



MA Water Resources Research Center

# Annual Report 2012-2013

March 1, 2012 – June 30, 2013

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## Executive Summary

During the Fiscal Year 2013, the Massachusetts Water Resources Research Center, with its staff of 3 FTE, managed a \$320,319<sup>1</sup> budget covering 13 projects.

Six research projects were supported through the USGS 104B Program.

- Dr. Andrew Ramsburg of Tufts University worked on "*Elucidation of the rates and extents of pharmaceuticals biotransformation during nitrification*," clarifying the degradation potential and rates of selected pharmaceuticals by nitrifying bacteria, which will be helpful to understand how pharmaceuticals can be removed from wastewater.
- "*Analysis of Charles River (MA) submerged aquatic vegetation (SAV) Using a prototype*" was led by Dr. Bruce Jackson at MassBay Community College, using robotic submersible technology to characterize submerged aquatic vegetation in order to better control its excessive spread.
- "*Modeling of road salt contamination and transport in ground water*" under PI Dr. Rudolph Hon of Boston College sought to better understand the pathways of road salt in aquifers to help design better management practices of both the de-icer application rates and the preservation of drinking water resources for the future.
- "*Land use, land cover and stormwater management in Massachusetts under conditions of climate change: Modeling the linkages*" was overseen by PI Dr. Elizabeth Brabec of UMass Amherst, who concluded that climate change adaptation is critical since the impacts from climate change are greater than land use impacts on streamflow, and that green infrastructure plays an important role to mitigate flooding.
- "*Elucidating the impact of upgrading wastewater treatment for nitrogen removal on eutrophication and toxic algal bloom in Long Island Sound*," under PI Dr. Chul Park of UMass Amherst, showed that reduction of Nitrogen in wastewater effluents via new mandatory biological nutrient removal processes does not bring a positive effect on reducing algal blooms in the Long Island Sound.
- "*Biopolymer sorbents for Tungsten removal*," under PI Dr. Jessica Schiffman of UMass Amherst, looked to develop environmentally benign sorbents (such as chitosan, a product developed from sea crustaceans skeletons) capable of removing the pollutant tungsten from our water supplies.

The 104B Program also supported four Technology Transfer projects: "*The Symposium on the Value of Water*" at Tufts University; "*The River's Calendar Symposium*," "*Growing Your Green Infrastructure Program*," and a "*Fluvial Geomorphology Workshop*" organized by the Water Center on the University of Massachusetts Amherst campus.

The USGS 104G Program supported a final year for the research project entitled "*Characterizing and quantifying recharge at the bedrock interface*" led by Dr. David Boutt of UMass Amherst, to understand the timing and nature of water recharge to bedrock aquifers.

The Massachusetts WRRC also administered two United States Army Corps of Engineers (USACE) awards to Dr. Casey Brown of UMass Amherst using supplemental funds passed through the USGS to the Water Resources

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<sup>1</sup> Does not include the two USACE projects



Research Center: “*Evaluation of adaptive management of Lake Superior amid climate variability and change*,” which devised a new way to conduct climate risk assessments for large water resource systems, and “*Climate risk assessment and management*,” which presents a new approach to describe flood risk under climate change for better flood risk reduction.

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 in Massachusetts.

Other projects conducted at WRRC include the continued collaboration with UMass Extension on the *Stream Continuity Project*. The Center also worked on a stormwater clearinghouse project that enables users to search the web for stormwater Best Management Practices that have been vetted through robust evaluation studies.

The *Blackstone River Water Quality Modeling project*, led by WRRC Director Paula Rees, continued to track river quality in the Blackstone River and study the impacts of the City of Worcester’s wastewater treatment plant on the river.

Finally the WRRC runs the Environmental Analysis Laboratory on the UMass Amherst campus to support our projects such as the Acid Rain Monitoring project, the Blackstone River project, and the Connecticut River Watershed Initiative, as well as volunteer monitoring groups across the state. EAL provides quality control samples and the analysis of chlorophyll *a* and total phosphorus.

Forty-nine publications and conference presentations resulted from this year’s projects. The projects supported 23 students and one post-doc: five students pursued PhD degrees, four were working toward a Master of Science, and fourteen were undergraduate students.



## Introduction

This report covers the period March 1, 2012 to June 30, 2013<sup>2</sup>, the 47<sup>th</sup> 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.

Six research projects were supported by the Massachusetts Water Resources Research Center through the USGS 104B Program. One research project, headed by Dr. Andrew Ramsburg of Tufts University, was entitled "Elucidation of the rates and extents of pharmaceuticals biotransformation during nitrification." "Analysis of Charles River (MA) submerged aquatic vegetation (SAV) Using a prototype" was led by Dr. Bruce Jackson at MassBay Community College. Four graduate student projects were also funded: "Modeling of road salt contamination and transport in ground water" under PI Dr. Rudolph Hon of Boston College; "Land use, land cover and stormwater management in Massachusetts under conditions of climate change: Modeling the linkages" under PI Dr. Elizabeth Brabec of UMass Amherst; "Elucidating the impact of upgrading wastewater treatment for nitrogen removal on eutrophication and toxic algal bloom in Long Island Sound" under PI Dr. Chul Park of UMass Amherst; and "Biopolymer sorbents for Tungsten removal" under PI Dr. Jessica Schiffman of UMass Amherst.

The 104B Program also supported four Technology Transfer projects: "The Symposium on the Value of Water" at Tufts University; "The River's Calendar Symposium," "Growing Your Green Infrastructure Program," and a "Fluvial Geomorphology Workshop" were organized by the Water Center on the University of Massachusetts Amherst campus.

The USGS 104G Program supported a final year for the research project entitled "Characterizing and quantifying recharge at the bedrock interface" led by Dr. David Boutt of UMass Amherst.

The Massachusetts WRRC also administered two United States Army Corps of Engineers (USACE) awards to Dr. Casey Brown of UMass Amherst using supplemental funds passed through the USGS to the Water Resources Research Center: "Evaluation of adaptive management of Lake Superior amid climate variability and change," and "Climate risk assessment and management."

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 continued collaboration with UMass Extension on the *Stream Continuity Project*. The Center also worked on a stormwater clearinghouse project that enables users to search the web for stormwater Best Management Practices that have been vetted through robust evaluation studies. The *Blackstone River Water Quality Modeling* project continued.

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

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<sup>2</sup> 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 2012 - June 30, 2013.





## **Research Program**

This year's research program includes eight projects, focusing on climate change effects on water quantity; wastewater treatment and emerging pollutants as well as nutrients; and water quality problems such as eutrophication, salt intrusion in groundwater, and stormwater. Individual reports for each project is detailed in the following pages.

Six new projects were funded through the 104B program and were completed this year.

### **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:** March 1, 2012 – June 30, 2013

**Funding Source:** USGS (104G)

**Research Category:** Groundwater Flow and Transport

**Focus Categories:** Groundwater; Water Supply; Water Quantity

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

The recharge of groundwater through glacial till is poorly understood (Cuthbert, 2010). Recharge occurs when the soil moisture deficit and matric potential is reduced sufficiently to allow for free draining water to enter the aquifer below the overburden layer (Rushton, 2005). The process is complicated by the presence of low permeability and often, anisotropic tills (Rushton, 2005). Researchers' attempts to characterize recharge through till are not new and have historically relied upon regional water balance approaches that lack resolution and assume that the potential recharging water volume is equal to actual recharge volume (deVries, 2002). To complicate matters further, an observed rise in the water table may be related to recharge or may be related to a pneumatic pressure response from an increase in the overlying weight of the wetting front in the overburden (Rodhe and Bockgard, 2006). Fitzsimmons and Missstear (2006) have shown recharge coefficients, that is the amount of effective precipitation that will cause a particular amount of recharge, to vary between 2% and 80% by varying the till hydraulic properties. The thickness of the till package that overlies the receiving bedrock aquifer is equally important especially when determining the vertical hydraulic gradient for Darcy flux calculations (Stephens, 1996). White and Burbey (2006) noted that recharge rates to bedrock aquifers are controlled by the permeability of the structures found within the bedrock aquifer.

Developing an understanding of bedrock recharge dynamics is imperative to future water sustainability in communities that rely upon bedrock aquifers. Continued withdrawal from bedrock aquifers without an understanding of the timing and rate at which the aquifer is replenished could result in stifled economic development and water shortage. The purpose of this project is to understand the timing and nature of recharge to bedrock aquifers.

#### **Project Update**

We are in the 4th year of this project after a no-cost extension. Our progress this last year has been tremendous. The major accomplishment is the establishment of a new fractured rock field site at the Smith College MacLeish



Field Station. We drilled two new wells into bedrock with the purpose of monitoring recharge processes into fractured bedrock. This has also enabled us to test some of the characterization and conceptualization from the field site at Gates Pond. During the drilling of the new bedrock well at MacLeish we obtained a 70 m rock core that will serve as an important data set for the PhD project of Amy Hudson. We have also been able to bring another MS student on board who will utilize some of the infrastructure to pursue his MS degree. In total this project has supported or partially supported 2 PhD students, 4 MS students, and at least 3 undergraduates to varying degrees. The following is a list of manuscripts that are in varying degrees of preparation that contain data collected with the support of the 104G funds:

#### **Manuscripts:**

Earnest, E.J. and Boutt, D.F., Hydromechanical Coupling in the Shallow Crust: In-situ stress and fracture deformability play a major role in flow and transport in fractured crystalline rocks, *Hydrogeology Journal*.

Boutt, D.F., A new conceptual model for the timing and nature of recharge into Fractured Bedrock Aquifers of the Northeast US, *Ground Water*.

Boutt, D.F. and Weider, M.K., Water Table Response to Decadal Climate Variability: A case study from the Northeastern United States, *Journal of Hydrology*.

It is anticipated that the results of the current PhD and MS students will be framed into additional peer-reviewed manuscripts. The following figures are some of the preliminary data collected at the field station. Excerpts follow this from the progress report from the prior year. We will compile a complete summary of all the data collected during the funded period of the project.

#### **Methodology**

##### **Site Description**

To investigate recharge mechanisms in this setting, a hillslope research area was developed at Gates Pond Reservoir, Berlin, Massachusetts within the Assabet River Watershed. The Gates Pond Reservoir (Gates Pond) is a 388,512 m<sup>2</sup> in area and provides drinking water to the town of Hudson, Massachusetts. The subwatershed that contributes to Gates Pond is 922,469 m<sup>2</sup> in area and is mainly forested with some tree fruit agriculture; pasture land, and low-density suburban development (MASSGIS, 2012). The Gates Pond site enjoys both thick and thin till deposits as well as post-glacial alluvium (FIG 1).



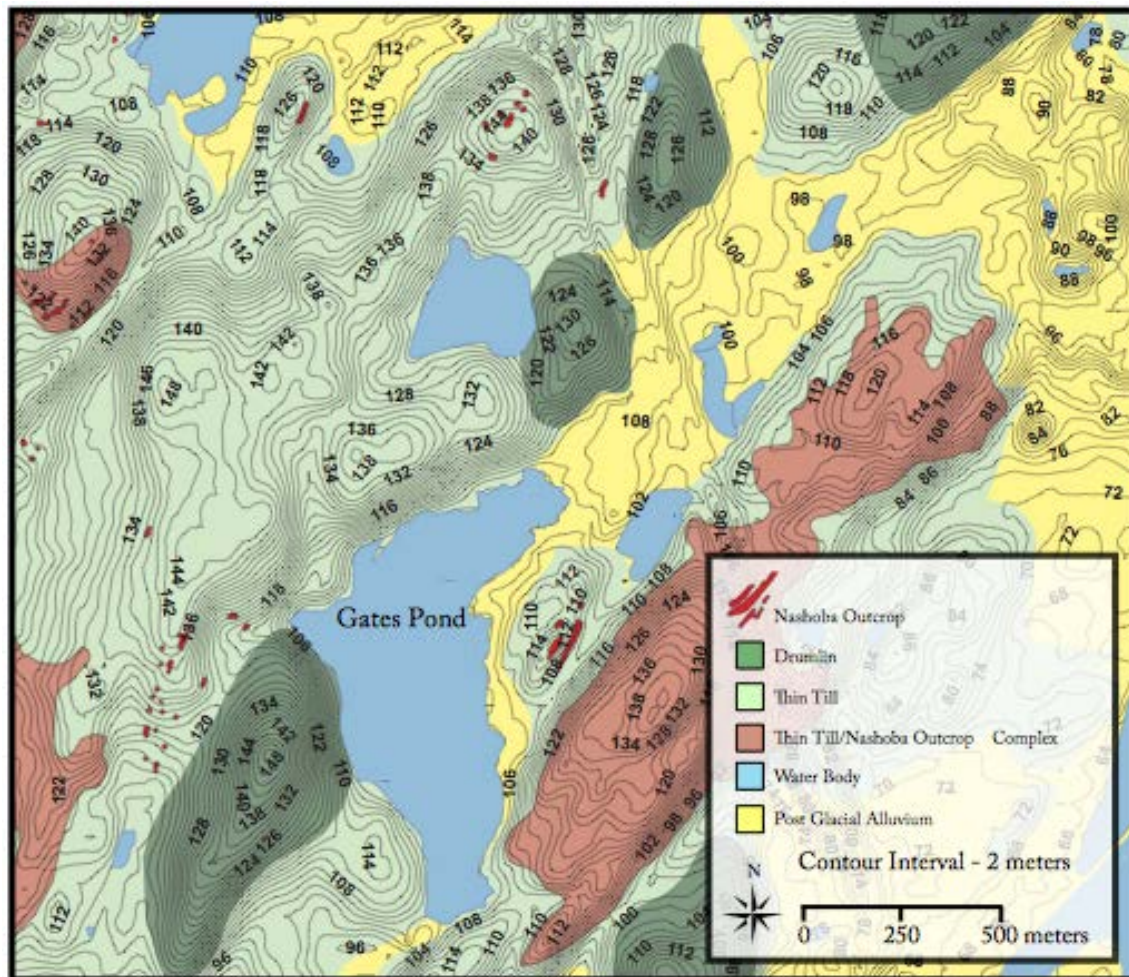


Figure 1 – Surficial geology/topography of the Gates Pond Reservoir field site.

Gates Pond also has four bedrock wells that range in depths from 178 m – 242 m below surface level (bsl).

To understand the timing and nature of bedrock recharge, two bedrock wells (BMW1 and BMW2) were respectively instrumented with Solinst® Levellogger pressure transducers that logged the water level within the wells continuously at 5 minute intervals from May 20, 2010 until August 30, 2011. The water levels were corrected for barometric pressure to obtain the potentiometric surface within the bedrock aquifer. Hourly precipitation data was obtained from the National Oceanic Atmospheric Administration's (NOAA) National Climatic Data Center (NCDC). Precipitation data was collected from the Fitchburg Municipal Airport (FMA) located approximately 13 miles to the northwest of Gates Pond Reservoir. Daily Potential Evapo-transpiration (PET) rates were determined using temperature data from the FMA weather station and calculated using methods developed by Thorthwaite (1939). Soil moisture was also monitored continuously at 5 minute intervals from October 27, 2010 until September 9, 2011 at depths of .5 meters and 1.5 meters bsl at the thin and thick till sites using a Decagon Devices® 5TM soil moisture probes. It was assumed that the 1.5 meter soil moisture data would approximate the soil moisture conditions at the surficial/bedrock interface. Soil samples were taken at a depth of 1.25 meters bsl at both the thin and thick till sites as well as the thin till deposit that overlies the

bedrock monitoring wells and were analyzed for unsaturated hydraulic properties (i.e. Van Genuchten parameters) using Decagon Devices'® HyProp instrument. The unsaturated properties taken from the HyProp instrument will be used to develop a time series of unsaturated conditions in the subsurface. Finally, a transient 1-dimensional infiltration model using the HYDRUS 1-D code (Simunek et al., 2008) will be developed using the unsaturated properties of the thin and thick tills to verify the timing and magnitude of fluxes beneath the approximated surficial/bedrock interface.

### Preliminary Findings and Significance

Work on this project began on September 1, 2009 with site selection and characterization and continues today with model development. Figure 2 includes a site locus as site map showing the location of monitoring equipment as well as geophysical survey lines. Time series data collected from wells BMW1 and BMW2 have captured bedrock recharge timing and magnitude at the Gates Pond Site (Fig. 3).

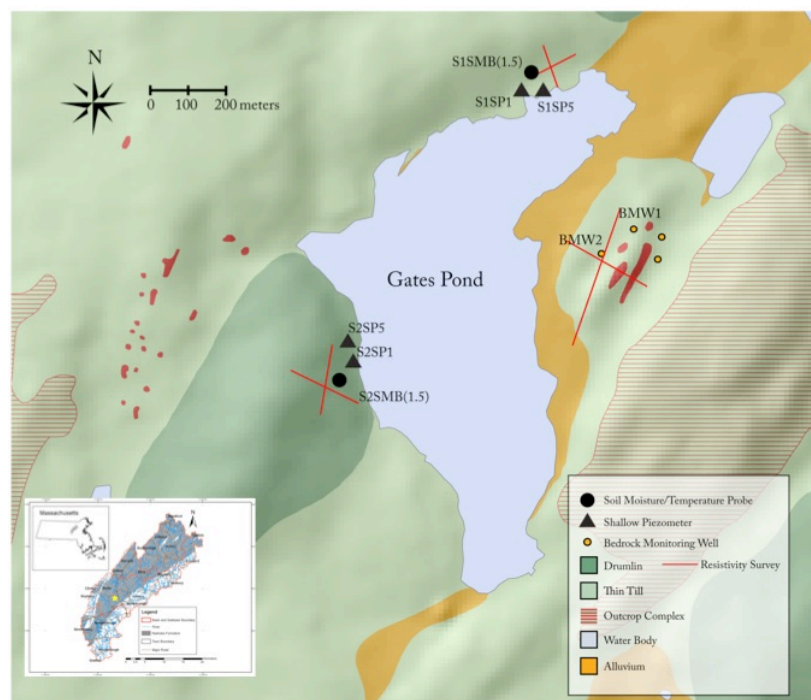


Figure 2. Site map of the Gates Pond Reservoir. In the lower left corner is a site locus showing the location of Gates Pond in relation ship to the Nashoba Formation in Massachusetts.

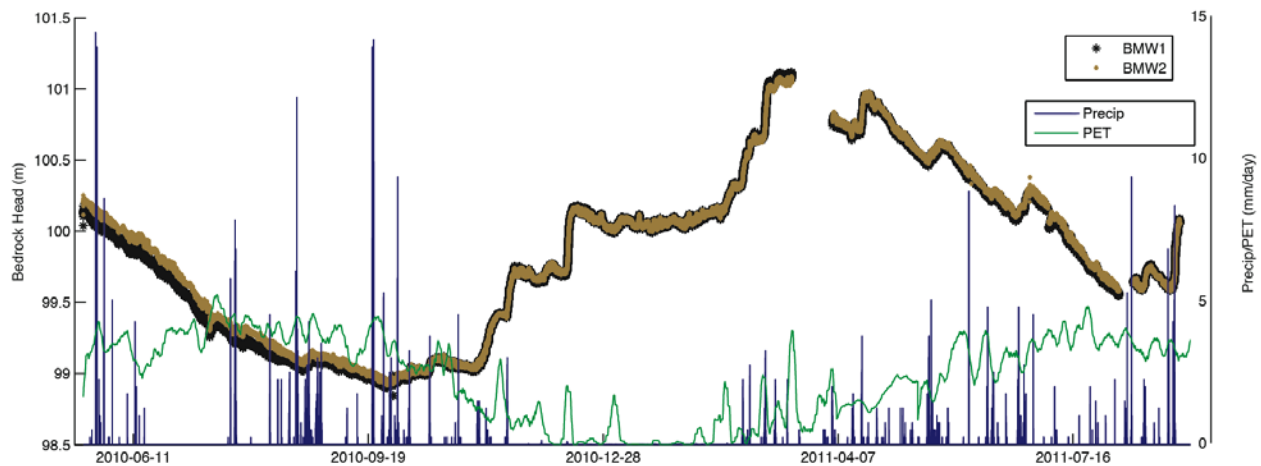


Figure 3. Time series of normalized head from BMW1 and BMW2. Potential evapotranspiration rate as calculated using the Thorthwaite approximation and precipitation rate are also plotted.

Summer precipitation events can have an appreciable effect on the trend of the bedrock head. Bedrock recharge occurs not only during times with reduced potential evapotranspiration but when there is a soil moisture gradient within the soil profile (Figure 4). It appears that there is a greater correlation between the soil moisture gradient and the magnitude of the recharge event than the magnitude of the precipitation and the magnitude of the recharge event (Figure 5a and 5b).

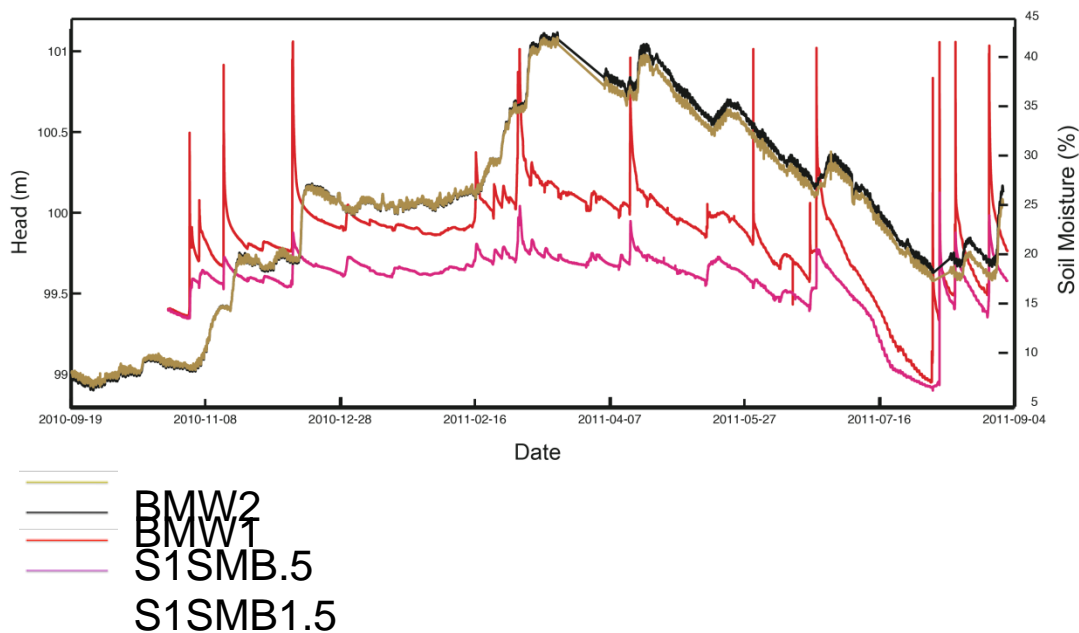


Figure 4. Plot of bedrock head within BMW1 and BMW2 along with the soil moisture gradient within thin till. Thin till is the deposit type that overlies BMW1 and BMW2. Soil moisture probes S1SMB.5 and S1SMB1.5 are collocated within the thin till at .5 meters bsl and 1.5 meters bsl respectively.

