microbial Loading to Source Waters. AWWA conference 12/7/06

Jianyong Wu, Paula Rees, Sara Storrer, Kerri Alderisio, and Sarah Dorner, 2009. Fate and Transport Modeling of Potential Pathogens: the Contribution from Sediemnts. Journal of the American Water Resources Association, vol 45, no 1, p 35 – 44.

Dissertations/MS Theses

James T. Mangarillo Jr, 2006. Basin-Scale Methodology for Evaluating Relative Impacts of Pollution Source Abatement. MS Thesis, Department of Civil and Environmental Engineering,University of Massachusetts, Amherst, September, 2006.

Megan M. Patterson, 2007. EVALUATION OF NUTRIENTS ALONG THE BLACKSTONE RIVER. MS Thesis, Department of Civil and Environmental Engineering,University of Massachusetts, Amherst, September 2007

Mangarillo, J.T., Jr., 2009. HSPF Modeling of the Blackstone River Watershed: A Tool for the Evaluation of Nutrient Based Watershed Management Strategies. PhD Dissertation. Department of Civil and Environmental Engineering, University of Massachusetts, Amherst, September 2009.

Other Publications and presentations

CDM (2008). *Blackstone Model Release Memo*. Camp Dresser & McKee, Cambridge, Massachusetts.

UMass, 2008. Blackstone River HSPF Model Scenario Report, Upper Blackstone Water Pollution Abatement District, October 2008.

Drs. Paula L. Sturdevant Rees, Daeryong Park, Kris Masterson, John Gall, Gary Mercer and Jeff Walker, 2009. Blackstone River HSPF Model 2009 Scenario Report. Upper Blackstone Water Pollution Abatement District, December 2009

MAWRRC (2008). Blackstone River HSPF Model Scenario Report. Massachusetts Water Resources Research Center, University of Massachusetts, Amherst, Massachusetts.

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Arizona Humanities Council Web Page (2001). "Moving Waters: The Colorado River and the West" http://www.azhumanities.org/movingwaters/index.html (January 24, 2006).

Barbaro, J.R. and Zariello, P.J. (2006). *A Precipitation-Runoff Model for the Blackstone River Basin, Massachusetts and Rhode Island*. U.S. Geological Survey Scientific Investigations Report 2006-5213.

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Shanahan, P. (1994). "A Water-Quality History of the Blackstone River, Massachusetts, USA: Implications for Central and Eastern European Rivers." *Water Science and Technology*. (30-5), p59-68.

11. Technical support for the development of a probabilistic water quality monitoring program for Massachusetts

Principal Investigator: Dr. Paula Rees, MA Water Resources Research Center, UMass Amherst
Start Date: 12/1/2009
End Date: 6/30/2010
Reporting Period: July 1, 2009 – June 30, 2010
Funding Source: MassDEP
Focus Categories: Water Quality; Hydrology
Descriptors: Probabilistic Monitoring; Water Quality

Problem and Research Objectives

The purpose of this project was to provide technical support for the design of a probabilistic water quality monitoring program for the Commonwealth of Massachusetts which would provide sufficient data to report on the overall quality of freshwaters in Massachusetts every two years and at the same time provide MassDEP with additional information to assess the condition of water quality in specific lakes and rivers to meet the Commonwealth's obligations under section 303d of the federal Clean Water Act.

Methodology

The Massachusetts Water Resources Research Center of UMass worked with MassDEP to support the development of a probabilistic monitoring program for wadable rivers, lakes and estuaries in the Commonwealth. Technical support was provided in the following areas:

- Preparation of an overview of relevant literature, including an evaluation of other state programs to determine if and how they have integrated probabilistic monitoring designs into their water assessment and management programs and, if so, the approximate number of FTEs allotted to those efforts; and
- Modifications to the high resolution (1:24,000) National Hydrography Dataset (NHD) within Massachusetts to allow for its use as the sample frame for river and lake probabilistic surveys.

The project included 3 main tasks:

1. Complete "Literature Review" of states' use of statistically valid monitoring surveys in their water assessment and management programs. Interview fifteen states to obtain details pertaining to their use of statistically valid surveys and to determine the number of FTEs allotted to probabilistically designed monitoring. A summary of findings including descriptions of how the data and information from probabilistic monitoring contribute to the value of the states' overall water management programs and to reporting to the EPA under the Clean Water Act.

2. Reduce the overcoverage in the NHD flow lines layer (rivers) by eliminating flow lines that would not be considered "natural streams or rivers" or "waters of the state," such as mosquito ditches, cranberry bog ditches, aqueducts, etc.

3. Assess feasibility of adding Strahler Order to the NHD flow lines attribute table. Add Strahler Order to the NHD flow lines attribute table for one or more pilot watershed(s). Determine error rate for the methodology used to determine Strahler Order (assumes the methodology is automated in GIS). Complete remaining watersheds statewide.

Principal Findings and Significance

Deliverables for the project included:

- Draft and Final technical memoranda summarizing the literature and state survey findings including contact information for state personnel interviewed.

- Draft and Final technical memoranda, e-files and other pertinent documents summarizing the process and results of the overcoverage reduction in the NHD flow lines layer (e.g., NHD datalayer with reduced coverage).

- Draft and Final technical memoranda, e-files and other pertinent documents summarizing the methodology utilized to determine Strahler Order, the GIS coverage attribute table for the state, and associated error rate for the methodology.

Publications and Conference Presentations

Rees, P.L.S., 2010. Technical Support for Probabilistic Sampling: Task 2 and 3 Final Report, Massachusetts WRRC, UMass Amherst.

Schoen, J.S., 2010. Technical Support for Probabilistic Sampling: Task 1 Final Report, Massachusetts WRRC, UMass Amherst, 29 pp.

Student Support

The project supported MS student Maili Page for 1 semester.

12. Growing a green community through neighborhood collaboration

Principal Investigator: Jerry Schoen, MA Water Resources Research Center, UMass Amherst
Start Date: 6/1/2010
End Date: 10/31/2010
Reporting Period: July 1, 2009 – June 30, 2010
Funding Source: Massachusetts Environmental Trust, subcontract from Town of Winchendon
Focus Categories: Water Quality; Volunteer Monitoring
Descriptors: Water Quality; Recreation; Bacteria

Problem and Research Objectives

Winchendon was first settled by Europeans around 1752 and incorporated in 1764. Early industry included water powered grain mills, saw mills and tanneries. It is still a vibrant, rural community with a population of approximately 10,000 residents. Winchendonians have always valued their natural environment and have pledged to protect and restore their wetlands and waterways. This intent has been reflected by Town Meeting votes of overwhelming support in the dedication of open space, a local wetlands bylaw, a new Low Impact Development Bylaw and a conservation design bylaw. The Winchendon Planning Board has dedicated itself to responsible, sustainable, low impact development wherever feasible.

The community is striving to plan proactively for its future growth and development, but municipal staffing is constrained by the current economic climate and have therefore partnered with a consultant and the University of Massachusetts Water Resources Research Center.

The Town of Winchendon proposed two efforts to improve the water quality and enhance stewardship of the Millers River:

1. Reduce stormwater flooding and nonpoint source pollution by educating residents in the use and construction of Low Impact Development (LID) practices.
2. Train volunteers and conduct water quality monitoring in the Millers River to enable recreational use. Methods employed will build local capacity for water protection and can be replicated in other communities.

Methodology

Long-term project goals are to:

1. Reduce nonpoint source pollution to the Millers River from stormwater runoff
2. Build local capacity to remedy stormwater pollution and advance stewardship of water resources
3. Restore the recreational use of the river for residents.

The following objectives will help realize these goals in the near-term:

1. Identify 30 sites where LID retrofits (rain gardens) would be most beneficial to reduce stormwater runoff to the Millers River

2. Reach 1,500 households to engage Town residents in the voluntary use of LID practices through outreach, education and a media campaign
3. Construct 3 demonstration rain gardens with volunteers from local service organizations, schools, municipal boards and the community
4. Train 10 volunteers to conduct water quality monitoring of the Millers River for one season so that the river can receive MassDEP designation for recreational use.

WRRC's Elizabeth Scotten Finn acts as Trainer in Task 4. Her tasks for this reporting period included:

- Travel to Winchendon in order to conduct planning sessions.