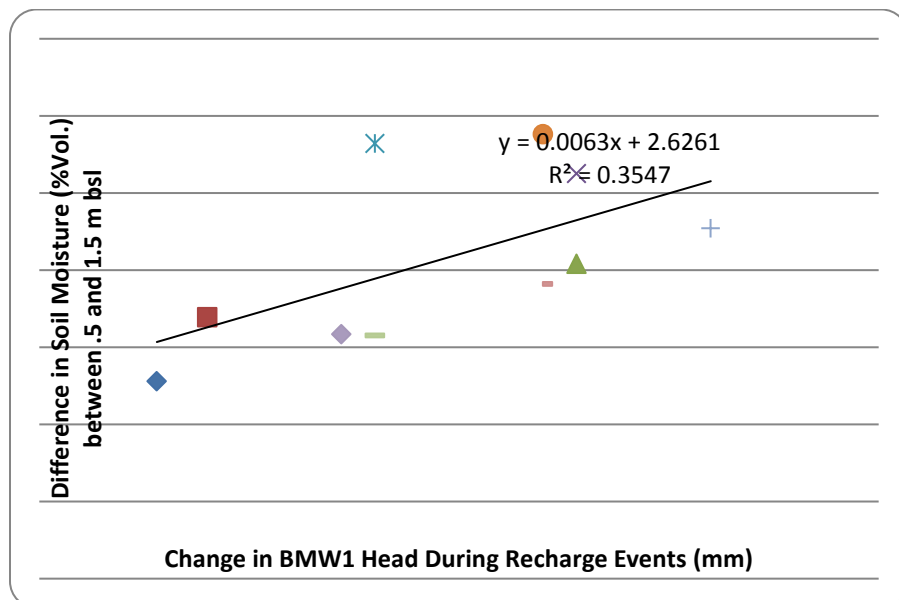


Figure 5a Correlations between soil moisture gradient and magnitude of bedrock recharge event.

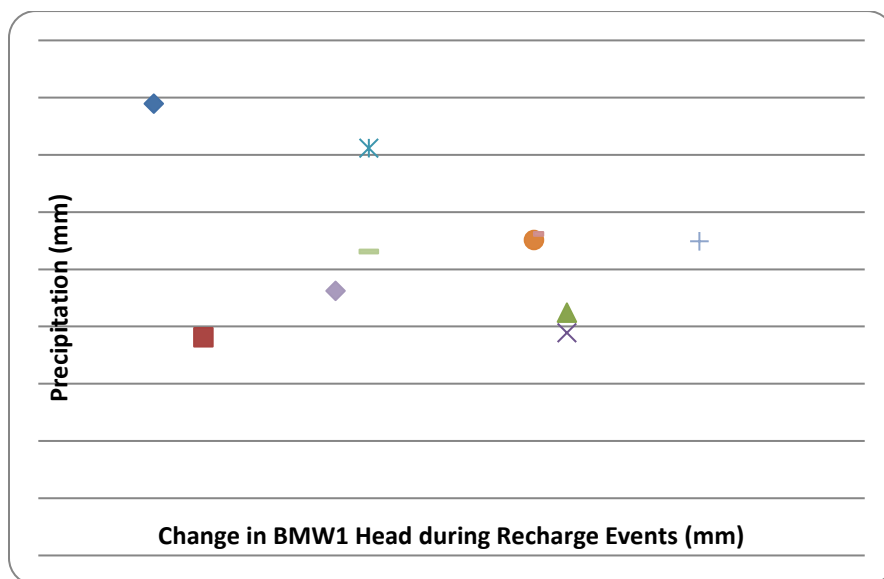


Figure 5b Lack of correlation between magnitude of precipitation event and bedrock recharge event.

Soil moisture retention curves of the thin and thick tills were also determined using the Decagon Devices HyProp device and the unsaturated hydraulic properties were determined using Brooks and Corey (year) (Figure 6)

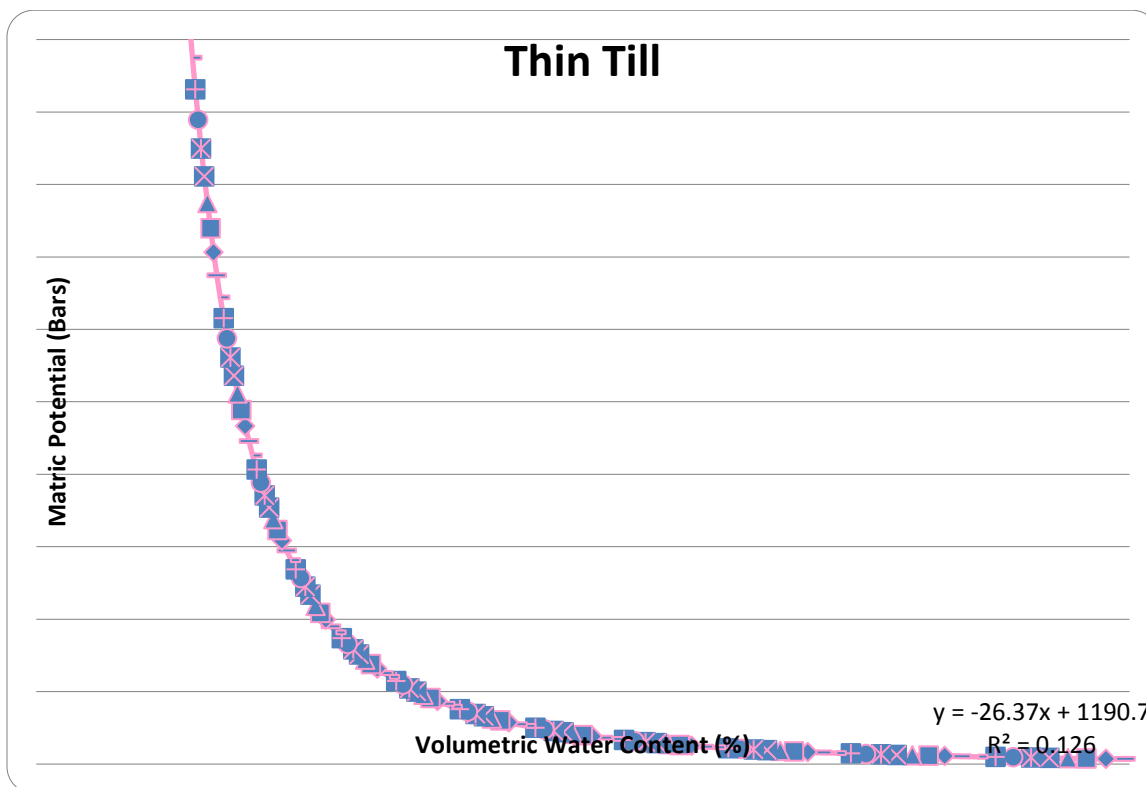


Figure 6a. Soil moisture retention curve for thin till deposits.

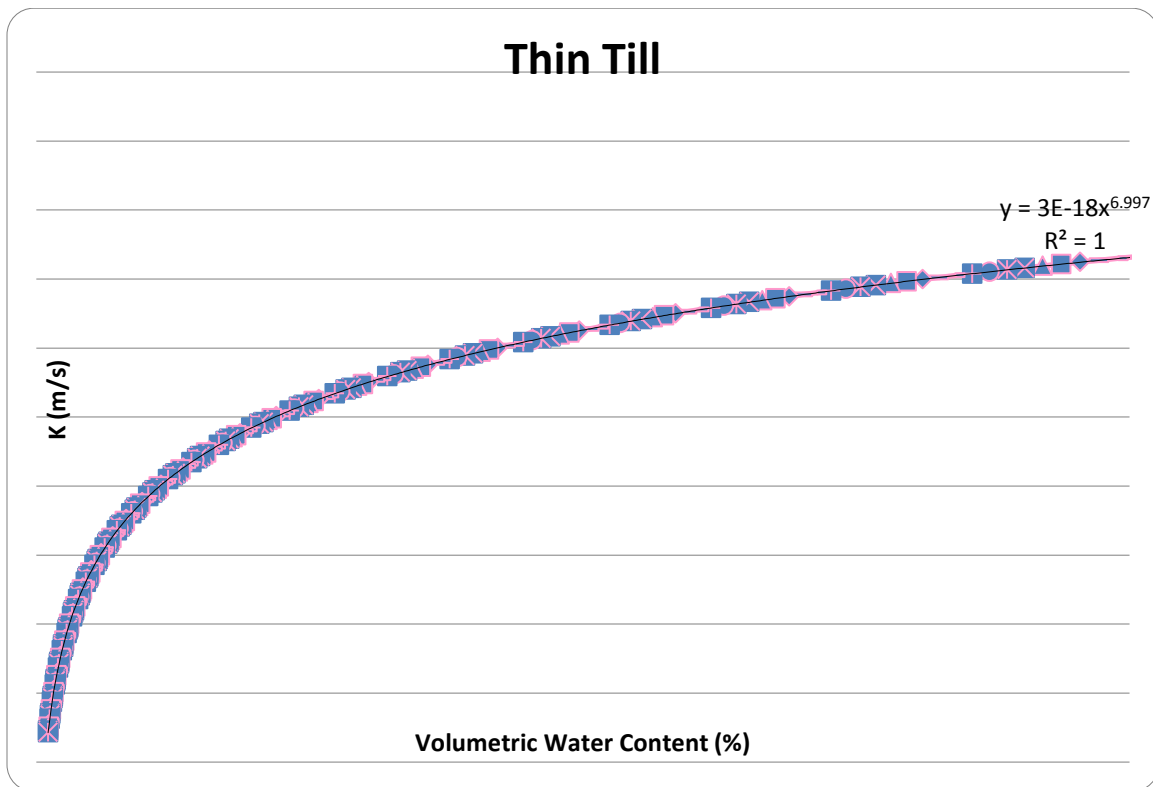


Figure 6b. Unsaturated hydraulic conductivity of the thin till.

Once the soil moisture retention and unsaturated hydraulic conductivity curves were developed, a time series of unsaturated hydraulic properties was developed (Figure 7).

— Soil Moisture ThinTill @ .5 m  
— Soil Moisture Thin Till @ 1.5 m



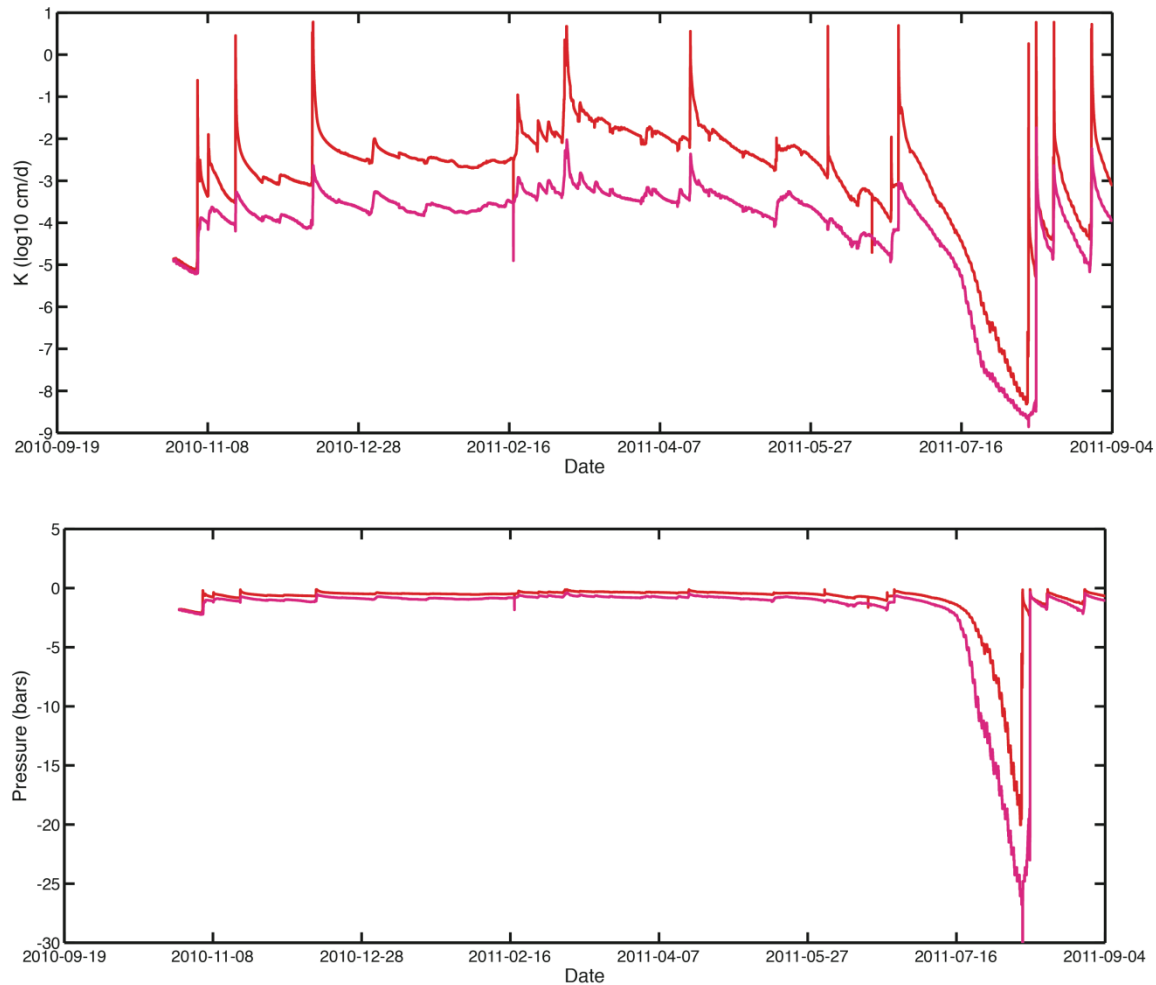


Figure 7. Time series of matric potentials and hydraulic conductivities.

**Bedrock Hydroclimatic response:** In order to constrain the regional subsurface response of bedrock ground water flow systems, we need to first understand relationships between hydroclimatic variables (such as temperature and precipitation) and surface and subsurface hydrology (i.e. streamflow and ground water) in overlying sediments. Research by the PI using distributed networks of ground water wells has yielded valuable information regarding hydraulic ground water response to climate. Following Weider and Boutt (2010) we calculate air temperature, precipitation, streamflow and ground water anomalies ( $A_i$ ), defined as  $A_i = m_i - \bar{m}$  where  $m_i$  is the monthly value,  $\bar{m}$  is the average for an individual month over a time series, and normalized anomalies ( $NA_i$ ), defined as  $NA_i = \frac{m_i - \bar{m}}{\sigma_m}$ , where  $\sigma_m$  is the standard deviation for the individual month over the whole time series. To look at longer term and seasonal averages, we use 12 month-moving averages fit to monthly normalized and anomaly values.

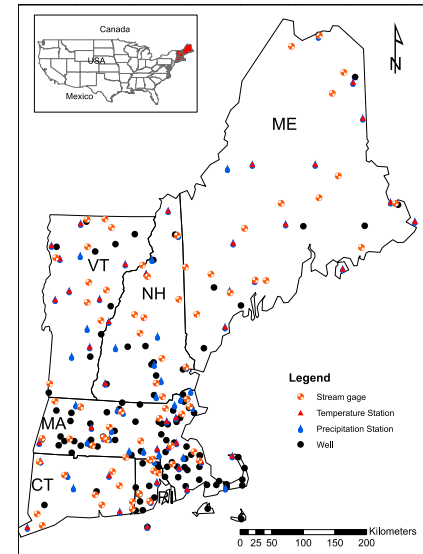


Following Weider and Boutt (2010) we calculate air temperature, precipitation, streamflow and ground water anomalies ( $A_i$ ), defined as  $A_i = m_i - \bar{m}$  where  $m_i$  is the monthly value,  $\bar{m}$  is the average for an individual month over a time series, and normalized anomalies ( $NA_i$ ), defined as

$$NA_i = \frac{m_i - \bar{m}}{\sigma_m}, \text{ where } \sigma_m \text{ is the standard deviation for the}$$

individual month over the whole time series. To look at longer term and seasonal averages, we use 12

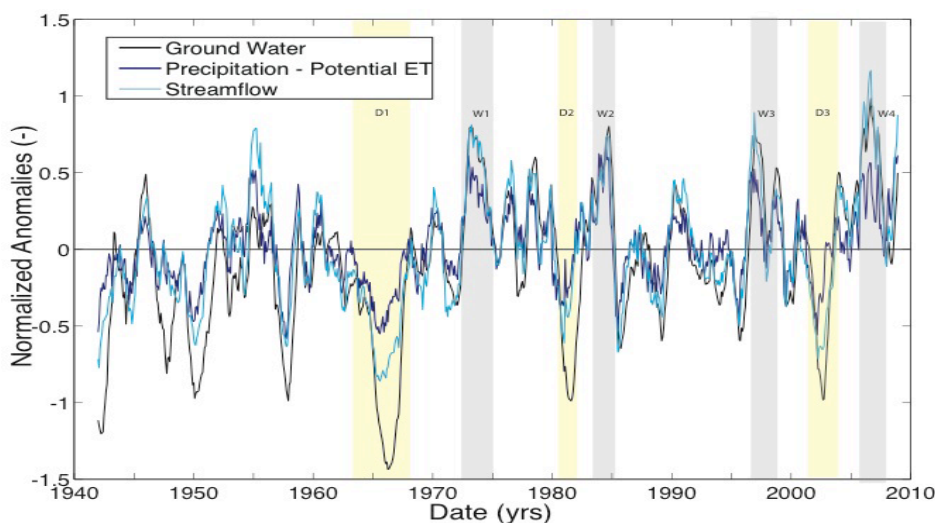
month-moving averages fit to monthly normalized and anomaly values. Weider and Boutt (2010) present ground water data from 100 well sites that span across the US New England region with sites selected to be within differing geologic, watershed, and climatic environments. Figure 2 displays all selected sites, which include 43 air temperature sites, 75 precipitation stations, 67 stream gages and ground water sites. Strong inter-relationships between the anomalies in climatic variables (temperature, and precipitation) and hydrologic variables (streamflow and ground water) exist for sites across the study region (Figure 3). Weider and Boutt (2010) showed that the ground water sites display more variation about the mean (i.e. standard deviation) and have almost twice as much variability as air



**Figure 8: Map displaying location of Weider and Boutt (2010) study sites.**

temperature, precipitation, and streamflow. We plan to utilize this set of wells to explore subsurface temperature variability due to the hydrologic and hydrogeologic factors discussed below.

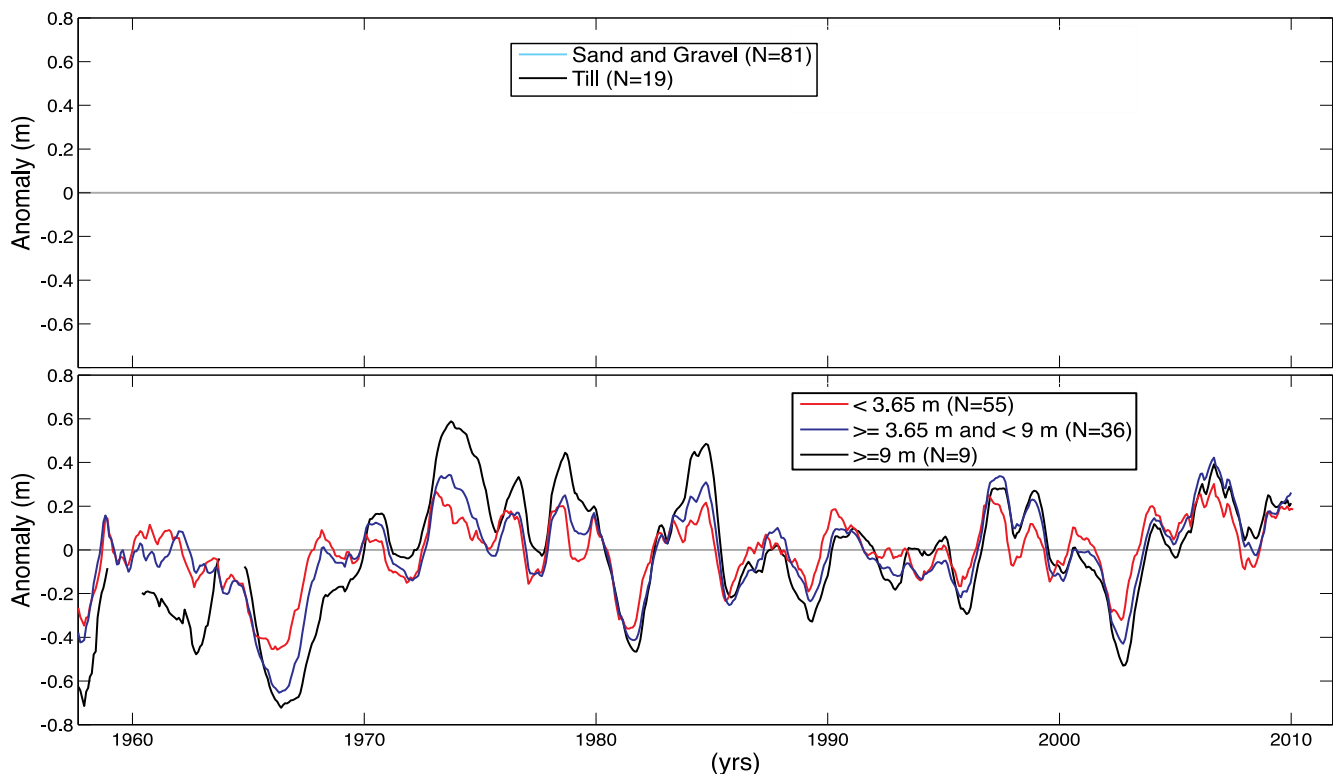
The region-wide anomalies depict strong relationships between precipitation, streamflow, and ground water and illustrate a strongly advective ground water environment. As discussed in Weider and Boutt (2010) a progression from small to large negative anomalies exists in increasing order from precipitation to streamflow to ground water anomalies, which is more obvious during periods with major droughts (i.e. 1960's and 1980's).



**Figure 9: Normalized anomalies for the hydroclimatic data presented in Figure 2. These lines represent the average of all sites and record periods of dry (D) and wet (W) times.**

During periods with positive anomalies, these differences are not observed and streamflow and ground water anomalies strongly track one another. A close examination of Figure 3 indicates that during times of negative anomalies, a consistent progression from low to high negative anomaly magnitude is apparent when comparing precipitation to streamflow and then to ground water anomalies (e.g. during the mid 1960s and early 1980s). During periods of positive anomalies these trends are also apparent, but the difference in magnitude between streamflow and ground water is not significant for reasons discussed above. The trend of increasing negative and positive anomaly magnitudes is puzzling, as climate drivers (such as precipitation) often show larger magnitude anomalies than ground water due to precipitation's highly non-autocorrelated nature (Eltahir and Yeh, 1999). Ground water systems are often called upon to moderate climate forcing, acting as a low-pass filter. Yet, these data suggest that ground water response is amplified relative to both air temperature and precipitation responses.

The regional water table hydraulic anomalies are controlled by the hydraulic properties of the material that the



**Figure 10: (Top) Ground water anomalies for wells screened in sand and gravel and till dominated aquifers. (Bottom) Anomalies for wells in aquifers as function of depth to water**

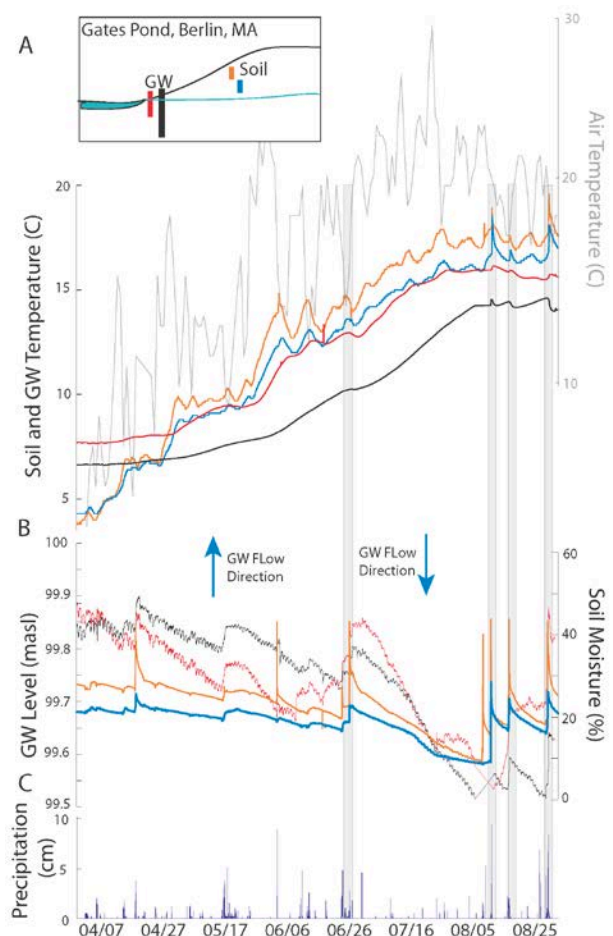
well is screened within and whether the well is screened in a recharge or discharge area of the aquifer. The hydraulic properties of the aquifer material influence the magnitude and rate of recovery of the water table anomaly. These include infiltration properties of the soil, specific yield, aquifer hydraulic conductivity, and regional hydraulic gradient. We anticipate that these factors will also influence the temperature characteristics of the subsurface. The time series presented in the top of Figure 5 are generated by taking the anomaly for an individual month and averaging them for well sorted sand and gravel and poorly sorted silt, sand, and gravel for the time period of 1956 to 2010. The two time series have similar overall patterns recording transitions between wet (positive) and dry (negative) periods in the record. For both composite series, the minimum anomaly is

always of a greater magnitude than the maximum anomaly. A distinct and measurable difference exists between wells screened in sand and gravel dominated aquifers and those screened in till (poorly sorted silt, sand, and gravel).

Water levels in discharge regions are influenced by nearby surface water and up-gradient groundwater conditions. In contrast recharge regions display large fluctuations in water level due to primarily vertical flow paths. In humid temperate climates, the water table strongly mimics topography: with shallow water tables in areas of low relative topography and deeper water tables in areas of higher relief (Gleeson et al., 2011). Averaged time series for 3 groupings are presented in Figure 5 (bottom). In general the time series are highly correlated and have similar trends during both dry and wet periods. A few important distinctions can be discerned: 1) deeper water tables have larger minima and maxima, 2) A lag of 2-5 months is apparent as the deeper water tables lag shallow water tables consistently, 3) this lag increases with the magnitude of the minima (drought severity), and 4) the slopes of the transitions for the three groupings are very similar. Since deeper water tables are assumed to be in recharge areas, these trends suggest that recharge areas and discharge areas have significantly different responses to climate variability. The lags and the timing of high and low anomalies imply a time-dependent water table response to climate that will also control how heat is advected into the subsurface.

### Local Soil-Ground Water Temperature Investigations

Multi-seasonal and distributed networks of subsurface temperature measurements yield valuable information on the hydrologic and hydrogeologic structure of shallow ground water basins but usually do not yield insight into local-scale recharge processes, their effects on the heat budget, or the degree of near-surface coupling between air and ground temperatures. Our research group has been intensively monitoring a local watershed adjacent to a water supply reservoir in Berlin, Massachusetts, USA to understand deep recharge processes and subsurface temperature responses. Figure 7A represents a time series of soil temperatures and ground water temperatures for the summer of 2011, when precipitation was almost 175% of normal. Ground water temperatures (red –shallow, black- deep) from two wells record the seasonal warming of the near-surface ground water. However, during periods of recharge (when shallow heads are greater than deep and soil moisture flux is high – gray boxes) these ground water temperatures are perturbed. During these conditions, shallow ground water temperatures are increased due to the inclusion of warmer recharge water, and deeper ground water temperatures are decreased, possibly due to advection of cooler water from depth reflecting a complex interplay of near-surface coupling and advection of water.



**Figure 11: Soil and ground water temperatures (A) respond to seasonal heating and recharge events due to advection of water (B).**

## Future Work

We are currently installing two additional bedrock monitoring wells at a new site in Whately, Mass. While installing the well, the bedrock/till interface will be cored and characterized. The new bedrock well will be instrumented with fiber optic DTS probes as well as instrumented to measure hydraulic head at multiple depths. The well will also be geophysically logged for resistivity, with a heat pulse flow meter, imaged and interpreted via optical televiewer and caliper. Time series data will continue to be collected and analyzed from all wells, soil probes and the pond. Stable isotope analysis will also be performed from regular sampling at the site. Stable isotopes will give the Investigators insight as to the origin of the water onsite and will allow the investigators to determine whether responses in bedrock wells are the result of advection across the bedrock/till interface or an expression of the pressure wave associated with hydraulic diffusion and surface loading of meteoric water mass.

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### **Publications and Conference Presentations**

Weider, K. and **D.F. Boutt**, *Heterogeneous water table response to climate revealed by 60 years of ground water data*, Geophys. Res. Lett., doi:10.1029/2010GL045561, 2010.

Boutt, D.F. and K. Weider, *Regional-Scale Water Table Response to Decadal Climate Variability*, In preparation for submission to J. Hydrology.

Boutt, D.F. and L.B. Bevan, *A conceptual model for the hydrologic connection of glacial derived surficial materials to fractured crystalline bedrock*, In preparation for submission to Ground Water.

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

*Developing a Conceptual Model for Bedrock Recharge in the Glaciated Northeastern US*. Bevan, L.B., D.F. Boutt, S.B. Mabee. American Geophysical Union Conference. December, 2010. (Poster session).

*Developing a Conceptual Model for Bedrock Recharge in the Glaciated Northeastern US*. Bevan, L.B., D.F. Boutt, S.B. Mabee. Massachusetts Water Research Center Annual Conference. April, 2011. (Poster session).  
First place poster submission.

### **Student Support**

Data collected from the bedrock core will be the centerpiece of Amy Hudson's PhD degree looking at fluid flow through fractures.

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.

Evan Earnest-Heckler is partially supported by this project. He has been assisting with field work and developing a detailed characterization of the fractured bedrock of the site. He is pursuing a PhD in geology in the Department of Geosciences at the University of Massachusetts, Amherst.

Shakib Ahmed used data collected from this project for his Senior thesis. He completed his B.S. in geology in the Department of Geosciences at the University of Massachusetts, Amherst.

## **2. Evaluation of Adaptive Management of Lake Superior amid Climate Variability and Change (USGS Award No. G10AP00091)**

**Principal Investigator:** Dr. Casey Brown, UMass Amherst

**Start Date:** 4/3/2010

**End Date:** 3/31/2012

**Funding Source:** Supplemental

**Reporting Period:** March 1, 2011 – March 31, 2012

**Research Category:** Climate and Hydrologic Processes

**Focus Categories:** Management and Planning, Climatological Processes, Surface Water

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

Provide a systematic, quantitative assessment of adaptive management strategies for the International Upper Great Lake Study using historical data, stochastic analysis and climate change projections.



### **Methodology:**

1. Using historical data and stochastic analysis, characterize the response of Lake Superior and the Upper Great Lake System (Superior-Michigan-Huron) to generalized climate variability and change
  1. Based on findings from ongoing and completed studies, identify the climate forcings of interest on the Lake System (e.g., monthly precipitation, annual mean temperature, etc.)
  2. Produce “response surfaces” of Lake System response to climate through simulation using parametrically varied climate forcings.
  3. Identify dominant climate variables based on the simulated impact of each variable on Lake System performance.
  4. Identify critical timescales of variability (including low frequency variability and trends) that significantly affect system performance. Identify threshold values of climate variable that significantly alter system performance.
2. Use climate information generated from General Circulation Model output, historical climate analyses and other model simulations to estimate risks associated with the dominant climate influences identified in Part 1.
  - a. Generate estimated probability density functions for variables of interest and timescales of interest using GCM output
  - b. Assign probabilities to ranges of climate variables of interest
  - c. Estimate risks associated with specific climate influences
3. Assess Adaptive Management Approaches in response to anticipated climate variability and changes.
  - a. Using current and proposed regulation plans including fence post plans, evaluate range of performance dominance for each strategy over ranges of climate variables of interest.
  - b. Identify climate thresholds where regulation plan optimality changes based on climate conditions using Bayesian decision model.
  - c. Assess performance of adaptive management strategies (including regulation plan switching in accordance with change points identified in part b) and static management strategies (a single optimal regulation plan) using historical data, stochastic analysis and climate change risk projections.
  - d. Estimate probable dominant adaptive and static management strategies for historical (stationary) and climate change (via GCM-based pdfs) conditions.

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

The analysis defined a new way to conduct climate risk assessments for large water resource systems.

### **Student Support**

The funding provided partial support for 1 MS and 1 PhD student.

### **Publications and Conference Presentations:**

Brown, C., Werick, W., Fay, D., and Leger, W. (2011) “A Decision Analytic Approach to Managing Climate Risks - Application to the Upper Great Lakes” Journal of the American Water Resources Association (in press).

Brown, C., Moody, P., and Werick, W. (2010) Abstract H23M-04, Decision Scaling to Aid the development of a dynamic regulation plan for the Upper Great Lakes, presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13-17 Dec.





Brown, C., Werick, W., Fay, D., and Leger, W. (2011) "A Decision Analytic Approach to Managing Climate Risks - Application to the Upper Great Lakes" Journal of the American Water Resources Association (in press).

Brown, C., Moody, P., and Werick, W. (2010) Abstract H23M-04, Decision Scaling to Aid the development of a dynamic regulation plan for the Upper Great Lakes, presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13-17 Dec.

Brown, C. and K. M. Baroang, 2011: Risk Assessment, Risk Management, and Communication: Methods for Climate Variability and Change, in Treatise on Water Science, Wilderer, P., Ed., Vol. 1, Elsevier, 189-199, doi: 10.1016/B978-0-444-53199-5.00018-X.

Brown, C., Werick, W., Fay, D., and Leger, W. (2011) "A Decision Analytic Approach to Managing Climate Risks - Application to the Upper Great Lakes" Journal of the American Water Resources Association (in press).

6.

Brown, C., Moody, P., and Werick, W. (2010) Abstract H23M-04, Decision Scaling to Aid the development of a dynamic regulation plan for the Upper Great Lakes, presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13-17 Dec.

Brown, C. and K. M. Baroang, 2011: Risk Assessment, Risk Management, and Communication: Methods for Climate Variability and Change, in Treatise on Water Science, Wilderer, P., Ed., Vol. 1, Elsevier, 189-199, doi: 10.1016/B978-0-444-53199-5.00018-X.

### **3. Elucidation of the Rates and Extents of Pharmaceutical Biotransformation during Nitrification (USGS 2011MA291B)**

**Primary Principal Investigator:** Andrew Ramsburg, Tufts University

**Start Date:** June 7, 2011

**End Date:** Feb. 28, 2013

**Reporting Period:** March 1, 2012– June 30, 2013

**Funding Source:** USGS (104B)

**Research Category:** Water Quality

**Focus Categories:** Water Quality, Nutrients, Waste Water

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

Reduction of nutrient discharges and, more generally, management of the nitrogen cycle are challenges currently faced by the Nation's community of water professionals (NAE, 2008). In the Northeast United States, impacts of excess nutrients on water quality in the Long Island Sound and Narraganset Bay have resulted in the promulgation of stringent limits on nutrient discharges within the States of Connecticut and Rhode Island, respectively. Within the Commonwealth of Massachusetts the Department of Environmental Protection (MADEP) has indicated that the development of total maximum daily loads for nutrients and the management of nutrient discharges are among its priorities for the next two decades (MADEP, 2008b). In fact, MADEP is evaluating options for stringent nitrogen standards total nitrogen (TN) < 5-8 mg/L for wastewater treatment



plants within the Connecticut River watershed, the Blackstone River watershed, and the Ten Mile River watershed (MADEP, 2008a).

Overlain in both space and time with the challenges related to nutrient control is the emerging challenge of understanding and mitigating the influence of microconstituents on environmental health (Schwarzenbach et al., 2006). The occurrence of microconstituents in the environment is now receiving significant attention across the engineering, science, and lay communities (e.g., Daughton and Ternes, 2000; Kolpin et al., 2002; Associated-Press, 2008). In its landmark national reconnaissance, the United States Geological Survey (USGS) established the presence of microconstituents in surface water bodies across the country including several water bodies located within the Commonwealth of Massachusetts (Kolpin et al., 2002). A more recent USGS project on Cape Cod detected 43 microconstituents among 14 sampling sites that included wastewater influents and drinking water supplies (Zimmerman, 2005).

Pharmaceutically active compounds (PhACs) are particularly concerning as microconstituents because the explosion of development and use of these chemicals over the last 30 years, and a growing body of evidence that suggests: (i) PhACs are neither fully removed nor fully transformed in conventional wastewater treatment plants (Heberer, 2002; Ternes et al., 2004; Stephenson and Oppenheimer, 2007); and (ii) chronic exposure, even at concentrations on the order of ng/L, may have adverse effects on ecosystems, such as impaired embryo development and modification of feeding behavior (Cleuvers, 2003; Kostich and Lazorchak, 2008; Quinn et al., 2009). Recent research suggests that PhACs may be better removed where wastewater treatment was designed to meet stringent regulations on nitrogen discharge (Clara et al., 2005; Joss et al., 2005; Kimura et al., 2005). Unfortunately, however, the vast majority of studies examining the fate of pharmaceuticals through the wastewater treatment process focus on the disappearance of the parent compound. Only a few studies have attempted to elucidate the biochemical processes responsible for PhAC degradation and the biodegradation products formed by these processes (Zwiener et al., 2002). Thus, there is a need for mechanistic research to elucidate the processes that degrade or remove pharmaceuticals during nutrient removal.

The overall objective of the project was to elucidate the degradation potential and rates of selected pharmaceuticals by nitrifying bacteria. This objective was achieved using a combination of laboratory scale experiments and mathematical modeling. Batch experiments were used to evaluate biodegradation of selected PhACs during nitrification. The batch experiments were conducted using a mixed biomass consortium from a nitrification enrichment culture. Where biodegradation of the PhACs was observed, mathematical modeling was used to: (i) evaluate the rate of PhAC degradation; and (ii) link the degradation rate to models of ammonia oxidizing bacteria (AOB) growth.

## **Methodology:**

### ***Materials***

Pharmaceuticals selected for this research were purchased from Sigma Aldrich (Saint Louis, MO) and included atenolol (ATN), metoprolol (MET) and sotalol (SOT). Purified water (resistivity  $\geq 18.2$  m $\Omega$ /cm and total organic carbon (TOC)  $\leq 8$  ppb) was obtained from a MilliQ Gradient A-10 station (Millipore Inc.). Unless otherwise specified, all chemicals were purchased from Fisher Scientific and Acros Organics.

### ***Nitrification Enrichment Consortium***

A sequencing batch reactor (SBR) was used to enrich sludge collected from a municipal wastewater treatment facility in Massachusetts. Seed biomass was collected from the second stage of a two stage facility (stage 1- BOD

removal followed by clarification, stage 2- nitrification with clarification). The nitrification enrichment SBR was generally operated on a 8-h cycle (90 min fill, 315 min react (aerobic), 60 min settle, 15 min decant) with pH between 7.5 and 8.0 and DO between 2.5 and 3.0 mg/L. The feed solution to the SBR comprised ammonium sulfate, potassium dihydrogen phosphate and nutrients to promote the growth of ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). No exogenous carbon was added to the SBR.

### Analytical Methods

ATN, MET and SOT were quantified with fluorescence detection subsequent to separation on an Agilent Series 1100 HPLC equipped with a Kinetix C-18 column (Phenomenex, 2.1 mm x 150 mm, 100 Å). Quantification of ATN was based on FLD excitation wavelength ( $\lambda_{EM}$ ) of 235 nm and emission wavelength ( $\lambda_{EX}$ ) of 314 nm. For MET and SOT,  $\lambda_{EX} / \lambda_{EM}$  were 228/324 nm and 235/319 nm, respectively. Method detection limits for ATN, MET and SOT (in picograms on column) were 100, 150 and 150, respectively. Ammonia nitrogen concentrations ( $S_{NH}$ ) were measured using a colorimetric assay: HACH method 10031 with UV absorbance at 655 nm measured using a Perkin Elmer lambda 25 UV/VIS spectrophotometer. Concentrations of nitrite ( $S_{NO2}$ ) and nitrate ( $S_{NO3}$ ) were quantified using Dionex ICS 2000 Ion Chromatograph. Total suspended solids (TSS) and volatile suspended solids (VSS) were measured using methods 2540D and 2540E of Standards Methods, respectively. DNA was extracted from the frozen biomass samples prepared from the batch experiments using MOBio Powersoil isolation kits (MOBIO, Carlsbad, CA) and stored at -80 °C until needed for further analysis. DNA concentration and quality were measured using a nanodrop lite UV spectrophotometer (Thermofisher Scientific). qPCR was used to estimate the abundance of total bacteria (EUB), ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). AOB abundance was measured using the ammonia monooxygenase gene subunit A (*amoA*). Abundance of both *Nitrospira* (NOB-Ns) and *Nitrobacter* (NOB-Nb) were measured by targeting the 16s rRNA gene (NOB-Ns; NOB-Nb). EUB abundance was measured using 16s rRNA gene targeted primers (see Table 1 for details). In addition to providing estimates of gene copy concentrations, qPCR data were used to estimate biomass (total bacteria, AOB and NOB) concentrations (in mg COD/L) using Equation 1 with conversion factors for each consortium as shown in Table 1.

$$X_{BIOMASS} \left( \frac{g-COD}{L} \right) = \left[ \frac{C_{SAMPLE-GENE-COPIES} \left( \frac{copies}{L} \right)}{C_{CELL-GENE-COPIES} \left( \frac{copies}{cell} \right)} \right] \left( \frac{cells}{L} \right) M_{BACTERIAL-CELL} \left( \frac{g-VSS}{cell} \right) \left[ 1.42 \left( \frac{g-COD}{g-VSS} \right) \right] \quad (1)$$

Table 1. Primers and conversions used in qPCR analyses.

Target	Primer Information				Cell Gene Copies Information		Cell Mass Information	
	Primer ID	Sequence (5′-3′)	Pos.	Primer Sequence Reference	C <sub>CELL-GENE-COPIES</sub> (copies/cell)	Reference	M <sub>BACTERIAL-CELL</sub> (g-VSS/cell)	Reference
EUB	1055f	ATGGCTGTCGTCAGCT	1055-1070	Ferris et al. (1996)	4.2	Klappenbach et al. (2001); Graham et al. (2007)	2.8x10 <sup>-13</sup>	Ahn et al. (2008)
	1392r	ACGGGCGGTGTGTAC	1392-1406					
AOB amoA	amoA-1F	GGGGTTTCTACTGGTGGT	332-339	Rotthauwe et al. (1997)	2.5	Norton et al. (2002)	1.6x10 <sup>-13</sup>	Farges et al. (2012)
	amoA-2R	CCCCTCKGSAAAGCCTTCTTC	802-822					
NOB-Ns	NTSPAf	CGCAACCCCTGCTTTCAGT	1081–1099	Kindaichi et al. (2006)	1	Graham et al. (2007)	1.4x10 <sup>-13</sup>	Farges et al. (2012)
	NTSPAr	CGTTATCCTGGGCAGTCCTT	1128–1147					
NOB-Nb	1198f	ACCCCTAGCAAATCTCAAAAAACCG	1198-1223	Graham et al. (2007)	1	Starkenbourg et al. (2006)	1.4x10 <sup>-13</sup>	Farges et al. (2012)
	1423r	CTTCACCCAGTCGCTGACC	1423-1443					

### Experimental evaluation of pharmaceutical sorption

Pharmaceutical sorption was evaluated using batch experiments setup in 30 ml foil covered glass vials closed with Teflon-lined caps. Vials contained mixed liquor from the nitrification SBR and one pharmaceutical at initial concentrations ranging from 0.5 to 50 µg/L. Sorption of the pharmaceutical at each concentration was assessed in triplicate. Homogenous samples are collected every six to eight hours. Samples are centrifuged and the pharmaceutical concentration in the aqueous phase was measured. The sorbed pharmaceutical concentration (µg-g-SS<sup>-1</sup>) was calculated. Equilibrium was considered to have been achieved when the measured aqueous PhAC concentration of three successive samples are the same. Positive controls are included to assess pharmaceutical sorption to the glass vial. Sorption isotherms are developed using the equilibrium sorption data; the sorption coefficient ( $K_D$ ) was calculated for each pharmaceutical.