It should be noted that the funding for this project was not recorded for this reporting period. The funds were released in July 2010, and the bulk of the tasks will be performed July 2010 through October 2010.

Information Transfer Program

1. Water resources conference 2010 (USGS 2009MA206B)

Principal Investigators: Paula Rees and Marie-Françoise Hatte, MA Water Resources Research Center, UMass Amherst
Start Date: 3/1/2009
End Date: 2/28/2010
Reporting Period: March 1, 2009 – June 30, 2010
Funding Sources: USGS (104B) and UMass Extension

The Water Resources Research Center organized the seventh annual Water Resources Research Conference: Monitoring and Responding to Water Resource Challenges. The Cooperative State Research, Education, and Extension Service New England Regional Program again cooperated in planning the conference. Seven co-sponsors helped underwrite the cost of the conference.

Thirty-one posters were presented and there were 32 platform presentations as well as a panel presentation in three concurrent sessions. The presentations were grouped into the following 12 sessions:

Climate Change and Precipitation

Climate Change and Water Resources Planning

Climate Change and Habitat Vulnerability

Coastal Issues

Pathogens in Water

Sustainable Water Resources

Environmental Monitoring

Harmful Algae Blooms

Streamflow

Stormwater Management

Hydrology and Ecosystem Services

Water/Energy Nexus

The Keynote Address was given by Cameron J. Brooks, PhD, Director, Solutions and Business Development, Big Green Innovations, IBM Corporation, on "Smarter Water Management: Whether Too Much or Not Enough, the World Needs a Smarter Way to Think About Water."

152 people registered for the event, representing 13 colleges and universities, 16 companies, 14 governmental agencies, 10 non-profit organizations, and 2 municipalities.

Students supported by project

1 BS student in Mathematics at UMass Amherst
1 BS student in Chemical Engineering at UMass Amherst

2. Innovative stormwater technology transfer and evaluation project

Principal Investigator: Jerry Schoen, MA Water Resources Research Center, UMass Amherst
Start Date: 1/1/2008
End Date: 6/30/2010
Reporting Period: July 1, 2009 – June 30, 2010
Funding Source: MassDEP
Descriptors: Stormwater; Water Quality; Nonpoint Pollution

The Massachusetts Dept of Environmental Protection (MassDEP) awarded WRRC a two and a half year grant to continue a previous project WRRC staff had contributed to in FY'05 and FY'06. The goal of this project is to provide technology transfer information about innovative stormwater Best Management Practices (BMP) to MassDEP, conservation commissions, local officials, and other BMP Users. The project maintains and updates the database already in place (www.mastep.net) and expands the database by adding information pertaining to twenty new proprietary BMPs and ten conventional and ten Low Impact Development BMPs. In the first six months of this project, WRRC staff met with the Massachusetts Stormwater BMP working group to get input on revision of BMP category rating system and redesigned the rating system. This project has been completed, all deliverables have been met. The MASTEP web site now has approximately 70 technologies profiled, including innovative proprietary BMPs, conventional and LID BMPs. A 3rd round of funding for MASTEP has been awarded to WRRC, to run from July 1, 2010 to June 30, 2011.

3. Stream continuity project

Principal Investigator: Scott Jackson, Environmental Conservation, UMass Amherst
Start Date: Spring 2000
End Date: Ongoing
Reporting Period: July 1, 2009 – June 30, 2010
Funding Source: UMass Extension
Descriptors: Stream Crossings; Water Quality; Fish Passage

Under a memorandum of understanding with UMass extension, WRRC staff worked to coordinate volunteers and manage the database for the Stream Continuity Project, a study looking at stream crossings and their status at creating barriers for fish and wildlife passage.

In 2005, three of the organizations/agencies that were key players in initiating and implementing the project joined to create the River and Stream Continuity Partnership. Founding members of the Partnership include:

- UMass Extension (University of Massachusetts Amherst)
- Massachusetts Riverways Program (Mass Department of Fish and Game)
- The Nature Conservancy

Members of the Partnership have made a commitment to the ongoing implementation of the River and Stream Continuity Project, including updates and revisions to the Mass River and Stream Crossing Standards, coordination and implementation of volunteer assessments, management of the Continuity database, and projects to upgrade or replace substandard crossing structures.