### Predictive models for pharmaceutical sorption during biological wastewater treatment

Reported values for distribution coefficients ( $K_D$ ) describing PhAC sorption during biological wastewater treatment were compiled from peer-reviewed studies (total of 388  $K_D$  values for 66 PhACs from 12 studies). The ability of single parameter models based on octanol-water partitioning coefficients ( $K_{OW}$ ) of the PhACs (Eq. 2) was examined. The single parameter model evaluated was extended to include models based on the apparent partition coefficients ( $K_D$ ) (i.e.,  $K_{OW}$  corrected to the experimental pH).

$$\log K_{D,PhAC} = \alpha \log K_{OW,PhAC} + \beta \quad (2)$$

We also evaluated two separate polyparameter predictive modeling approaches for PhAC sorption: (i) Linear Free Energy Relationship (LFER) employing predictors developed by Abraham (1993) and (ii) quantitative structural activity relationship (QSAR) models of the form shown in Eq. 3 utilizing PhAC chemometric properties which are typically available early in the drug development/design process. We found that LFER models were not robust enough to describe PhAC sorption (Sathyamoorthy and Ramsburg, 2013).

$$\begin{aligned} \log K_{D,PhAC} = & \chi + a[\log K_{OW,PhAC} \text{ or } \log D_{PhAC}] + b[(\log MW \text{ or } \log MV)] \\ & + c[\log(vdWSA)] + d[\log(TPSA)] + e(nAroC) + f(Pi.Energy) \\ & + g(nHBD) + h(nHBA) + i(nRB) \\ & + j(Dom.Species) + k(\alpha_+) + l(\alpha_-) \end{aligned} \quad (3)$$

Polyparameter QSARs of increasing complexity were systematically developed by addition of a new predictor to the previously best model until the addition of another predictor was not statistically significant (i.e.,  $p > 0.05$ ). A leading coefficient ( $\chi$ ) was included in models evaluated – omission of the leading coefficient would imply that the sorption mechanism can be entirely described by the predictor variables, which has limited physical meaning. For each model, the statistical significance of predictors was evaluated at  $p < 0.05$ , residuals were checked for homoscedasticity, and multicollinearity between predictors was evaluated.

Models were developed and evaluated using Minitab 16.1.1, and assessed using a suite of statistics. The ability of each model to capture the variance in the data set used to develop the model was evaluated using the correlation coefficient ( $R^2$ ) and adjusted- $R^2$  (adj- $R^2$ ). The predictive capability of models was assessed through predicted- $R^2$  (pred- $R^2$ ) and Nash-Sutcliffe Efficiency (NSE) (Nash and Sutcliffe, 1970). Unlike  $R^2$  which describes the goodness of correlation, pred- $R^2$  is a goodness of prediction statistic based upon the prediction residuals of

sum squares (Myers et al., 2010). The NSE ranges from  $-\infty$  to 1 and is typically greater than 0. Negative NSE values are possible and indicate that the mean of the measured KD values from the data set was a better predictor than the predictive model. Strong predictive capability is generally characterized by  $\text{pred-R}^2 > 0.7$  and  $\text{NSE} > 0.7$  (McCuen et al., 2006).

### Experimental evaluation of pharmaceutical biodegradation

A series of batch experiments was conducted to evaluate the biodegradation of the three, selected beta blockers (ATN, MET, SOT) by a nitrification activated sludge system. Selection of these three beta blockers permitted assessment of biodegradation within a family of pharmaceuticals that differ by one-to-two functional groups. Biomass for all experiments was taken from a nitrification enrichment sequencing batch reactor (Nit-SBR) maintained in the PI's laboratory. The Nit-SBR was continuously operated with a feed with ammonia and without the any exogenous organic carbon. Our experimental protocol included controls (in the absence of pharmaceutical) for nitrification (i.e., ammonia + nitrite oxidation) and nitrite oxidation. These controls characterize the microbial consortia obtained from our nitrification sequencing batch reactor before each experiment. Nitrification experiments that contain pharmaceutical were conducted in duplicate. Controls were also included to evaluate pharmaceutical degradation when nitrification was inhibited using allylthiourea (ATU). Time course samples are collected to quantify pertinent solutes during each experiment (i.e., each set of four reactors - two experimental replicates and two controls).

### Modeling of pharmaceutical degradation and ammonia oxidation

PhAC biodegradation was modeled using two approaches: a pseudo first order model based on reactor total biomass concentration as measured using VSS (Eq. 4) and a consortium level cometabolic model that incorporates the relevant modules from the Activated Sludge Model framework (Henze et al., 2000) with nitrification modeled as a two-step process (Chandran and Smets, 2000; Hiatt and Grady, 2008). The pseudo first order approach (Eq. 4) is frequently used to model microconstituent degradation despite its lack of mechanistic or process significance (Urase and Kikuta, 2005; Joss et al., 2006; Fernandez-Fontaina et al., 2012; Helbling et al., 2012). Although such a formulation is convenient, it is of limited value when comparing systems with different design or operating conditions. The principal shortfall of this approach is that it does not link PhAC degradation to a specific process occurring within the mixed culture.

$$\frac{dS_{PhAC}}{dt} = -(k_{BIO} X_{TOT}) S_{PhAC} \quad (4)$$

To address this shortcoming, a consortium level model was developed. Existing approaches for cometabolic biodegradation modeling (Criddle, 1993; Alvarez-Cohen and Speitel, 2001) were adapted to integrate PhAC biodegradation into the ASM framework. Three PhAC biodegradation scenarios were explored using the consortium level model as shown in Eq. 5: (i) cometabolic biodegradation linked to ammonia oxidizing bacteria (AOB) growth; (ii) biodegradation by AOB in the absence of growth; and (iii) biodegradation due to heterotrophs (HET) present in the mixed culture.

$$\frac{dS_{PhAC}}{dt} = - \left\{ \left[ \left\{ T_{PhAC-AOB} \mu_{AOB} \right\} + \left[ k_{PhAC-AOB} \right] X_{AOB} \right] + \left[ \left\{ \alpha_{PhAC-HET} \right\} X_{HET} \right] \right\} S_{PhAC} \quad (5)$$

Here  $T_{PhAC-AOB}$  is a PhAC transformation coefficient linked to AOB growth [ $L^3 M_{COD}^{-1}$ ],  $\mu_{AOB}$  is the AOB growth rate [ $T^{-1}$ ],  $k_{PhAC-AOB}$  is a biomass normalized PhAC degradation rate coefficient in the absence of AOB growth

$[L^3M_{COD}^{-1}T^{-1}]$  and  $X_{AOB}$  is the AOB concentration  $[M_{COD}3^{L^{-1}}]$ . PhAC degradation is linked to  $X_{HET}$  using a single biomass normalized PhAC degradation rate coefficient  $\mu_{PhAC-HET}$   $[L^3M_{COD}^{-1}T^{-1}]$  because heterotroph growth was not modeled (i.e., the analogous transformation capacity was not evaluated for heterotrophs). It is important to note that while this research places emphasis on evaluating biodegradation by nitrifying organisms, the model framework proposed here is flexible and readily adapted to other consortia and processes. For instance, as data related to role of heterotrophs in biodegradation of those PhACs evaluated in this research, it may be possible to replace  $\mu_{PhAC-HET}$  with more explicit parameters linked to growth as done herein for AOB.

### Principal Findings and Significance:

#### Sorption of pharmaceuticals during biological wastewater treatment

Evaluation of the sorption of the three beta-blockers (ATN, MET, and SOT) during nitrification in batch experiments suggested that sorption holds limited potential as an attenuation mechanism for these pharmaceuticals. Of the three beta-blockers, only MET sorbed to the inactivated nitrification SBR mixed liquor to an extent that permitted calculation of a statistically non-zero distribution coefficient ( $K_D$ ). The measured sorption coefficient for MET was highly dependent on experimental conditions. Two separate experiments produced  $K_D$  values of  $0.26 \pm 0.03$  and  $0.09 \pm 0.01$  L/g-SS.

Based upon these results we undertook a more significant assessment of pharmaceutical sorption during biological wastewater treatment. The assessment examined all available (published) data for sorption of pharmaceuticals during biological wastewater treatment - a total of 309 measured  $K_D$  values for 65 pharmaceuticals. Principal findings are reported here. Full details from this research are available in Sathyamoorthy and Ramsburg (2013). One of the aspects we evaluated was the role of experimental protocols (i.e., experiment type and biomass inactivation method) on measurements of  $K_D$  values. While the data are limited, our meta-analysis suggests the experiment type (batch or continuous flow) and inactivation method (chemical, physical, or no inactivation) (see Figure 1 and Figure 2) does not explain the large variation in measured  $K_D$  values. Therefore, large ranges in the reported values for  $K_D$  are unrelated to differences in experimental conditions. Rather, they are related to variations in the interaction between the pharmaceutical and the biosolids surface.

Conventional wisdom suggests that the hydrophobic interactions dominate the sorption of organic chemicals to biomass. It is also common to assume equilibrium and apply a linear isotherm to describe the sorption. The combination of these assumptions has led many researchers to attempt to correlate pharmaceutical sorption (described using the  $K_D$ ) to the octanol-water distribution coefficient for the pharmaceutical ( $K_{ow}$ ) (Stevens-Garmon et al., 2011; Hyland et al., 2012). Results from our research suggest that one parameter models based on octanol-water partitioning (even when  $\log K_{ow}$  was corrected to the experimental pH conditions, i.e.,  $\log D$ ) are generally ineffective at describing sorption of negatively-charged, uncharged, and positively-charged PhACs during biological treatment (Figure 3).

Polyparameter quantitative structural activity relationship (QSAR) models were explored as an alternative means of predicting the observed sorption extents. The QSAR models employed a suite of molecular descriptors that are readily available during drug design and development process. The predictor variables included molecular weight (MW), molecular volume (MV), aromaticity, number of rotatable bonds (n.RB), hydrogen bonding capacity (hydrogen bond donors- nHBD and acceptors- nHBA) and polar surface area (PSA). Models of increasing complexity were systematically developed by adding one of the aforementioned predictors to the best model of with a given number of predictor variables. The performance of each model was evaluated using



two main statistics – adjusted r-square ( $\text{adj-R}^2$ ) and predicted r-square ( $\text{pred-R}^2$ ). As noted in the methodology section, model residuals were checked for homoscedasticity and multicollinearity between model variables was evaluated. The polyparameter QSAR models developed in this research provide a significant improvement in the ability to predict  $K_D$  values (see Figure 4 and Table 3 for model details). The plateau in predictive capability at approximately 50% - 60% (Figure 4), however, suggests that while the best polyparameter QSAR models offer improvement over previously established correlations, none can be characterized as having strong predictive power. Importantly, QSAR models with a higher degree of predictive capability ( $\text{pred R}^2 > 0.80$ ) can be developed for scenarios where the uncharged species is greater than 85% of the total PhAC mass present in a system. But, restrictions on the fraction of uncharged species degrade model utility and practicability, especially in the case of acidic PhACs. For example, only 12 of the 66 PhACs tested to date would meet this threshold under normal treatment conditions. We hypothesize that the performance plateau results from only including solute-based descriptors, and suggest future research focus on characterization of the sorbent surface to better characterize the mechanistic interactions between sorption sites on biosolids and pharmaceuticals (Sathyamoorthy and Ramsburg, 2013).



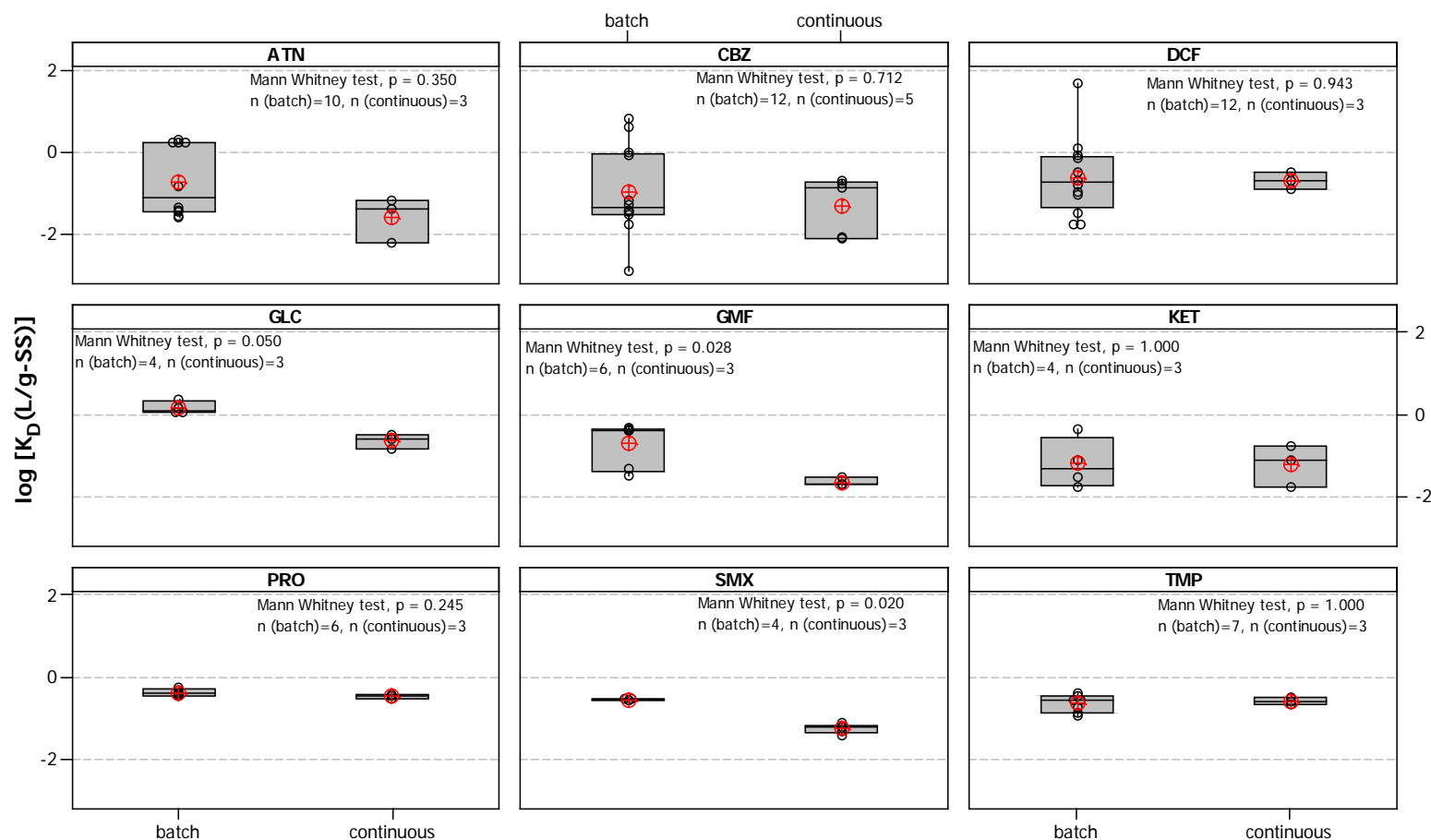


Figure 1. Comparison of measured sorption coefficients for atenolol (ATN), carbamazepine (CBZ), diclofenac (DCF), glibenclamide (GLC), gemfibrozil (GMF), ketoprofen (KET), propranolol (PRO), sulfamethaxazole (SMX) and trimethoprim (TMP) from batch and continuous experiments. Individual data points shown using small black circles; horizontal line indicates median; mean indicated by large red circle with cross-hairs. Box extents indicate 25th (Q1) and 75th (Q3) percentile with whiskers extending to upper limit [ $Q3 + 1.5(Q3 - Q1)$ ] and lower limit [ $Q1 - 1.5(Q3 - Q1)$ ]. Also shown are p-value of one-tailed Mann Whitney test and number of data points from batch [n (batch)] and continuous [n (continuous)] experiments.

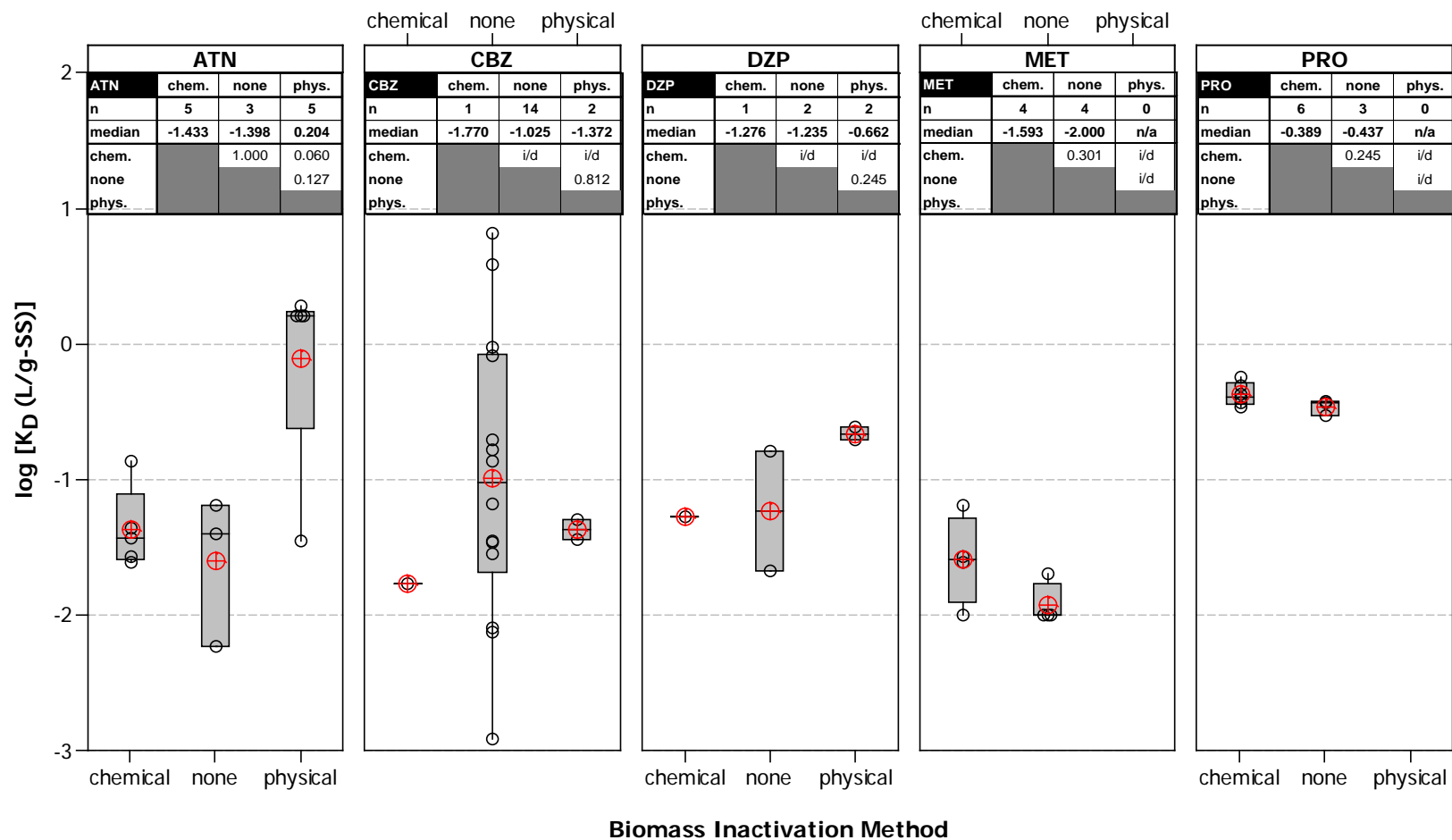


Figure 2. Measured Sorption Coefficients for atenolol (far left), carbamazepine, diazepam (middle), metoprolol and propranolol (far right) from batch and continuous experiments using chemical inactivation (e.g.,  $\text{NaN}_3$ ) no biomass inactivation, and physical inactivation (e.g., lyophilization). Individual data points shown using small black circles; horizontal line indicates median; mean indicated by large red circle with cross-hairs. Box extents indicate 25th (Q1) and 75th (Q3) percentile with whiskers extending to upper limit  $[Q3 + 1.5(Q3 - Q1)]$  and lower

limit  $[Q1 - 1.5(Q3 - Q1)]$ . Also shown are number of data points ( $n$ ), median  $\log[K_D(L/g-SS)]$  and p-value of one-tailed Mann Whitney test evaluating differences between inactivation methods (note: n/a = not applicable, i/d = insufficient data available for statistical evaluation).

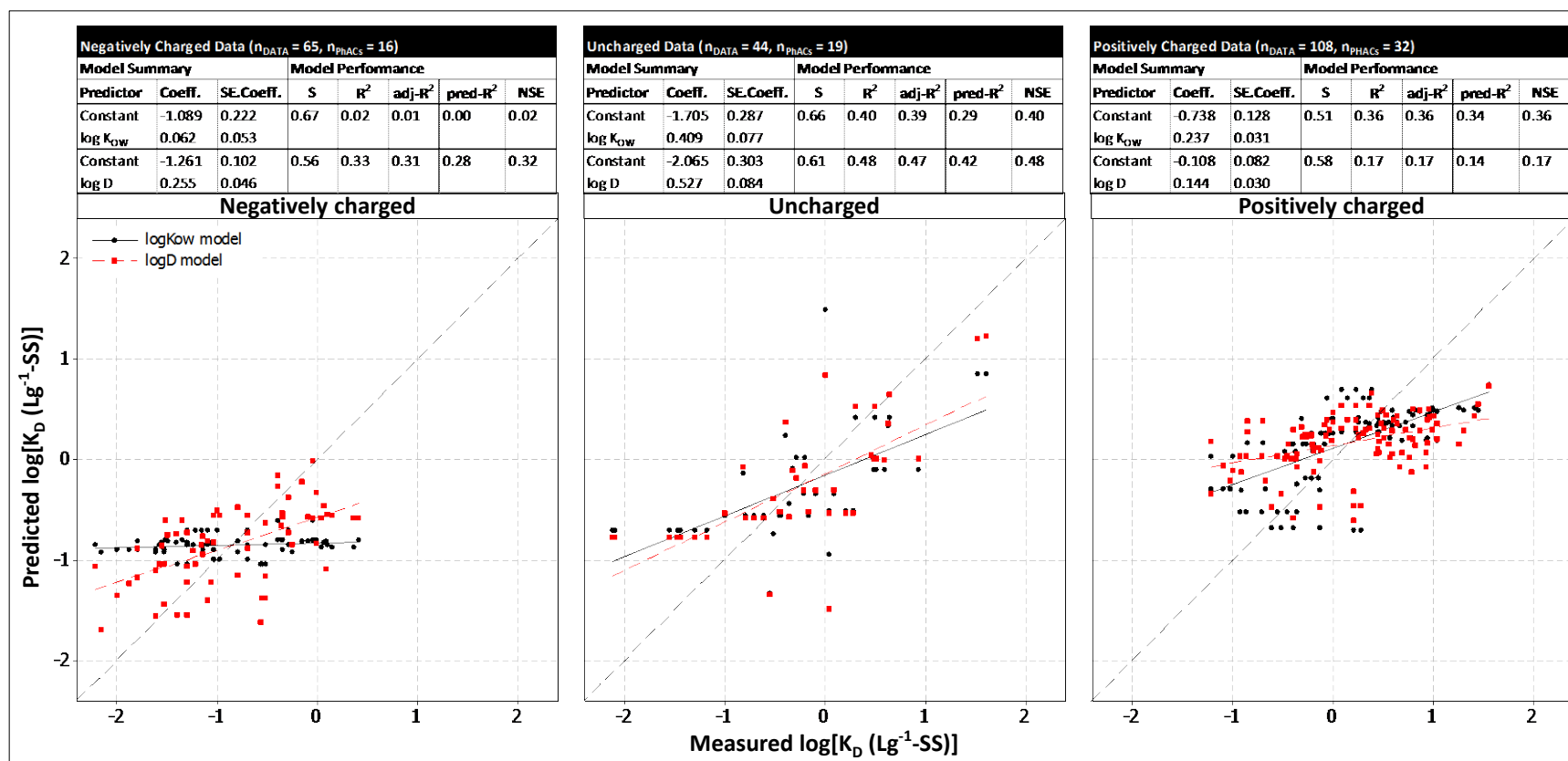


Figure 3. Reported  $\log K_D$  values with predictions using one-parameter models based on  $\log K_{OW}$  (black) and  $\log D$  (red) for negatively charged (left), uncharged PhACs (middle) and positively charged PhACs (right). Model coefficients and performance is shown in the overlying tables.

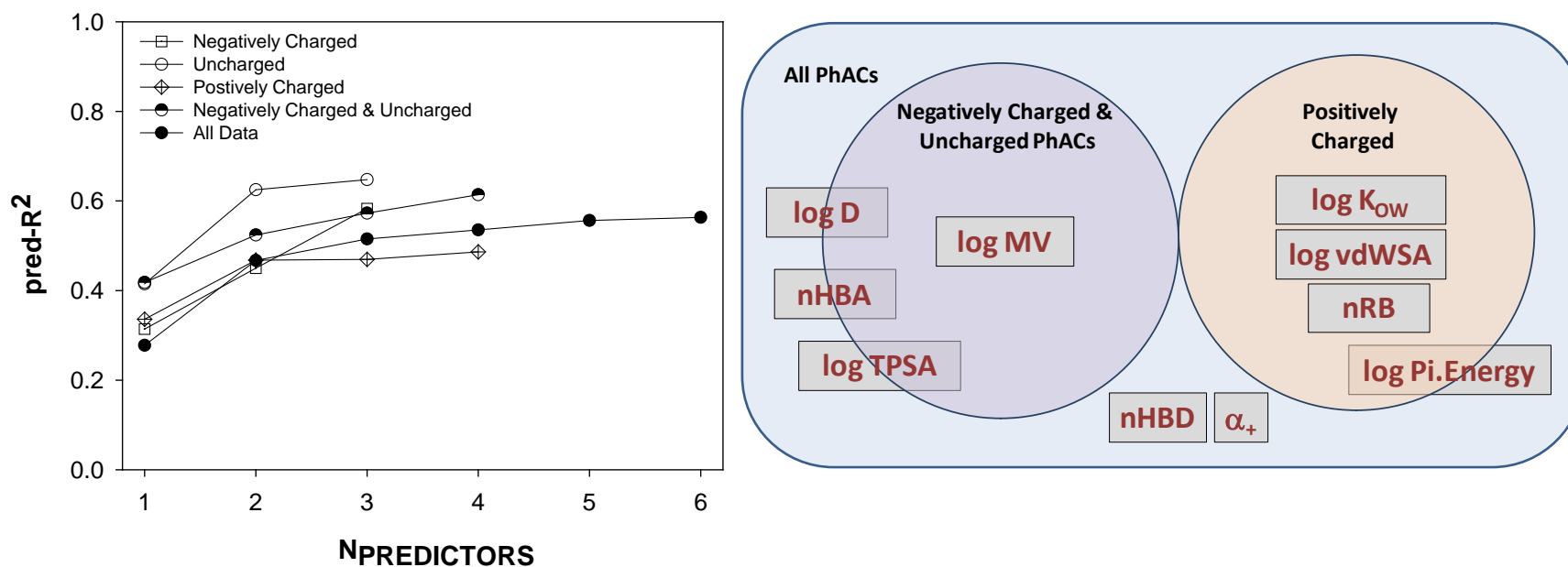


Figure 4. Left: Predictive capability (pred-R<sup>2</sup>) of polyparameter QSAR models with increasing number of statistically significant predictors. Note that correlation for uncharged PhACs can be improved when the fraction of uncharged mass is > 85% (see discussion in text). Right: Predictors which are significant in predictive models for sorption of negatively charged/uncharged pharmaceuticals, positively charged pharmaceuticals and all pharmaceuticals. Model details and summary statistics are provided in Table 2.

Table 2. Summary of best fit polyparameter QSAR models developed to describe the sorption of pharmaceuticals to suspended solids biological treatment.

N <sub>PRED.</sub>	Model Summary: log[K <sub>D</sub> (Lg <sup>-1</sup> -SS)] =	Model Performance				
		S	R <sup>2</sup>	adj-R <sup>2</sup>	pred-R <sup>2</sup>	NSE
Uncharged PhACs (n <sub>DATA</sub> = 44; n <sub>PhACs</sub> = 19)						
3	QSAR Model: [-3.12±0.29] + [(0.63±0.07)log D] + [(0.30±0.06)nHBA] + [(-0.07±0.03)nRB]	0.45	0.73	0.71	0.65	0.73
Negatively Charged PhACs (n <sub>DATA</sub> = 65; n <sub>PhACs</sub> = 16)						
3	[5.88±1.69] + [(0.37±0.05)logD] + [(0.30±0.05)nHBA] + [(- 3.56±0.78)logMV]	0.44	0.60	0.58	0.56	0.61
Positively Charged PhACs (n <sub>DATA</sub> = 108; n <sub>PhACs</sub> = 32)						
4	(7.65±2.24) + [(0.34±0.04)]log(K <sub>OW</sub> ) + [(1.65±0.31)]log(PiEnergy)] + [(-4.34±0.94)]log(vdWSA)] + [(0.05±0.02)]log(nRB)]	0.44	0.54	0.52	0.49	0.54
Models for Grouped PhACs						
Negatively Charged and Uncharged PhACs (n <sub>DATA</sub> = 109; n <sub>PhACs</sub> = 16)						
4	[ 4.54±1.36) + [(0.39±0.04)logD] + [(0.32±0.04)nHBA] + [(-2.41±0.59)logMV] + [(-0.86±0.25)log(TPSA)]	0.48	0.64	0.63	0.61	0.64
All PhACs (n <sub>DATA</sub> = 217; n <sub>PhACs</sub> = 54)						
6	(-1.74±0.46) + [(0.22±0.03)logD] + [(0.92±0.10)logTPSA] + [(0.99±0.28)log(Pi.Energy)] + [(-0.85±0.17)log(TPSA)] + [(0.14±0.05)nHBD] + [(0.08±0.03)nHBA]	0.53	0.59	0.58	0.56	0.59

Parameter values are reported with the standard error of the estimate. See Table 1 for definition of the predictors.

### **Biodegradation of beta-blockers during nitrification**

Several studies have reported that WWTPs operated at long solids retention times (SRTs  $\geq$  8-10 days) demonstrate improved removal of PhACs (Kreuzinger et al., 2004; Clara et al., 2005; Joss et al., 2006), yet it remains unclear if this observation is related to the presence of slow growing bacteria (e.g., nitrifying bacteria) or an increase in the microbial diversity (Shi et al., 2004; Batt et al., 2006; Reif et al., 2008; Tran et al., 2009; Suarez et al., 2010; Falas et al., 2012; Fernandez-Fontaina et al., 2012). Thus, the role of nitrification processes in the biodegradation of three beta blockers – atenolol (ATN), metoprolol (MET) and sotalol (SOT) was evaluated (see Table 3 for the structure and properties of each pharmaceutical). Full details of this research are available in a forthcoming manuscript (Sathyamoorthy et al., in preparation). Focus in this report is placed on the key findings.

#### ***Results related to characterization of biomass in batch experiments***

The qPCR in this research targeted the *amoA* gene of AOB and the 16s rRNA gene of EUB, NOB-Ns and NOB-Nb using a composite DNA sample from each reactor. Results from these analyses indicate that AOB are the dominant nitrifying consortium in these samples, making up between ~75% and 85% of the nitrifying population (i.e., AOB + NOB). This is within the range noted in previous studies of nitrifying populations (Li et al., 2006). Nitrobacter are dominant NOB effectively accounting for the remainder of the nitrifying population. Nitrospira NOB account for less than 0.1% of the nitrifying population. The negligible fraction of Nitrospira results from the high ammonia concentrations used in the nitrification enrichment SBR which was the seed biomass source for these experiments. High ammonia levels result in high nitrite concentrations during the SBR cycle which favors Nitrobacter over Nitrospira (Schramm et al., 2000).

#### ***Results related to pharmaceutical biodegradation***

Results indicate that ATN was degraded during nitrification whereas no degradation was observed for MET or SOT (see Figures 5, 6 and 7). Interestingly, atenolol biodegradation was also noted in the nitrification inhibition control (275  $\mu$ M ATU for nitrification inhibition). The extent of ATN biodegradation in the experimental reactors was ~80% compared to ~30% in the nitrification inhibition control. The extent of ATN degradation in a follow up experiment conducted to evaluate biodegradation of ATN during nitrite oxidation was comparable to the nitrification inhibition control (~28%). Collectively, these data suggest that although ATN was biodegraded by non-nitrifying bacteria present in the culture (presumably heterotrophs), nitrifying bacteria had a substantial role in ATN degradation. Furthermore, this research demonstrates that not all pharmaceuticals within the same compound or therapeutic class are biodegraded by the same group of bacteria.

The pseudo-first-order biodegradation rate coefficient for ATN fit using data from replicate experimental reactors ( $k_{\text{BIO,NIT}}$ ) was  $2.39 \pm 0.21 \text{ L.g-VSS}^{-1}.\text{d}^{-1}$ . The analogous rate coefficient using data from the Nit.Inh.Control ( $k_{\text{BIO,NIT,INH.}}$ ) was  $0.56 \pm 0.10 \text{ L.g-VSS}^{-1}.\text{d}^{-1}$  (see Figure 8 for model fits). The biodegradation rate of ATN under nitrification conditions was approximately four times greater than when nitrification was inhibited using ATU. This was consistent with the hypothesis that the activity of nitrifying bacteria controls the degradation of ATN in this nitrification enrichment culture. The  $k_{\text{BIO,NIT}}$  values for ATN determined in this research are comparable to those reported by Maurer et al. (2007) ( $0.98 \text{ L.g-SS}^{-1}.\text{d}^{-1}$  in batch experiments using biomass from an MBR operated at 20 d SRT) and Wick et al. (2009) ( $1.90$  and  $1.10 \text{ L.g-SS}^{-1}.\text{d}^{-1}$  in batch experiments using sludge from a suspended growth system operated at 18 d). Neither Maurer et al. nor Wick et al., however, report nitrogen concentration data which prohibits elucidation of any link between nitrification processes and PhAC biodegradation within their experiments. Both studies also reported attenuation of MET and SOT as resulting from nitrification though this was not observed in our experiments (Figures 5 and 6).



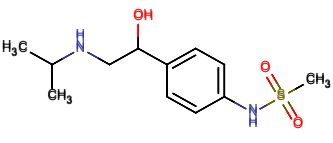
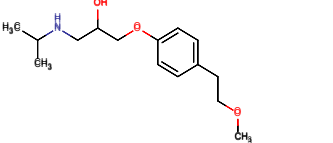
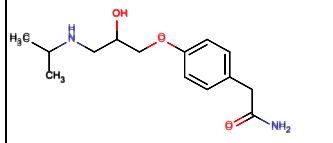
A coupled nitrification cometabolic PhAC degradation model was used to evaluate the role of ammonia oxidizing bacteria in ATN degradation noted in the replicate nitrification experiments and the nitrification inhibition control. Using the data from Nit.Inh.Control,  $\mu_{\text{ATN-HET}}$  was estimated to be  $12.6 \pm 2.50 \text{ L-g-COD}^{-1}\text{d}^{-1}$ . This estimate was utilized to model ATN biodegradation in the replicate experimental reactors and estimate values for the transformation capacity of ATN by AOB (i.e.,  $T_{\text{ATN-AOB}}$ ) and the rate associated with ATN biodegradation by AOB in the absence of growth through  $k_{\text{ATN-AOB}}$ . The best fit values determined for  $T_{\text{ATN-AOB}}$  and  $k_{\text{ATN-AOB}}$  were to be  $71.5 \pm 22.7 \text{ L-g-COD}^{-1}$  and  $16.1 \pm 5.58 \text{ L-g-COD}^{-1}\text{d}^{-1}$ , respectively. Shown in Figure 8 is a comparison of the model fits and experimental data for the two replicate experiments and the nitrification inhibition control. To our knowledge, this research is the first to report transformation coefficients for cometabolic biodegradation of any PhAC by nitrifying communities. Consequently, no existing data are available to compare with the results from this research. However, there is a significant body of knowledge related to cometabolic biodegradation processes in environmental systems (Chang et al., 1993; Criddle, 1993; Alvarez-Cohen and Speitel, 2001) and nitrifying communities more specifically (Ely et al., 1997; Kocamemi and Cecen, 2005, 2010b, a). The  $T_{\text{ATN-AOB}}$  value obtained herein ( $71.5 \pm 22.7 \text{ L-g-COD}^{-1}$ ) is similar to those reported for TCE at concentrations below  $350 \mu\text{g-L}^{-1}$  ( $\sim 50 \text{ L-g-COD}^{-1}$ , Kocamemi and Cecen, 2010a). Note here that Kocamemi and Cecen (2010a) estimated the transformation capacities they report in their Table 2 by taking the slope of the line formed between the origin and the highest reported degradation rate shown in their Figure 1. In fact, there is a theoretical basis for and evidence of a non-zero intercept based upon cometabolic degradation when there is no growth (e.g., Ely et al. 1997). Thus, the data from Kocamemi and Cecen (2010a) were refit to produce both a slope (indicative of  $T_{\text{ATN-AOB}}$ ) and intercept (indicative of  $k_{\text{ATN-AOB}}$ ). Our estimates of the  $T_{\text{TCE-AOB}}$  based upon the data from Kocamemi and Cecen (2010a) assume a yield coefficient for ammonia oxidation of  $0.15 \text{ mg-COD-mg-N}^{-1}$ .

### **Results related to nitrification**

Ammonia, nitrite and nitrate concentrations during the batch nitrification experiments with ATN, MET and SOT are shown in the left panels of Figures 5, 6 and 7. Complete nitrification was achieved in all control and replicate reactors for each experiment. No accumulation of nitrite was observed in any of the experiments and the highest nitrite concentration observed was less than  $5 \text{ mg-N/L}$  which is below levels where nitrification of PhACs is considered relevant (Gaulke et al., 2008). Successful inhibition of nitrification was achieved with ATU addition to the inhibition control reactors in each experiment as demonstrated through no production of either nitrite or nitrate during the course of the experiment.

The discrepancy between measured and modeled concentrations of ammonia, nitrite and nitrate concentrations in the ATN experiment were found to be larger at low ammonia concentrations. That is to say, in the case of ATN, the model was unable to satisfactorily predict the nitrification process when the ammonia concentration was at or below the half saturation value. Interestingly, the same effect of the PhAC on ammonia oxidation rates at low ammonia concentration was not observed in predictions from MET or SOT experiments. The predictive capability for the nitrification process was significantly improved when the nitrogen specie data were refit assuming competitive inhibition of AOB growth by ATN (Bailey J.E and Ollis D.F, 1986). These data suggest that ATN may competitively inhibit ammonia oxidation in these batch experiments. The inhibition constant  $K_{i,\text{ATN-AOB}}$  was determined to be  $1.84 \pm 0.39 \mu\text{g-L}^{-1}$ . This suggests that the presence of ATN, at levels consistent with those found in wastewater treatment facilities, in the range of  $0.2$  to  $2.0 \mu\text{g-L}^{-1}$  (Lee et al., 2007; Wick et al., 2009; Jelic et al., 2012), may reduce the growth rate of AOB.

Table 3: Properties of pharmaceuticals selected for this research with reported concentrations in environmental systems

		SOT	MET	ATN
Basic Parameters	Formula	C <sub>12</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub> S	C <sub>16</sub> H <sub>21</sub> NO <sub>2</sub>	C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub>
	MW (g/mol)	272.4	259.3	266.3
	Structure			
Partitioning	Log K <sub>ow</sub>	0.24	3.48	0.16
	pK <sub>A</sub>	8.35, 9.98	9.7	9.6
Geometry & Stereochemistry	TPSA (Å <sup>2</sup> )	78.4	50.7	84.6
	%Aro.C	50%	40%	43%
	No. Rot.Bonds	6	6	8
	H-bond Don.	3	2	3
	Acc.	5	4	4
Environmental concentration	VdW SA (Å <sup>2</sup> )	430.76	474.69	440.41
	WWTP influent (ug/L)		0.21-0.25 (Siemens et al., 2008) 1.80-2.60 (Siemens et al., 2008)	-- (Miege et al., 2008) 2.3 (Ternes et al., 2007)
	Prim. Effluent (ng/L)	180-567 (Lee et al., 2007)	214-664 (Lee et al., 2007)	1,180-2,210 (Lee et al., 2007)
	WWTP Effluent (ng/L)	162-429 (Lee et al., 2007)	177-402 (Lee et al., 2007)	642-1,680 (Lee et al., 2007)

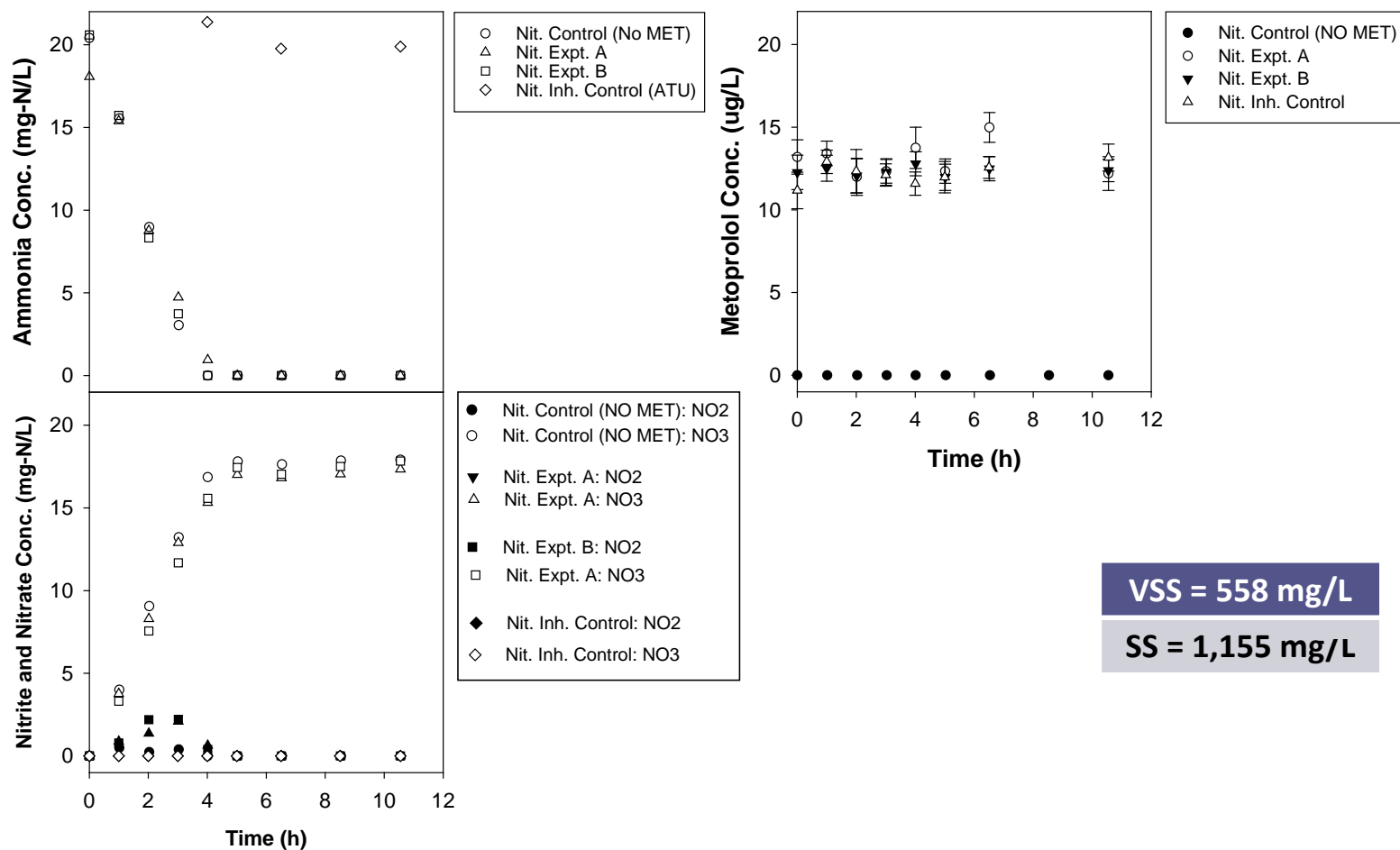


Figure 5. Results from experiment evaluating biodegradation of metoprolol during nitrification: concentration in the aqueous phase of ammonia (top left panel), nitrite and nitrate (bottom left panel) and metoprolol (top right panel). Each plot contains data from four reactors: one nitrification control reactor which has no metoprolol (Nit. Control (No MET)), two experimental reactors (Nit. Expt. A and Nit. Expt. B) and one nitrification inhibition control reactor (Nit. Inh. Control) where ATU is used to inhibit nitrification. Also shown in the bottom right are VSS and SS for reactors.