Representatives of Partnership organizations as well as other agencies and organizations that have been providing input and advice to the project make up the River and Stream Continuity Advisory Committee.

In this reporting year, WRRC staff reviewed entered data for inconsistencies and to account for a change in field measurements. We also wrote a manual for survey coordinators, and continued acting as database coordinator.

4. Other Information Transfer/Outreach

Jerry Schoen completed a research project for the UMass IT Minor program in winter/spring 2010. He researched IT Certificate programs of other colleges around the US, drafted recommendations for an IT Certificate program at UMass. His draft was used by IT minor program to develop a proposal for Faculty Senate's consideration.

WRRC maintains a web site at www.umass.edu/tei/wrrc and a listserv of about 2500 members to inform the public of latest water resources research news.

5. EPA Workshop: Invited workshop on monitoring and responding to impacts of climate variability and change on water resources in New England

Principal Investigator: Dr. Paula Rees, MA Water Resources Research Center
Start Date: 7/1/2009
End Date: 12/31/2009
Reporting Period: July 1, 2009 – June 30, 2010
Funding Source: USEPA New England
Descriptors: Climate Change; Outreach
Focus Categories: Education; Management & Planning; Climatological Processes

On September 30, 2009 MA WRRC hosted a workshop for invited participants to increase coordination among governmental agencies, Universities, and NGOs and to lay a framework for monitoring, detecting, and responding to climate change in New England. Invitees were leading experts, senior scientists and researchers from federal and state government, academia, NGOs, and other stakeholders with expert knowledge regarding the monitoring approaches and data sets currently used by their agencies.

The focus of the workshop was to establish ways to share existing data so that efforts are not duplicated by multiple organizations, to identify information gaps, to reach a consensus on future data needs, and to develop a range of options for meeting these needs. Workshop participants:

1. Developed a comprehensive list of environmental indicators that would indicate changes in the environment due to a warming climate and be appropriate at watershed scales
2. Evaluated the utility of these indicators/available data for a wide range of applications and sectors
3. Identified existing state/federal/non-profit environmental monitoring programs that currently address these needs
4. Identified historical data sets that are critical for documenting observable changes to-date
5. Recommended modifications of existing monitoring and/or data procurement efforts to better detect impacts of climate change in New England's watershed basins
6. Recommended appropriate strategies for interpreting and utilizing data in order to develop effective responses, including the development of user-friendly tools for communities
7. Identified funding needs and potential sources for implementation of recommendations.

While not a focus area, participants in the workshop also considered adaptation strategies that might be formulated and implemented to respond to climate variability and change impacts in New England.

6. Information Technology

WRRC is involved in two projects using information technology for environmental research, teaching and outreach. In both projects, WRRC is partnering with the UMass Center for Educational Software Development.

1) An eQuest program, funded by the Department of Elementary and Secondary Education, engages Athol middle-school students in learning phenology and biodiversity concepts by exploring natural and built areas of the North Quabbin region, aided by location-aware handheld computers and web-based mapping programs such as Google Earth. This project is a collaboration among WRRC, the Athol-Royalston Regional School District, Harvard Forest, and the Millers River Environmental Center. WRRC participated in teacher training and public outreach sessions in this fiscal year. Students linked to the Connecticut River Targeted Watershed Initiative(CT TWI) project by creating virtual tours of natural places around the Athol-Royalston Middle School property. These were loaded on to a CT TWI Virtual Tour web page. WRRC participation in this project is now concluded.

2) For the EPA-funded Tri-State Watershed Initiative in the Connecticut River watershed, the Center, working with the UMass Center for Educational Software Development, developed a digital map-based virtual tour of the watershed and handheld-computer mobile tours of selected areas where environmental restoration work is occurring in the watershed. http://www.cesd.umass.edu/TWI/TWI_Projects/Virtual_Tours/index.html

Other Activities

1. Environmental Analysis Laboratory

Reporting Period: July 1, 2009 – June 30, 2010

The Environmental Analysis Laboratory (EAL) was created in 1984 by WRRC to assist the Acid Rain Monitoring Project (ARM) by analyzing more than 40,000 samples for a suite of 21 parameters. Since 1988, the Lab has provided services to a wide range of off-campus and on-campus researchers. EAL provided chemical analysis of water, soils, tissue, and other environmental media for University researchers, public agencies, and other publicly supported clients. The EAL conducts a wide variety of analyses to support environmental research, management, and monitoring activities. EAL provides high quality analytical services for inorganic substances in water including nutrients, inorganic anions, and metals and has especially distinguished itself in the analysis of trace levels of phosphorus.