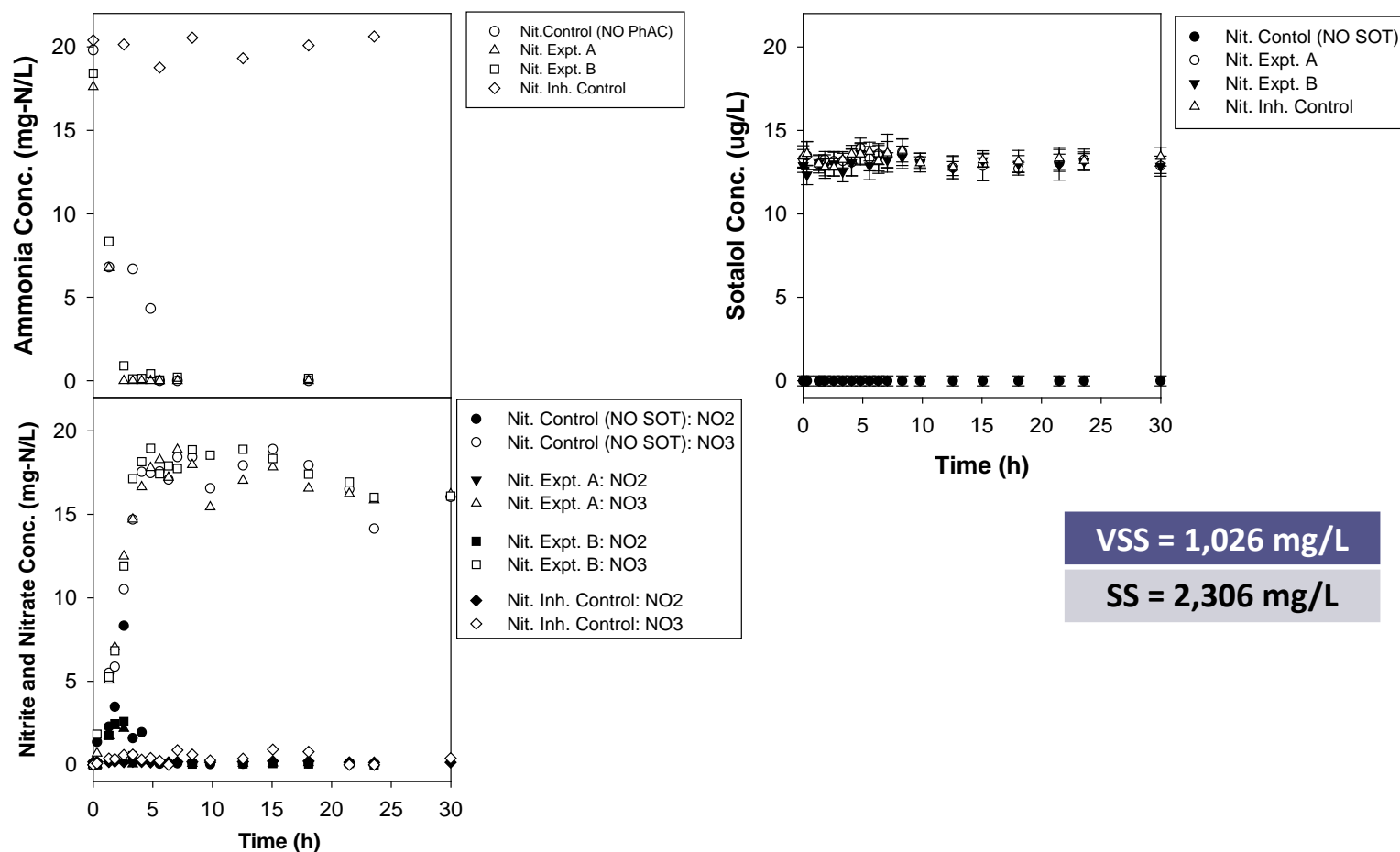


Figure 6. Results from experiment evaluating biodegradation of sotalol during nitrification: concentration in the aqueous phase of ammonia (top left panel), nitrite and nitrate (bottom left panel) and sotalol (top right panel). Each plot contains data from four reactors: one nitrification control reactor which has no sotalol (Nit.Control (No SOT)), two experimental reactors (Nit.Expt. A and Nit.Expt. B) and one nitrification inhibition control reactor (Nit.Inh.Control) where ATU is used to inhibit nitrification. Also shown in the bottom right are VSS and SS for reactors.

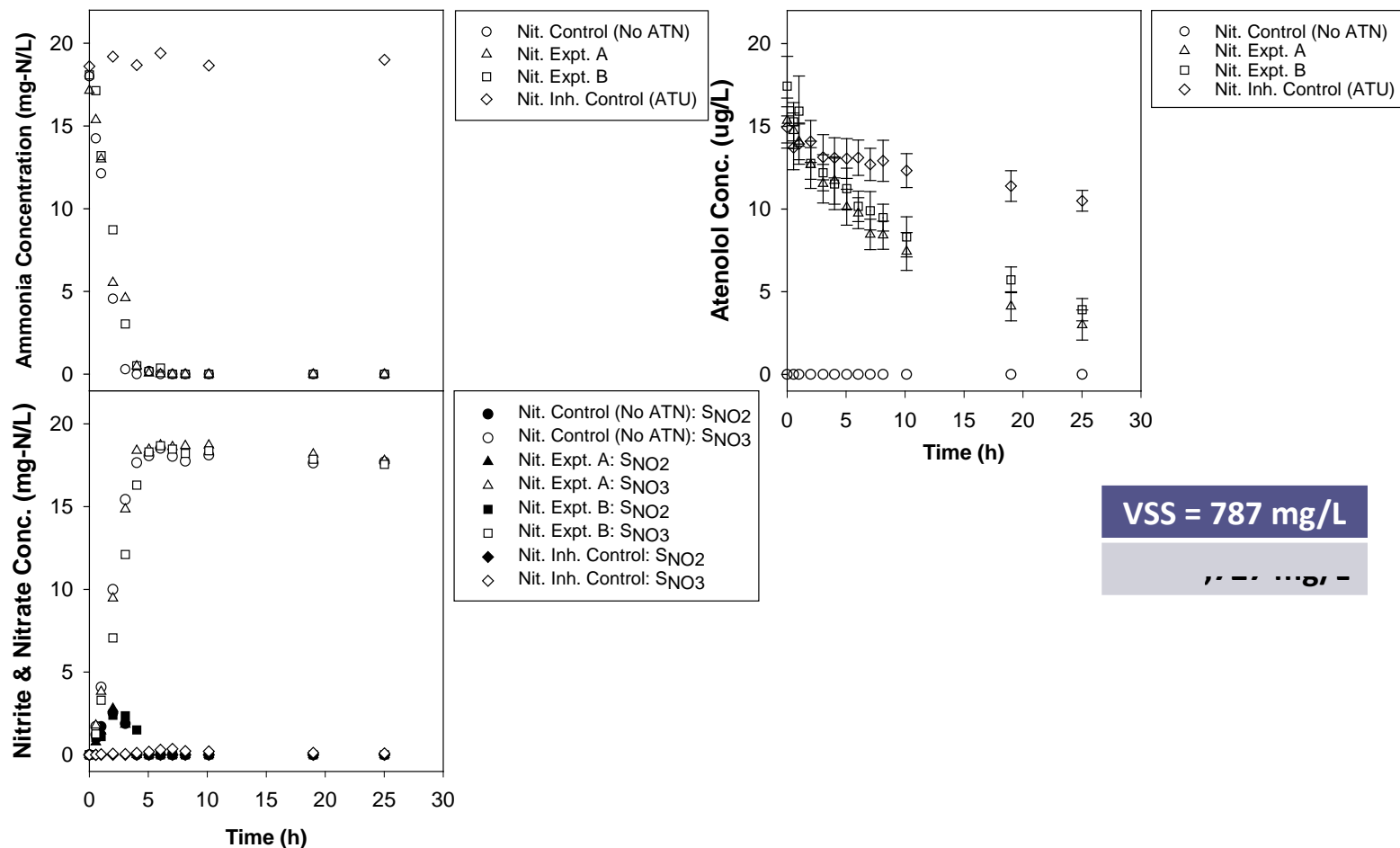


Figure 7. Results from experiment evaluating biodegradation of atenolol during nitrification: concentration in the aqueous phase of ammonia (top left panel), nitrite and nitrate (bottom left panel) and atenolol (top right panel). Each plot contains data from four reactors: one nitrification control reactor which has no atenolol (Nit.Control (No ATN)), two experimental reactors (Nit.Expt. A and Nit.Expt. B) and one nitrification inhibition control reactor (Nit.Inh.Control) where ATU is used to inhibit nitrification. Also shown in the bottom right are VSS and SS for reactors.

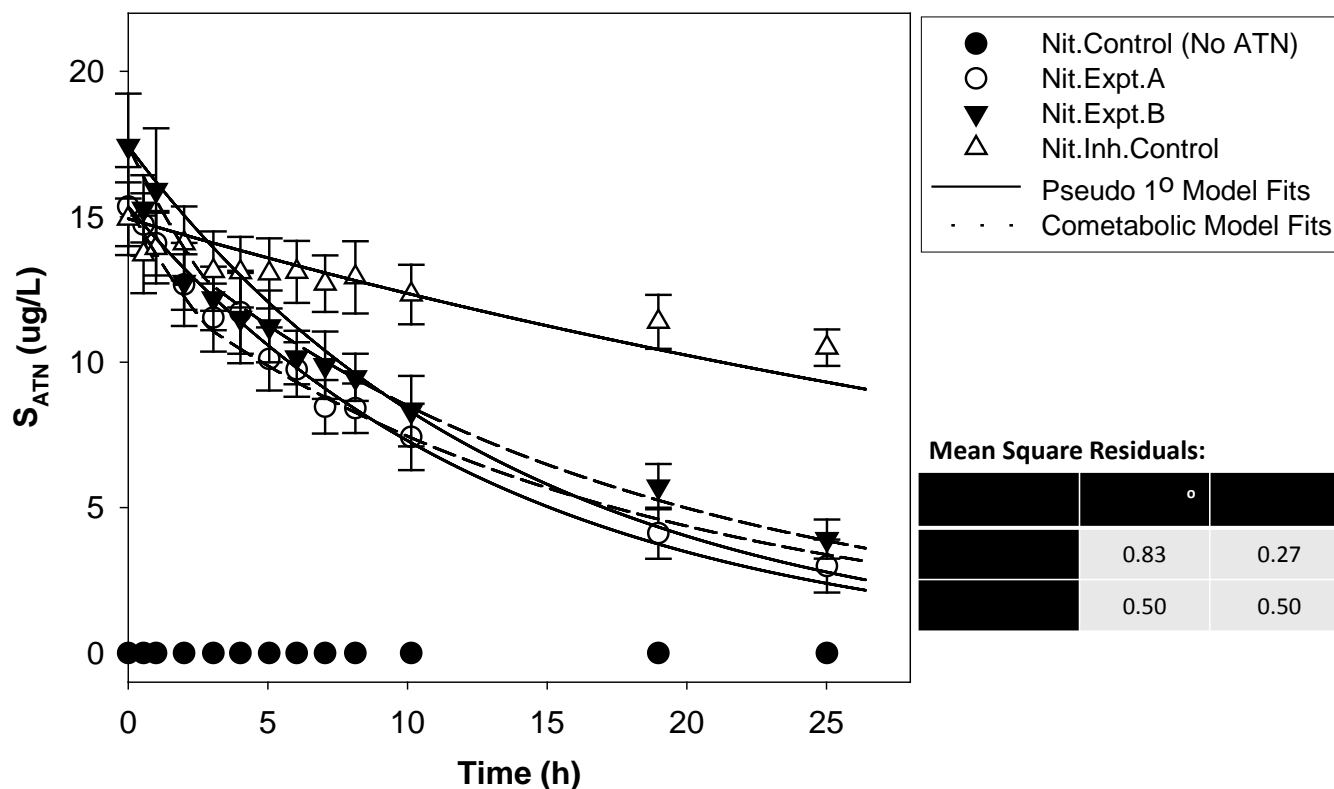


Figure 8. ATN concentration in batch experiments evaluating ATN degradation during nitrification. Results from Nit.Expt.A Nit.Expt.B and Nit.Inh.Control are shown with model simulations a using pseudo-first-order model with  $k_{BIOL,NIT.} = 2.39$  and  $k_{BIOL,NITINH.} = 0.56 \text{ L.g-VSS}^{-1}\text{d}^{-1}$  and cometabolic model with for  $T_{PhAC-AOB} = 0.060 \pm 0.017 \text{ L mg-COD}^{-1}$  and  $k_{PhAC-AOB} = 0.017 \pm 0.004 \text{ L mg-COD}^{-1} \text{ d}^{-1}$ . Also shown is a comparison of the mean square residuals for each model based on the experimental data (Nit.Expts.) and inhibition control data (Nit.Inh.Control).

### Summary and Implications

The goal of this research was to evaluate the role of sorption and degradation of PhACs in wastewater treatment facilities aimed at meeting stringent nutrient standards. Sorption was evaluated using both batch experiments with specific PhACs and predictive modeling that is more generally applicable. The role of nitrifying bacteria and nitrification processes in PhAC biodegradation was evaluated using a nitrification enrichment culture.

Our experiments indicate that only MET appreciably sorbed to the biosolids in the nitrifying enrichment culture. Broader evaluation of PhAC sorption, across a range of processes and unit operations, using existing values of the PhAC distribution coefficient suggests that the conventional use of single-parameter models based on octanol-water partition coefficients has limited predictive capability. To overcome this limitation, polyparameter QSAR models were developed using chemometric properties of PhACs. These polyparameter models suggest that the single best predictor for PhAC sorption is the charge of the dominant species. Other important predictors include molecular weight (MW), molecular volume (MV), aromaticity, number of rotatable bonds

(n.RB), hydrogen bonding capacity (hydrogen bond donors- nHBD and acceptors- nHBA) and polar surface area (PSA). While results indicate that the polyparameter models developed herein significantly enhance predictive capability, the best models can only explain approximately 60% of the variance in the available PhAC sorption data. More research is therefore required to assess the role that biosolids surface properties have in PhAC sorption.

The relevance of sorption as an attenuation mechanism is illustrated in Figure 9 which shows the fraction of PhAC mass that is associated with biosolids for various distribution coefficients and biomass concentrations. For a conventional activated sludge (CAS) system operating at a typical mixed liquor suspended solids (MLSS) concentration of  $3,000 \text{ mg L}^{-1}$ , PhACs with a  $K_D$  equal to  $0.37 \text{ L g}^{-1} \text{ SS}$  will be evenly distributed between the biosolid and aqueous phases. For a membrane bioreactor (MBR) operating at  $10,000 - 11,000 \text{ mg L}^{-1}$  MLSS the same distribution occurs for at much lower values of  $K_D$  ( $0.10 \text{ L g}^{-1} \text{ SS}$ ).

Laboratory experiments were coupled with mathematical modeling to evaluate the biodegradation of the beta blockers ATN, MET and SOT. Results indicate that only ATN was readily degraded by the nitrification enrichment culture used herein. Thus, care should be taken to avoid assuming that the occurrence of nitrification in WWTPs operated at long solids retention times leads to greater biodegradation of PhACs due to a greater presence of nitrifying organisms. It remains an open question; however, if the greater biodiversity associated with longer solids retention times can be relied upon to aid degradation of PhACs. Certainly, additional research is warranted to evaluate the biodegradation of those beta blockers studied here by microbial consortia that are more indicative of wastewater treatment facilities.

Results from the biodegradation experiments conducted with ATN indicate that ATN degradation resulted from ammonia oxidation. In fact, the ATN results suggest that the role of ammonia oxidizing bacteria in PhAC biodegradation may be more relevant than previously estimated. It is conventionally assumed that the role of nitrifying bacteria in PhAC biodegradation is limited by the fact that these organisms represent only a small fraction of the biomass in a wastewater treatment plant. Our research suggests that even when AOB make up 5% of the total biomass in a WWTP reactor, they contribute between 7% - 17% to the biodegradation rate of ATN (Figure 10). That is to say, their contribution outweighs their proportion in the biomass. Additional research is necessary to evaluate the extent to which this observation holds true for other PhACs co-metabolically degraded by the biochemical processes responsible for nitrification.

ATN degradation was accurately described through the use of a coupled nitrification-cometabolic PhAC biodegradation model. The model represents a novel use of an integrated cometabolic biodegradation module within the ASM model framework. This approach is particularly relevant considering the widespread utility of the ASM modeling framework in industrial WWTP process simulators (e.g., Biowin, GPSx, etc.). Consortium level assessments of PhAC biodegradation offer increased sophistication and greater generalizability over pseudo first order biodegradation rate coefficients which offer no mechanistic insight. Additional research is therefore warranted to elucidate cometabolic transformation capacities for a host of PhACs undergoing degradation by heterotrophs and nitrifiers. Development of a suite of transformation capacities for a number of PhACs under a wide range of conditions will provide the foundation necessary for the development of models which can predict PhAC fate in wastewater treatment facilities based upon chemometric properties.



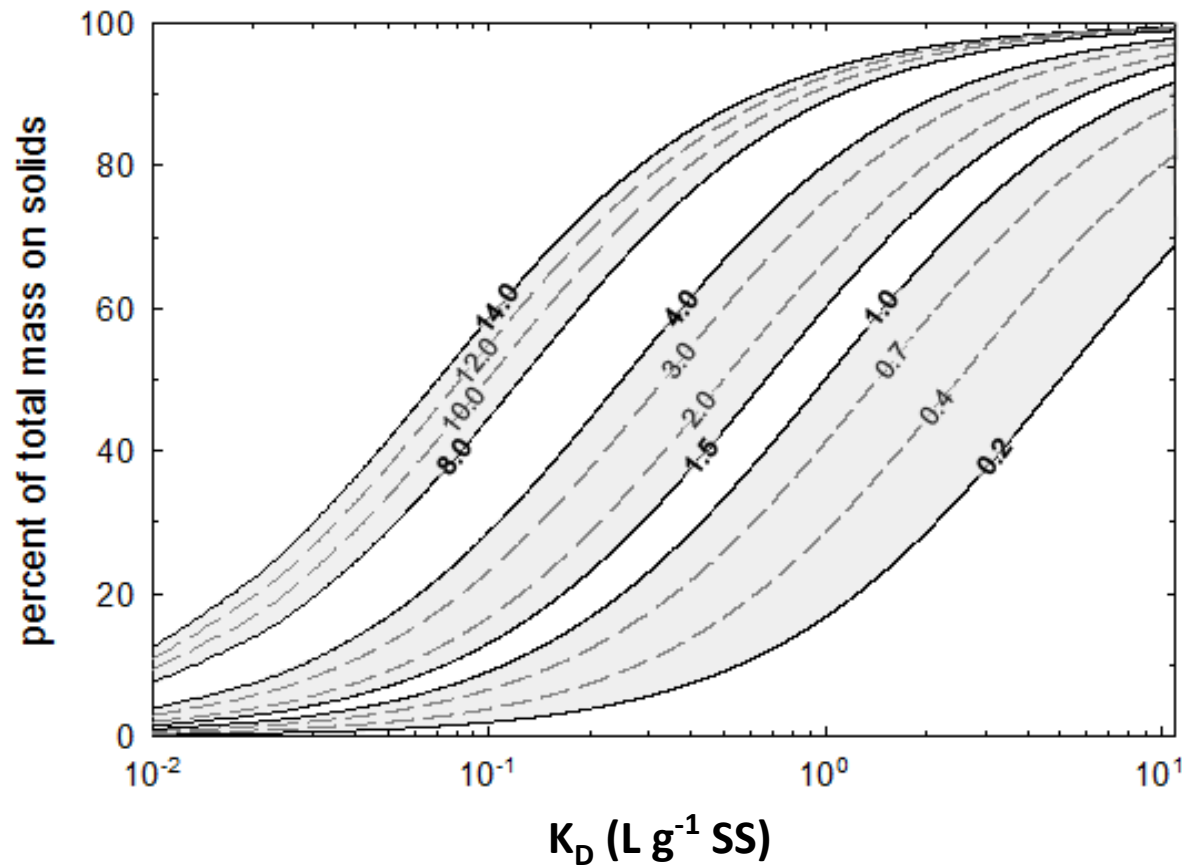


Figure 9. Fraction of PhAC sorbed to mixed liquor solids for PhACs with  $K_D$  values ranging from 0.01 to 10  $\text{L g}^{-1}$  SS. Lines are shown for different reactor mixed liquor concentrations (indicated on the plot in  $\text{g L}^{-1}$ ). Three data bands are shown for (from left to right): membrane bioreactors (MLSS = 8.0 – 14.0  $\text{g L}^{-1}$ ), suspended growth/conventional activated sludge systems (MLSS = 1.5 – 4.0  $\text{g L}^{-1}$ ) and lab scale systems (MLSS = 0.2 – 1.0  $\text{g L}^{-1}$ ).

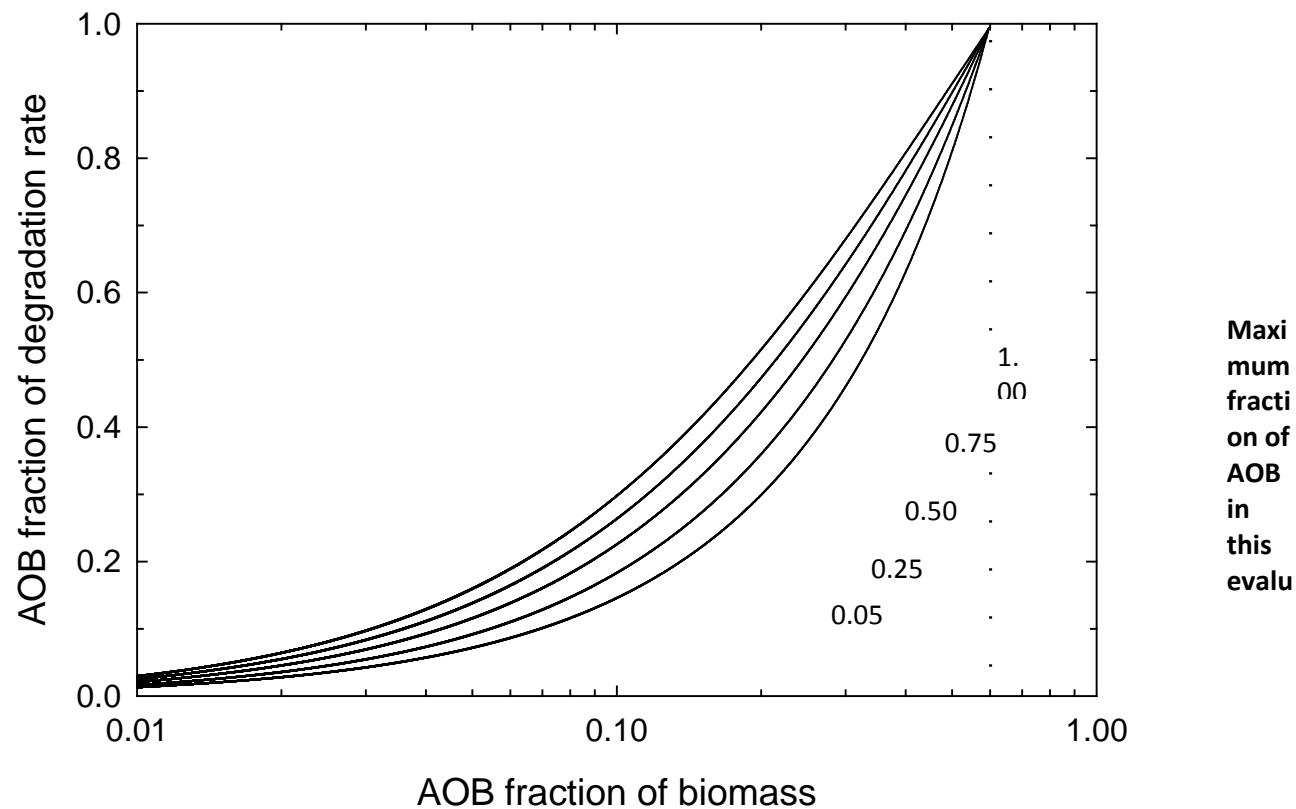


Figure 10. Fractional contribution of AOB to the rate of ATN biodegradation. Each curve represents a fraction of the maximum specific growth rate of AOB on ammonia (taken here to be  $0.5 \text{ d}^{-1}$ ). Note that the plot assumes that AOB comprise 60% of nitrifiers which is, therefore, the maximum fraction of the biomass that AOB can represent (vertical line).