In this past year, EAL continued to provide laboratory support for the Acid Rain Monitoring Project, including a quality-control program for pH and alkalinity and analytical determinations for a suite of 15 parameters. The quality-control program for volunteer-monitoring groups continued for pH, alkalinity and dissolved oxygen. Analytical services were provided for nine Massachusetts volunteer groups, and one university researcher, primarily for Total Phosphorus and Chlorophyll-*a*. Collaboration with Dr. Julian Tyson of the Chemistry Department continues and his lab has been responsible for sample analyses and for new methods development.

The management structure of the lab offered a unique opportunity to provide both the campus community and others with specialized methods development as well as basic analytical services.

Students Supported

1 PhD Student, Chemistry Department.

2. Working Groups

Reporting Period: July 1, 2009 – June 30, 2010

The WRRC has been participating in the coordination of interdisciplinary working groups on themes such as "Water" and "Environmental Contaminants." Each year the working groups help identify several seminar speakers and host their visit as part of The Environmental Institute (TEI) sponsored seminar series.

The Fall 2009 TEI Lecture series theme was "Water Sustainability" and featured several topics of interest to the Water Working Group:

- Christopher Jarrett, Professor and Director, School of Architecture, College of Arts and Architecture, University of North Carolina, Charlotte. PowerHouse.
- Eric Strauss, Director, Boston College Environmental Studies Program. Science Advisor, Urban Ecology Institute Research. Associate Professor, Biology Department. Editor in Chief, Cities and the Environment Journal Urban Ecology. The Challenge of Rejuvenating America's Cities.
- David Foster, Harvard Forest and Department of Organismic and Evolutionary Biology, Harvard University. Reading and Conserving New England. Insights from History and Ecology.

- Riley Dunlap, Regents Professor of Sociology, Oklahoma State University. Climate-Change Denial and Conservatism: Exploring the Connections.

During each visit, Water Working group members had opportunities to interact with the speaker to discuss emerging issues and trends in research and education. These interactions have assisted in proposal development and will hopefully lead to future collaborations.

In addition, members of the working groups worked on one IGERT proposal during the reporting period:

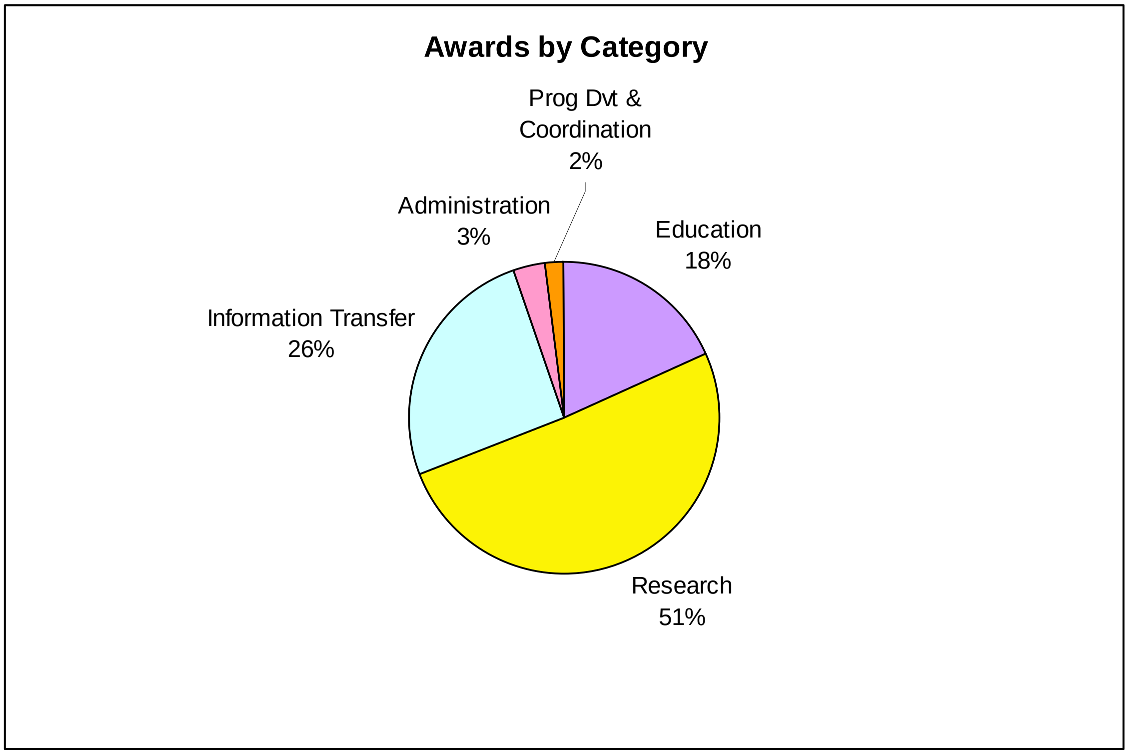
- **Full Proposal IGERT: Sensing, Modeling and Policy for Water Sustainability.** The water sensing IGERT was not selected for funding.
- **Pre-Proposal for IGERT:** Societal Interaction with and Response to Complex Engineered Systems (SIRCES). This IGERT was invited to the full proposal stage.

Financial Overview

Center revenues come strictly from grants and contracts. The University of Massachusetts contributes 27% of the salary for a half-time Director and also provides physical facilities for the WRRC.

Total revenues amounted to $506,960:

USGS 104G:	$92,936
USGS 104B:	$92,335 broken down as follows:
	$29,998 Park research project
	$21,192 Conference
	$16,867 Administration
	$9,402 ARM Project
	$5,000 Rooney-Varga research project
	$4,976 Xing research project
	$4,900 Mathisen research project
CT River Tri-State Initiative	$77,034
ARM Project	$50,000
MASTEP	$48,997
Blackstone River	$40,171
Probabilistic Monitoring	$39,996
UMass (Director)	$20,369
Extension	$20,000
EPA workshop	$10,687
Conference Revenues	$ 8,640
EAL	$ 5,795


Awards by Category
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Coordination
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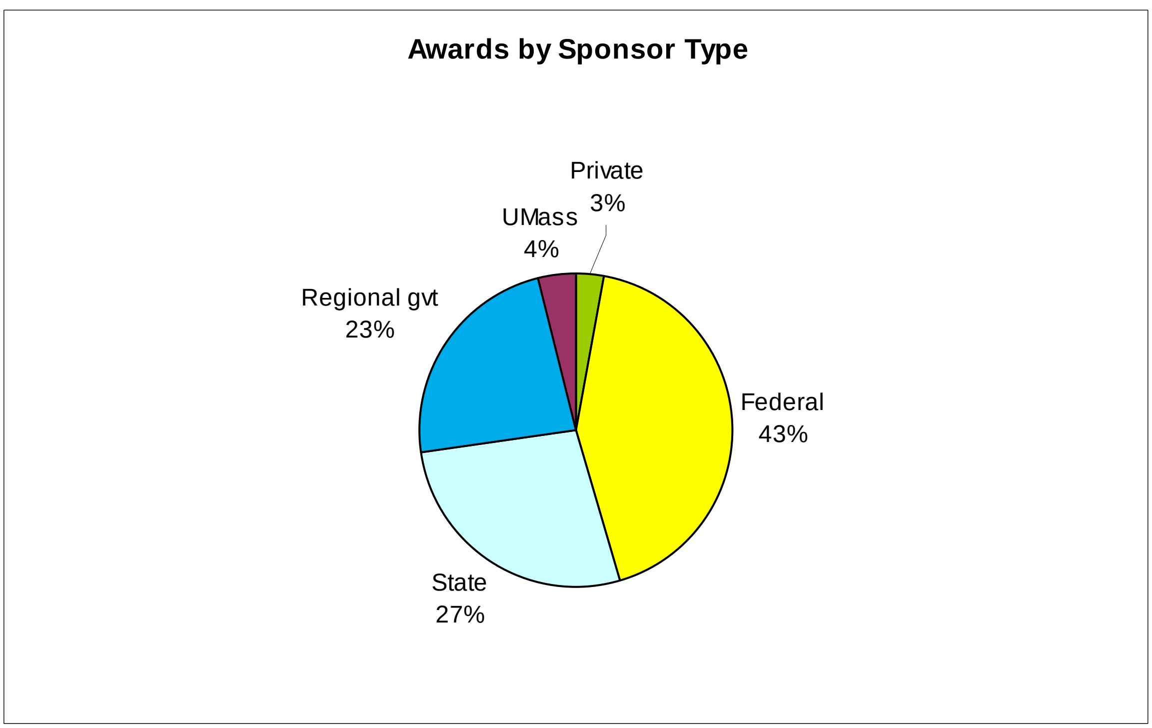
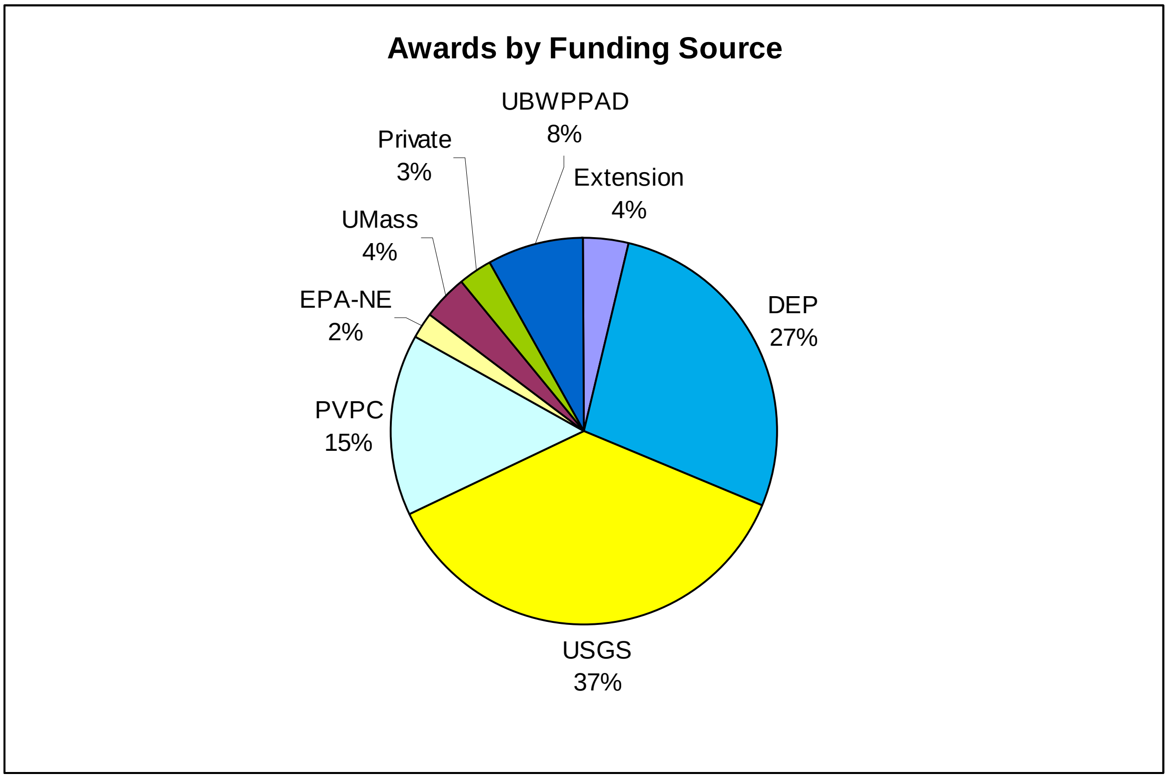
Administration
3%
Education
18%
Information Transfer
26%
Research
51%


Awards by Sponsor Type
Private
3%
UMass
4%
Regional gvt
23%
Federal
43%
State
27%


Awards by Funding Source
UBWPPAD
8%
Private
3%
Extension
4%
UMass
4%
EPA-NE
2%
DEP
27%
PVPC
15%
USGS
37%