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#### **Student Support**

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#### **Publications and Conference Presentations:**

Sathyamoorthy S. and Ramsburg C.A., Assessment of Quantitative Structural Property Relationships for Prediction of Pharmaceutical Sorption during Biological Wastewater Treatment, *Chemosphere*, In Press (DOI: <http://dx.doi.org/10.1016/j.chemosphere.2013.01.061>)

Sathyamoorthy, S., Chandran K. and Ramsburg C.A., Degradation of Beta Blockers during Ammonia Oxidation, *In Preparation*.

Sathyamoorthy, S., A Laboratory and Modeling Investigation of Pharmaceutical Attenuation through Biodegradation and Sorption in Single Sludge Nitrification Systems, Anticipated completion date: August 2013

Sathyamoorthy S. and Ramsburg C.A., Degradation of selected pharmaceuticals during nitrification, in Proceedings of: WEFTEC 2012, WEF, New Orleans, LA, 2012

#### **4. USGS Award No. G11AP20228 Climate Risk Assessment and Management (USGS 2011MA316S)**

**Principal Investigator:** Casey Brown, UMass Amherst

**Start Date:** 9/16/2011

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**Reporting Period:** March 1, 2012 – February 28, 2013

**Funding Source:** Supplemental

**Research Category:** Climate and Hydrologic Processes

**Focus Categories:** Climatological Processes, Management and Planning

There is a concern among the climate science community that increased global temperatures will accelerate the hydrologic cycle, leading to more intense and frequent storms and greater flood risk. The ability to plan and implement resilient flood risk reduction strategies has been impeded because of a host of uncertainties associated with future climate, the hydrologic response, and relationships between flood levels and damages. Deep uncertainty in future climate conditions has confounded long-term planning efforts in flood risk management that have previously relied on an assumption of stationarity in the climate system. The vast array of information available from the current set of climate projections can often paralyze the decision-making process as users debate the credibility of projections and their utility at the scale of the impacts of interest. A need exists for a clear methodology that can derive decision-relevant information from the available sources of climate evidence without depending too greatly on any one sources' accuracy or acceptability.

In addition to the uncertainty surrounding future climate, there is also significant uncertainty surrounding our ability to estimate the hydrologic response, especially the flood response, of a local watershed. This uncertainty should not be ignored when considering the adequacy of flood protection projects under future climate change. The purpose of this study is twofold: 1) to present a new approach to describing flood risk under climate change that better facilitates the development of robust adaptation strategies for flood risk reduction projects; 2) to present a framework for assessing the effects of hydrologic modeling uncertainty on the estimation of future flood risk within the context of a changing climate.

### **Methodology:**

To account for the uncertainty of future climate change in flood risk planning, this report utilizes the Decision-Scaling methodology introduced by *Brown et al.* (2012). The approach is stakeholder and decision-centric and includes the use of climate projections and other sources of climate information in the decision-making process. At its core, the Decision-Scaling methodology can be characterized by two primary components: 1) the identification of climate conditions that lead to unacceptable flood control problems (i.e. a vulnerability assessment), and 2) an examination of different sources of climate evidence (e.g. climate projections, the historic record, paleodata) to determine whether those problematic climate changes are likely to occur. By separating the vulnerability assessment from the analysis of likely climate changes, the approach ensures that the performance of the current system and a set of proposed adaptation strategies are tested over a sufficiently wide range of possible futures to identify important vulnerabilities. When coupled with information regarding the likelihood of different climate changes, the vulnerability analysis provides the decision-maker with an assessment of climate-based risks facing the system, as well as an appraisal of how robust different adaptation strategies are to those risks. The framework presented here consists of four primary steps: 1) the identification of key stakeholder concerns and decision thresholds, 2) a vulnerability assessment to identify the climate states that lead to unacceptable system performance, 3) an analysis of the likelihood of different types of problematic climate changes, and 4) an appraisal of the robustness of alternatives to inform decision-making. Extensive details on each step can be found in the report of Brown (2012).

This report accounts for parameter and structural hydrologic modeling uncertainties using a comprehensive error modeling approach. A lumped-parameter, conceptual hydrologic model (HYMOD) is used to simulate the catchment response of the Coralville watershed. Structural uncertainty in the model is accounted for by fitting a formal probability distribution to the model residuals. An innovative error model is chosen to accommodate the non-Gaussian, auto-correlated, and heteroscedastic nature



of daily hydrologic model errors. Input uncertainties are lumped together with structural uncertainties in the error model. Error model parameters are estimated based on a traditional hydrologic model fit using standard optimization procedures. After the error model is estimated, the parameters of the hydrologic model are inferred using Bayesian methods. Prior distributions are set for all hydrologic model parameters and Markov Chain Monte Carlo (MCMC) sampling techniques are used to explore the posterior distributions of all parameters considered. This calibration approach allows for an assessment of hydrologic model parameterization uncertainty. The error model parameters are then re-estimated based on the mean response of the hydrologic model under the Bayesian calibration. The components of the hydrologic uncertainty analysis are described in detail in the report of Brown (2013). The Coralville Reservoir system located in eastern Iowa was chosen as a case study for demonstrating usefulness of our methodologies.

## **Principal Findings and Significance:**

### **1) Key findings from hydrological uncertainty evaluation**

The 49 different climate sequences produced by the weather generator are used as input to two hydrologic models (HYMOD and VIC), which in turn are used to drive the Coralville Reservoir simulation model. For the HYMOD model, 100 different ensemble streamflow traces are used to characterize model uncertainty. For all model runs, expected annual flood damages are recorded and used to assess system performance. Figure 1 shows the expected annual flood damages produced under a range of potential precipitation changes. Expected damages are shown for the hydrologic model outputs from both the HYMOD and VIC models. For the VIC model, each climate change is associated with one sequence of predicted streamflow. For the HYMOD model, the mean flood damage is shown from the ensemble HYMOD traces, as well as the 95% uncertainty bounds. Three main conclusions emerge from these results.

- First, it is clear that regardless of the hydrologic model, flood damages increase substantially as the average precipitation increases, suggesting that the current system is very sensitive to changes in regional precipitation. For both hydrologic models, a 10% increase in precipitation over climatology (i.e. from 100% to 110%) more than doubles the expected annual flood damage.
- Secondly, the annual flood damages predicted under the VIC simulations are contained within the uncertainty bounds associated with the HYMOD simulations, suggesting that the structural differences between the two models is no more influential with respect to damage estimates than the fully quantified uncertainty within one model. This implies that for hydrologic modeling, multi-model approaches alone may be insufficient to characterize the true uncertainty in predicted streamflows.
- Finally, the results suggest that the uncertainty from the HYMOD model contributes significantly to the uncertainty in future flood damages when compared against the range of damages associated with uncertainty in climate change. This is especially true as future precipitation increases, as the uncertainty in damage originating from the hydrologic model grows substantially with changes in precipitation. For instance, consider the shift in flood damage associated with precipitation mean increases between 110% and 120% of historic norms. The annual flood damages, as predicted using the mean HYMOD model hydrologic response, increase from \$700,000 to \$1,400,000 between these two scenarios. Yet under the scenario with a 20% increase in mean precipitation, the 95% uncertainty bound for flood damage ranges from \$750,000 to \$1,800,000. That is, the range in flood damage due to hydrologic modeling uncertainty at a high level of precipitation change (e.g. 120% of climatology) is 50% *greater* than the range of flood damage between the mean responses under two climate scenarios of future precipitation increases. In this case, the hydrologic model is clearly contributing substantially to the total uncertainty surrounding future flood damages under a shifting climate.

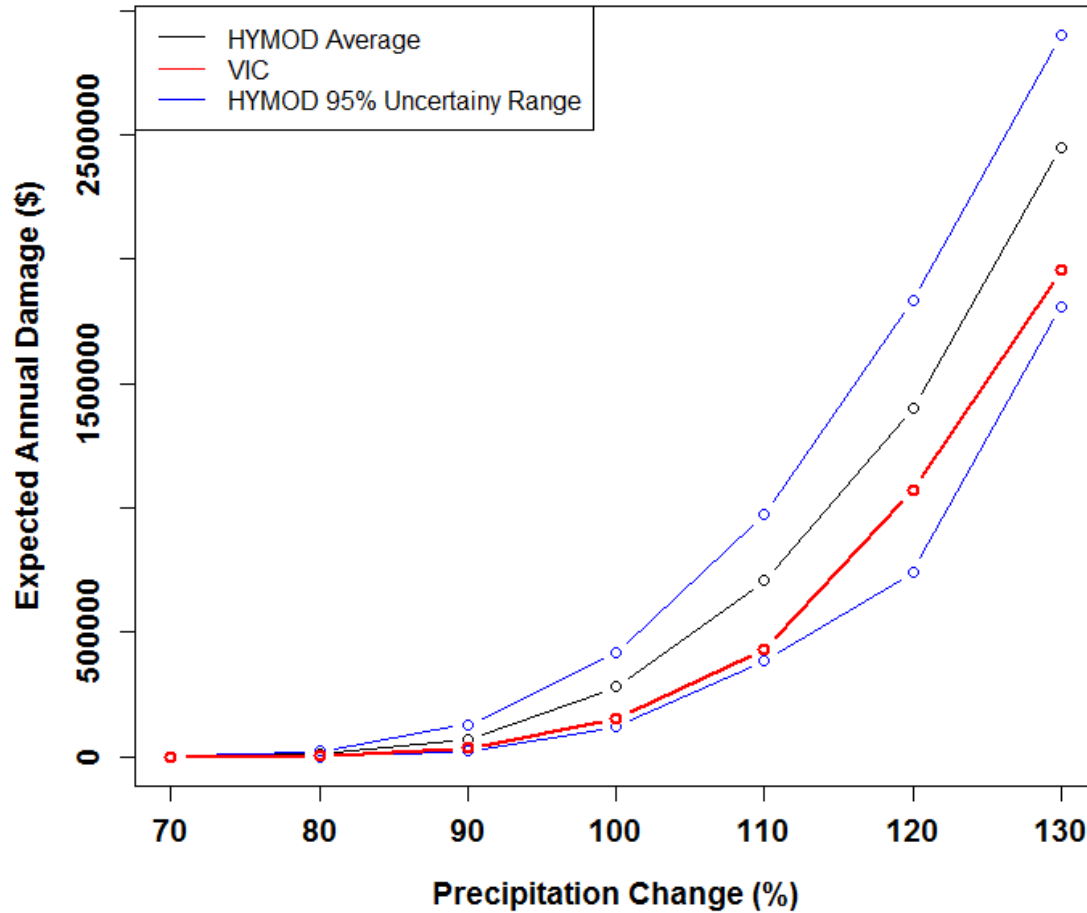


Figure 1. Expected annual flood damages produced under a range of potential precipitation changes

The influence of hydrologic model uncertainty on system robustness can also be compared against the combined influence of temperature and precipitation changes. Figure 2 shows a climate response surface of expected annual damages below the Coralville Reservoir. Damages are calculated for each of the 49 combinations of temperature and precipitation change using the HYMOD model. Here, a threshold value of \$280,000/year of damage is considered a “tipping point” with respect to the decision-process and is plotted in bold on the response surface. That is, we assume that decision-makers and stakeholders consider expected annual damages above \$280,000/year unacceptable and use the risk of damages exceeding this threshold as a trigger that would support adaptation actions. This particular damage threshold was chosen because it is the baseline level of damage that emerged under no climate changes. The threshold corresponding to the mean HYMOD model response is shown on Figure 2 as the dark black line. The 2.5<sup>th</sup> and 97.5<sup>th</sup> percentile damage values across the ensemble of HYMOD traces are also shown on the surface by the dotted blue lines. Finally, future climate projections were taken from the Coupled Model Intercomparison Project Phase 5 (CMIP5) global climate model runs and superimposed on the figure. These projected changes in precipitation and temperature were first bias corrected for the Coralville region and are developed using a 30-window centered about the year 2050.

Figure 2 shows how a critical decision-centric metric can vary due to hydrologic modeling uncertainty in the context of future climate projection uncertainty. Several insights emerge from this figure. First, the diagonal orientation of the damage threshold suggests that the influence of precipitation increases on flood damage is slightly offset from increases in temperature. That is, as temperatures increase, slightly more precipitation is needed to cause the same level of flood damage. This result emerges because increases in temperature lead to increases in potential evapotranspiration, which in turn remove some of the water from the basin and reduce the overland flow during large storm events. In addition, high temperatures reduce the water stored in snowpack that can lead to some of the larger springtime flood events. Figure 2 also shows a large range in the location of the critical damage threshold in climate space due to the uncertainty of the HYMOD model. The 95% confidence bounds for the threshold due to hydrologic uncertainties spans a 15% change in precipitation. In fact, a majority of CMIP5 projections lie within this range of uncertainty, indicating that the differences between many of these projections, at least in terms of aggregate climate statistics, are less consequential than the uncertainty stemming from the hydrologic model. We do note, however, that some CMIP5 projections do lie outside this uncertainty range, indicating that the full range changes from the projections provide some information beyond the noise imposed by the hydrologic modeling process.

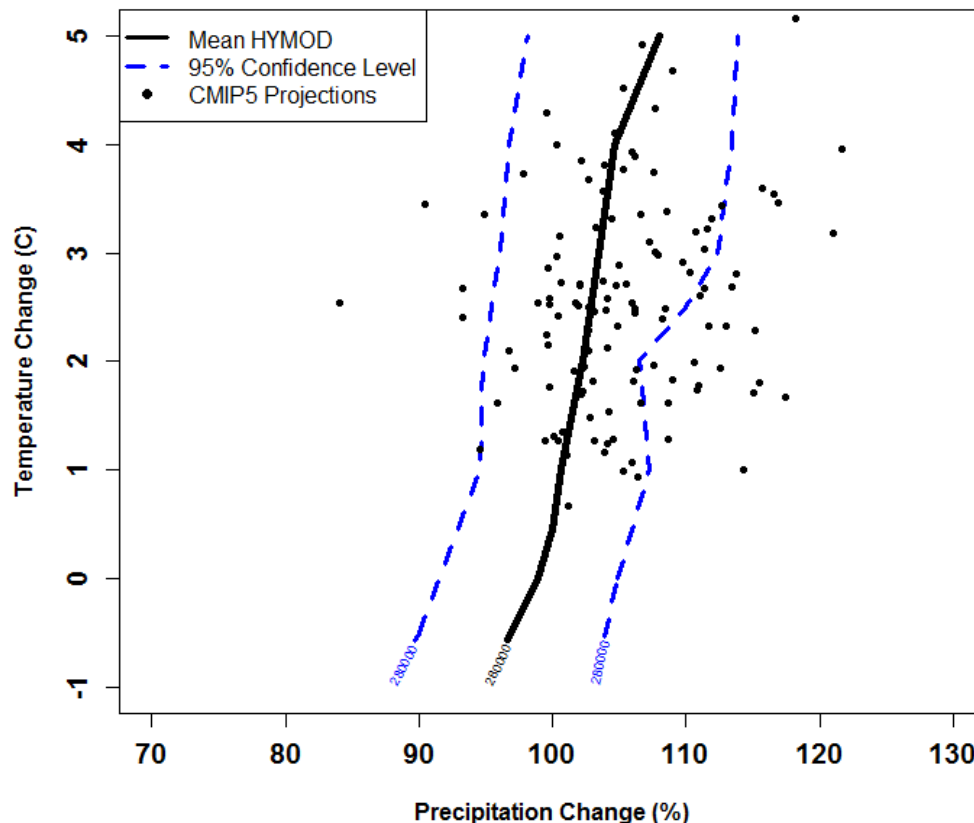


Figure 2. A climate response surface of expected annual damages for the Coralville Reservoir

## 2) Key findings from appraising the new flood risk assessment framework

The primary contribution of this part is to present the climate risk assessment framework which is designed to generate insightful guidance from the often confusing and conflicting set of climate information available to decision makers. The approach generates information that is tailored to the

actual decisions facing managers and planners, helping to ensure that the results of the analysis are relevant to the objectives of the system. Through the use of a climate stress test, the approach helps to develop insights into the critical system sensitivities to climate within the context of stakeholder-developed concerns. Information from all available climate sources, including the latest generation of climate projections produced from the scientific community, is integrated into the analysis in a transparent manner that allows decision-makers to include their own judgments on the relative credibility of different sources of information and understand what different assumptions about future climate imply about the preferences of available adaptation actions. The case study application to the Coralville Lake system demonstrated how the approach can be used to highlight the robustness of current infrastructure and operations across a wide range of potential climate changes and then contextualize this robustness in terms of current trends in the observed record and projected climates generated by an ensemble of GCMs. The approach produced easy-to-interpret results that indicate under which climate conditions a given adaptation strategy (e.g. the purchase of farmland in the floodplain) would be preferred over the status-quo system, and then showed whether different sources of climate evidence suggested that these climate states were likely to occur in the future. The principal findings are well illustrated in Figure 3 and 4.

The results from the climate stress test revealed that the current system is vulnerable to certain types of climate change, particularly for precipitation. This sensitivity indicates that adaptations for this system should be considered. Therefore, the stress test was conducted again on the adapted system after farmlands are purchased in the floodplain to reduce flood risk. In order to appraise and compare the robustness of the current Coralville flood control system and the adapted system, the climate states under which thresholds for expected annual damages are exceeded are identified for both systems. Since there are two thresholds considered in the study (concerning damage (\$10 million per year) and unacceptable damage (\$20 million per year)), the climate change space is partitioned into three zones for the current system and the adaptation strategy considering the purchase of farmland in the floodplain. By comparing the climate change space over which expected annual damages remain in the acceptable zone (i.e. below \$10 million per year in expected damages), the robustness of the status quo and adapted systems can be compared. Examining the extent to which the threshold of \$20 million per year in expected damages is surpassed across climate change space can reveal the robustness of each option against unacceptable damage. To assess the climate-informed robustness of each option, the range of GCM projections, as well as the historic trend, can be compared against the regions of climate change space that prove to be acceptable, challenging, and unacceptable in terms of expected annual damages for each system.

The robustness of the adaptation plan considered in this study (the purchase of farmland) is compared against the status quo system in Figure 3. To conduct this comparison, Figure 3 shows the two threshold levels of damage for both the status quo system (solid black lines) and the system with an additional buffer zone from the purchase of land in the floodplain (dashed red line). These thresholds are shown for climate changes with altered precipitation and temperature means but precipitation variability held at historic levels. Also shown are historic climate means from the periods 1951-1980 and 1981-2010, as well as projections for these mean values for the year 2050 from an ensemble of GCMs. Uncertainty ellipses at the 95% confidence level are also shown for the historic statistics.

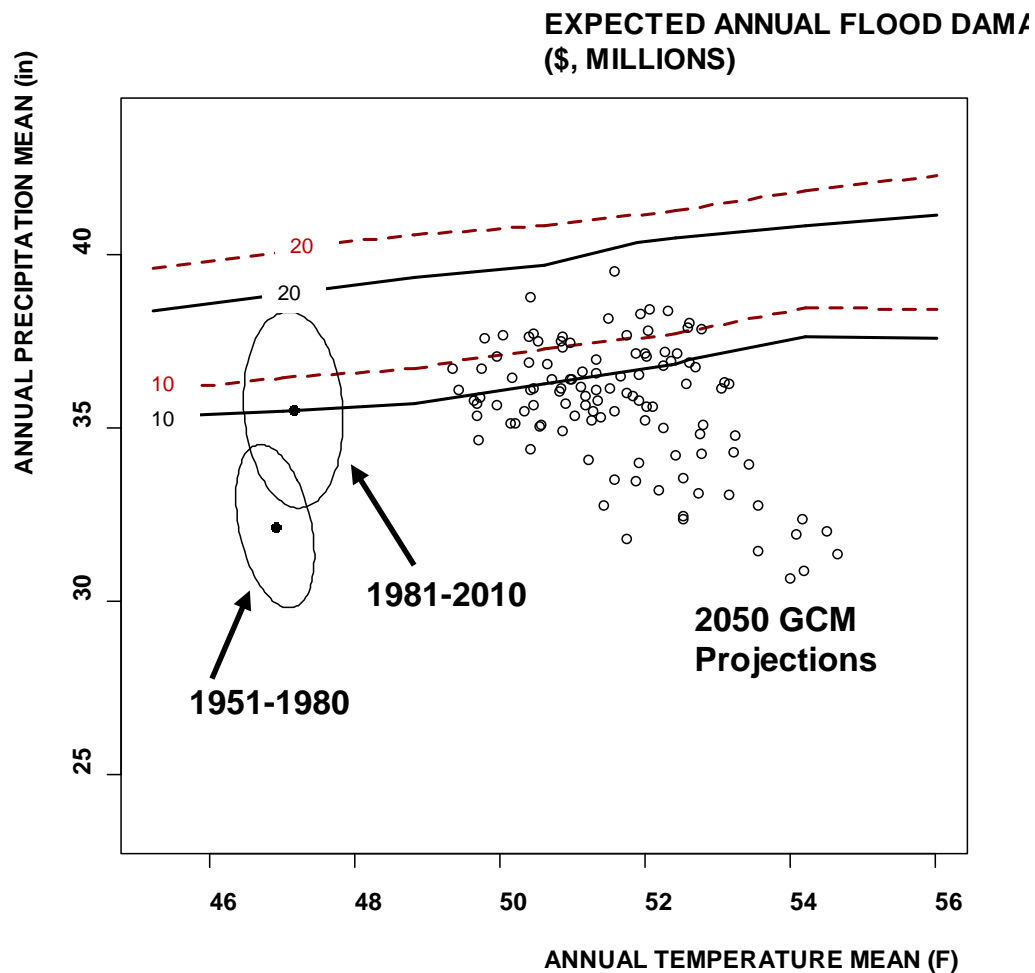


Figure 3. Critical (\$10 million/year) and breaking (\$20 million/year) thresholds of damage for the status quo (black solid) and adaptation-based (red dashed) systems across climate space. The critical and breaking lines depict the types of climate change under which expected annual flood damages are acceptable to stakeholders (below the critical line), stressing but manageable (between the critical and breaking lines), and intolerable (above the breaking line). The upward shift of the lines for the adaptation-based system above those of the status quo indicate how much more robust the adapted system is compared to the status quo across climate space. The climate changes considered here include changes in mean temperature and mean precipitation levels. The historic climate and its associated uncertainty for 1951-1980 and 1981-2010 are shown as solid points with 95% uncertainty ellipses. Open circles indicate an ensemble of GCM climate projections for the year 2050.

Figure 3 shows that when an additional buffer zone in the floodplain is added to the flood control system on the Iowa River, flood risk moderately decreases. The same level of critical flood damages (\$10 million/year) for the status quo can be maintained under approximately 1 inch of additional rainfall per year when the adaptation is introduced (i.e. the dashed red critical level for the adaptation-based system resides above that of the status quo system by about 1 inch of rainfall, as measured on the y-axis). Also, the portion of climate space classified in the breaking zone moderately decreases when the adaptation is considered. We note that under the status quo system, the historic shift in climate between 1951-1980 and 1981-2010 moved the system into a critical damage zone (i.e. between \$10 and \$20 million/year in damages), but when the adaptation is applied to the system, the system under 1981-2010 climate returns back to an acceptable zone of flood damage. We also note that

significantly fewer of the climate models project precipitation and temperature changes for 2050 that would enter the critical zone of flood damage if the adaptation is employed; under status quo conditions, many more of these projections show futures in the critical zone. It is important to recognize, however, that if the uncertainty of the 1981-2010 climate is considered, there is still considerable risk that even the adapted system remains in the critical zone of damages, suggesting that this adaptation is likely insufficient in isolation to provide the necessary protection needed to reduce flood damages to acceptable levels.

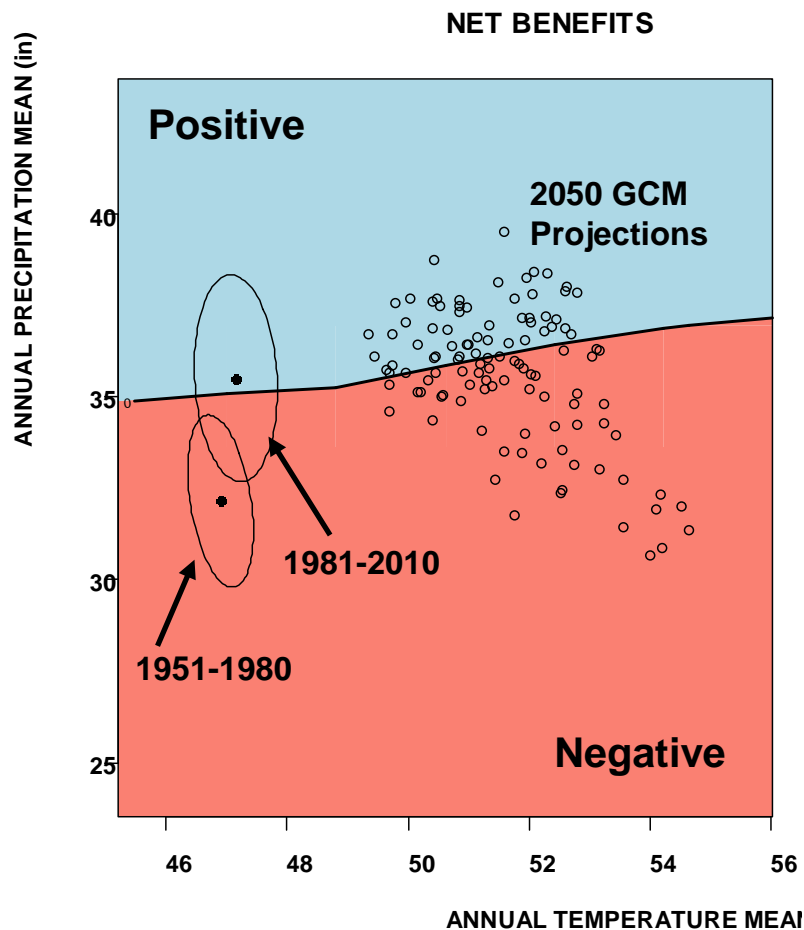


Figure 4. Net benefits (reductions in damage less annualized costs) afforded by the purchase of farmland in the floodplain of the Iowa River across climate space. The climate changes considered here included changes in mean temperature and mean precipitation levels. The blue region indicates climate changes under which net benefits are positive for the adapted system, while the red region depicts types of climate change under which the adaptation leads to negative net benefits. Zero net benefits are indicated by the black line. The historic climate and its associated uncertainty for 1951-1980 and 1981-2010 are shown as solid points with 95% uncertainty ellipses. Open circles indicate an ensemble of GCM climate projections for the year 2050.

While the purchase of farmland clearly improves flood protection on the Iowa River, it is not clear under which future climate states it would be preferable to employ this adaptation because the costs have not yet been compared to reductions in damage. This information is shown in Figure 4. This figure displays the net benefits accrued from the purchase of farmland in the floodplain across climate space. Net benefits are defined here as the reduction in expected annual flood damage between the adaptation-based and status quo systems less the annualized costs for the purchase of the land. Areas

in Figure 4 that show positive net benefits (blue) indicate climates under which the reductions in flood damage outweigh the cost of the adaptation, while areas with negative net benefits (red) indicate that the investment was not preferable for that region of climate space. Again, the historic climate for two time periods and projected climate for 2050 are also shown. Figure 4 indicates that the flood damage reduction benefits afforded by the adaptation outweigh the cost for most climates with greater than approximately 35 inches of precipitation a year, although as temperatures increase, more precipitation is needed to justify the investment. The adaptation appears to be a good investment when just considering the historic shift in the climate already seen, as the net benefits move from being negative to positive as the climate shifted from the 1951-1980 to the 1981-2010 climate regime. The purchase of floodplain farmlands also seems like a worthwhile investment under about 50% of future GCM projections.

### **Student Support**

1 Postdoctoral Research Scientist

### **Notable Achievements and Awards**

PI Brown was named College of Engineering Outstanding Junior Faculty Member

### **Follow-on Funding**

During this period PI Brown received a \$1.8M grant from DoD SERDP program for climate risk assessment.

### **Publications and Conference Presentations:**

1. Steinschneider, S., and C. Brown, A semiparametric multivariate, multi-site weather generator with low-frequency variability for use in climate risk assessments, *Water Resources Research*, under review.
1. Brown, C. Climate Risk Assessment of Coralville Reservoir: Demonstration of the Decision-Scaling Methodology, Report to the Institute of Water Resources, US Army Corps of Engineers, Submitted November 2012.
2. Brown, C. Climate Risk Assessment of Coralville Reservoir: System Robustness under Future Climate and Hydrologic Uncertainty, Report to the Institute of Water Resources, US Army Corps of Engineers, Submitted May 2013.
1. Steinschneider, S., and C. Brown, Climate stress test: A novel approach to bottom-up vulnerability assessments under climate change in the water sector, EWRI May 2013, Cincinnati, OH.

### **References**

- Brown, C., Y. Ghile, M. Laverty, and K. Li (2012), Decision scaling: Linking bottom-up vulnerability analysis with climate projections in the water sector, *Water Resour. Res.*, 48, W09537, doi:10.1029/2011WR011212.
- Brown, C. Climate Risk Assessment of Coralville Reservoir: Demonstration of the Decision-Scaling Methodology, Report to the Institute of Water Resources, US Army Corps of Engineers, Submitted November 2012.
- Brown, C. Climate Risk Assessment of Coralville Reservoir: System Robustness under Future Climate and Hydrologic Uncertainty, Report to the Institute of Water Resources, US Army Corps of Engineers, Submitted May 2013.



## **5. Analysis of Charles River (MA) Submerged Aquatic Vegetation (SAV) Using a Prototype (USGS 2012MA318B)**

**Principal Investigator:** Bruce A. Jackson, Biotechnology, MassBay Community College

**Start Date:** 3/1/2012

**End Date:** 2/28/2013

**Reporting Period:** March 1, 2012 – February 28, 2013

**Funding Source:** USGS (104B)

**Research Category:** Biological Sciences

**Focus Categories:** Invasive Species; Water Quality; Education

**Descriptors:** None

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

This project utilizes robotic submersible technology (RUSS-2) to characterize submerged aquatic vegetation (SAV) blooms in the Charles River (MA) at the organismal, molecular and atomic levels. Data from this research has been useful in devising methodologies to control SAV contamination in the waterways of Massachusetts and other regions of the United States and its territories; specifically the San Juan Estuary of Puerto Rico.

Seven converging interdisciplinary studies on the Estuary are enabled (^) or significantly enhanced (+) by RUSS-2:

- 1) Collection of [fresh] urban water algae that are promising candidates as biofuel sources^;
- 2) Genetic assessment and DNA data-basing of urban water algae and bacteria+;
- 3) Assessment of Charles River and San Juan Estuary bed mineral content^;
- 4) Determining contaminant indices in river and estuary aquatic plant root systems^;
- 5) Analysis of Charles River and San Juan Estuary snails as an environmental indicator species^;
- 6) Geology and topographical survey of the Charles River and San Jan Estuary bed^; and
- 7) Detection and quantification of coliforms in the Charles River and San Juan Estuary.

### **Scientific Relevance of this Project**

This Project is scientifically aligned with the United States Environmental Protection Agency's (USEPA) Joint Initiative on Urban Sustainability (USEPA Report, 2011), West Coast Estuaries Initiative (USEPA Report, 2008), and Puerto Rico National Estuary Program (USEPA Report, 2007). Our Project is educationally aligned with the USEPA's "Science to Achieve Results (STAR)" Program and 'Environmental Education and Training Partnership (EETAP)" and other related public and private efforts to create this nation's future environmental scientists. It is in the interest of our nation and its territories to include urban waterways in environmental sustainability practices and to achieve the mutual goal of protecting all of the nation's natural resources. Urban community colleges are perfectly positioned to accomplish this goal. This is because 60 percent of all Americans and 80 percent of minorities begin their undergraduate careers at community colleges (Mullin and Phillipe, 2009). These large enrollments portend that a significant percentage of this nation's future scientists will begin their careers at these burgeoning institutions. Community colleges are central to President Obama's educational reform movement, which, relevant to this project, coincides with the President's national environmental initiatives. A national effort by community colleges to transform STEM curriculums through research-based learning that teaches science as a process began with MassBay's Biotechnology Program in 1993, spread nationally and gave rise to the PI's 2009 *Presidential Award for Excellence in Science, Mathematics and Engineering Mentoring* (awarded to him by President Obama in the Oval Office). This reform entails engaging community college scholars in research early in their collegiate careers and that is relevant to their community. Taken together, community colleges are ideal institutions to lead a national study of urban waterways.

Our interdisciplinary research entails an expansive and ongoing study of the Charles River and subsequently the San Juan Estuary, which were enabled or enhanced by RUSS-2. The collaborators that comprise our research team are well established in their respective disciplines. We utilize submersible technology that was developed at two Massachusetts' community colleges, MassBay and the Benjamin Franklin Institute of Technology (BFIT). Scientifically, RUSS-2 adds an analytical rigor to our research by allowing the study of aquatic regions inaccessible or dangerous to boats and/or research divers. RUSS-2's GPS and hovering capabilities allow precise regions of the Charles River and San Juan Estuary to be studied for extended periods. In temporal experiments, this capability allows water, sediment and biological samples to be collected from the same position with insignificant variation in the submersible's position, thus assuring experimental reproducibility.

The Charles River is a waterway that traverses several communities in Massachusetts and has significant historical, environmental and recreational importance. Likewise, the San Juan Estuary is a key ecological and economic resource for Puerto Rico and serves as a model for environmental studies of other urban waterways of America and its territories. The waterways contain extensive wetland forests, diverse biological communities, tidal basins, dunes and salt flats. The San Juan Estuary is also the breeding ground for numerous species that are on the Federal Endangered Species List, including the brown pelican, least tern, peregrine falcon, roseate tern and leatherneck sea turtle (USEPA Report, 2007). Both waterways possess valuable wetland and aquatic habitats, and are the gateways to commercial fishing areas and shipping lanes. Their urban locations, wide-ranging importance and fragile ecosystem validate our multidisciplinary research of the environmental issues affecting these urban waterways. Importantly, our research on the Charles River and San Juan Estuary is relevant to any other urban estuarial system in the world.

Our Specific Research Aims are to:

1. Utilize a prototype submersible "Robotic Underwater Sampling and Surveillance (denoted RUSS-2)" vehicle to measure the levels of SAV, specifically the blue green algae, *Microcystis*, along the 80-mile (129 km) stretch of the Charles River of Massachusetts. During this funding period we expanded our research area to include the San Juan Estuary, Puerto Rico because of its similarity to the Charles River Basin with regards to its egress to Boston Harbor;
2. Employ RUSS's specialized "multibeam" sonar transducer system to measure and define the acoustic characteristics of SAV and map SAV blooms in the Charles River and San Juan Estuary;
3. Utilize RUSS's water and riverbed collection capabilities to measure the relative phosphorus and microstatin levels in water and riverbed soil in regions of heavy, moderate and light SAV in both waterways;
4. To determine if bloom-specific and/or region-specific polymorphisms occur in the hypervariable regions (HVR) I and II of *Microcystis* mitochondrial (mt) DNA. If so, we will create a mtDNA profile database of *Microcystis* collected from the Charles River and San Juan Estuary by RUSS-2 for our use and for other researchers conducting similar studies;
5. Involve 25 nontraditional community college and nontraditional high school (HS) scholars for environmental science and submersible technology through our long-time educational partners, "Eco-Academy" and Boston Green High School Academy by their direct involvement in the research proposed in this project;

Analysis of SAV, water and riverbed soil samples from the Charles River and San Juan Estuary was conducted in the state-of-the-art Biotechnology laboratories at MassBay. This project revealed identifying characteristics of SAV blooms at the macro- and molecular levels. Information from this project enhanced our understanding of the persistence of SAV and elucidate more effective processes for its control. Genomic and mitochondrial DNA sequencing of algae and prokaryotes from the Charles River and San Juan Estuary are in progress.

#### **Methodology:**

The projects which have been proposed under this Award have been advanced except the geological survey of the Charles River and San Juan Estuary floors. These will be completed after the modification of RUSS-2 as described below.

**Biological Sample Collection:** Because *Microcystis* thrives at permissive temperatures in the shallows of slow moving or calm waters containing high levels of phosphorus and nitrogen, samples were collected from water and riverbed samples at SAV sites of low, moderate and heavy bloom in the Charles River and San Juan Estuary. Collected water and riverbed samples are assayed for phosphorus and microcystin in MassBay's BT laboratories using Gas Chromatography (GC) and ELISA, respectively.

**Genetic Analysis:** Algae and prokaryotic DNA were extracted and purified using the Epicentre™ method. PCR templates were prepared as described by Kondo *et al.* (1999). Polymerase chain reaction (PCR) amplifications are performed using a single set of primers for each of the hypervariable (HV) 1 and HV2 regions of Algae mtDNA using the thermo-cycling conditions described by Wilson *et al* (2010).

After amplification, all algae samples plus controls are typed by direct DNA sequencing across the HV1 and HV2 regions. In order to sequence the PCR product, fragments are then cycle sequenced in the forward and reverse directions using the same PCR primers with the BigDye Terminator V1.1 chemistry kit (Applied Biosystems (ABI), Foster City, CA). After cycle sequencing, samples are ethanol precipitated and nucleotide base sequences determined in an ABI PRISM 377 DNA Sequencer. Editing and alignment of the sequences are performed using Sequencher 4.7 Forensic Edition software (Gene Codes Corp, Ann Arbor, MI) and a similar sequence alignment protocol developed and used by MassBay's Biotechnology Program.

Species origin and phylogeny were assigned by DNA sequencing of the hypervariable (HV) region I and II of the D-loop and determining the polymorphisms against a reference sequence. With regard to Charles River *Microcystis* this technology is not without limitations due to the small size of algae DNA databases, undefined mutation rates in various species of algae and an absence of uniform algae sampling methodologies for genetic analysis. We are interested in whether *Microcystis* blooms in the Charles River differ in HV1 and HV2 haplotype depending on their location and/or to the levels of phosphorus to which they are exposed.

Because mtDNA persists in dead organisms for considerable periods of time we are preparing to perform nucleotide sequence analysis of the HVr1 and II regions of *Microcystis* cells recovered from low, moderate and high bloom sites. We will analyze and compare mtDNA sequences to determine if bloom-specific sequence variations can be identified. If identified we will establish a public mtDNA database of Charles River *Microcystis* mtDNA for research purposes.

A significant research effort established under MWRA support by participating MassBay Biotechnology Scholar, Carolyn Lanzkron (See "Student Support", below), was entitled *Experimental Model for Separation of the West Nile Virus from its Insect Vector*. RUSS-2 will be a major collection vehicle of the

mosquito larvae utilized in this study. Of importance, MS. Lanzkron was awarded the 2013 Barry M. Goldwater Scholarship for this study (See “Student Support”).

Briefly, insect-borne diseases have had a significant impact on humans and human evolution. Insects such as flies, fleas, mosquitoes, and lice serve as prolific vectors of diseases, transmitting their pathogens to humans through their blood meals. The insects transmitting these diseases commonly begin their life cycles in waterways similar to the Charles River and San Juan Estuary. Ms. Lanzkron’s research establishes a molecular model for abating the virulence of one such disease, West Nile Virus (WNV), through the creation of a genetic barrier that separates the causative pathogen from its insect host. This is achieved by 1) determining and characterizing the co-evolutionary factors that govern pathogen-insect host selectivity at the DNA level; and 2) developing, in collaboration with Olaf Pharmaceuticals, Inc., a Massachusetts biotechnology company, a panel of drugs that target and disrupt the obligate molecular linkage(s) between pathogen and host.

Current mosquito vector control measures focus on habitat control (draining rivers, removal of local pools of stagnant water, etc.), insecticides, larvicides, and the introduction of infertile male mosquitoes. This research seeks to establish a molecular alternative.

#### **Submersible Engineering and Design:**

WRIP support allowed us to test our submersible engineering concepts and the impact on our research projects to which this technology is linked. Given the multiple uncertainties associated with underwater studies of urban waterways our efforts were to determine if our designs would perform in the difficult environs typical of shallow urban waterways.

Several resolvable problems occurred with RUSS-2 under this Award. Several design changes of the submersible occurred and addressed these problems. RUSS-2 possesses the same basic design as its [prototype] predecessors but with these additions:

RUSS-2 was fitted with a larger propulsion system that uses 7 thrusters that are directly driven brushless electric motors. The major reason that we replaced the propulsion system used on RUSS-2 is to significantly enhance the maneuverability of RUSS-2. The primary purpose of thrusters on a submersible is to surmount the resistive hydrodynamic forces placed on the vehicle, in particular in descents and sudden collision avoidance maneuvers (a common event in urban waterways). These forces are magnified in urban waterways where pervasive submerged natural and manmade objects further impede the movement of the submersible. The speed and maneuverability provided by direct drive is greatly superior to that produced by small thrusters fitted fore and aft of vehicles, as is the case with RUSS-2. Another reason for the change in propulsion systems is power conservation. Smaller thrusters are a considerable draw on the lithium batteries that were the original power source. This draw on power is increased when thrusters must be throttled up in order to propel the vehicle through submerged vegetation such as milfoil. The new thruster systems will make the RUSS-2 extremely maneuverable. Two main thrusters will control forward and backward movement. We will add two angled thrusters, one each on the port and starboard sides of the submersible, giving increased capability side-to-side movements, and ascents and descents. The new thrusters system will allow RUSS-2 the ability to travel underwater at a speed of 9 to 13 knots in any direction.

RUSS is connected to a cabin cruiser (“chase boat”) by a tether that contains guidance, power and communications cables. RUSS-1’s tether is problematic to its mission for several reasons: 1) as the length of the tether increases a significant proportional drag is placed on the submersible as it moves through the water. This drag decreases the submersibles maneuverability especially in tight turns or ascents made to avoid submerged obstacles. Deployment and recovery of the submersible is also problematic because entanglement is common due to the substantial natural and manmade debris submerged in urban waterways. A narrow but accurate analogy to this type of entanglement is that experienced by a person fishing for Bass in a pond with dense milfoil and/or lily pad growth; 2) the tether length required for RUSS-1’s activities in urban waterways is only 300 feet. However, the power

cable component of the tether is aluminum wire. This is because aluminum has a significantly higher conductivity to weight ratio than copper, a factor that is important in signal transmission. However, aluminum wire requires a larger gauge than copper to carry the same current, which increases tether weight and rigidity. Also, aluminum wire is subject to a phenomenon known as "cold creep" in which the metal expands proportionately with increases in temperature and contracts as temperatures decrease (Jenkins and Willard, 1966). This effect is most prominent when the tether is exposed to seasonally changing temperatures and/or temperature gradients in a body of water. "Cold Creep" causes the tether to lose its flexibility and degrades submersible's maneuverability, deployment and recovery over time. Further, marine grade aluminum is exceedingly expensive. Its use in the hull of RUSS-1 and RUSS-2 is imperative. However, its use in a key cable component of the tether is problematic. RUSS-2 is now soft tethered and will have two operation systems that can be operated by a single pilot. The first will be a remote computerized control system (CCS) in which operational signals are relayed to RUSS-2 via a single small gauge wire that will not affect any aspect of the submersible's movements. The second is a programmable guidance system (PGS) that requires no connection to the surface and renders the vehicle under complete computerized control. Both the CCS and PGS systems will utilize a standard 486 computer as the brain and a subsystem control interface. A 486 computer is ideal for RUSS-2's underwater functions because its software, though older, was designed more efficiently and maintains the simplicity, reliability and serviceability of the submersible. The CCS will manage the control input from the pilot at the surface into the submersible's actions under the water. All data required by the pilot on the surface to know RUSS-2's precise position under the water will be collected by GPS sensors on its foredeck and continuously transmitted back to the pilot's control console.

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

The academic and industry collaborators that comprise our estuary research team are well established in their respective disciplines. We utilize submersible technology that was developed at 2 Boston community colleges, MassBay and the BFIT.

Scientifically, RUSS-2 adds an analytical rigor to our research by allowing the study of estuarial regions inaccessible or dangerous to boats and/or research divers. RUSS-2's GPS and hovering capabilities allow precise regions of the estuary to be studied for extended periods. In temporal experiments, this capability allows water, sediment and biological samples to be collected from the same position with insignificant variation in the submersible's position.

Of all the tasks RUSS-2 will be capable of, its usefulness lies in the ability to provide a platform for researchers and scholars to make personal observations in previously inaccessible urban waterways. Our ability to directly observe the environment of the Charles River and San Juan Estuary is beneficial to the multiple STEM disciplines operating in our study. We made operation of the submersible [generationally] intuitive by using as its control system the same joystick technology familiar to anyone born after 1980. Our submersible-based research, though still evolving, reveals scientific wonders of underwater ecosystems to nontraditional scholar-explorers as much as it does seasoned field scientists.

The Charles River and San Juan Estuary are key ecological and economic resources for Massachusetts and Puerto Rico, respectively and serve as a model for environmental studies of other urban waterways of America and its territories. The San Juan Estuary is the breeding ground for numerous species that are on the Federal Endangered Species List, including the brown pelican, least tern, peregrine falcon, roseate tern and leatherneck sea turtle (USEPA Report, 2007). Both waterways possess valuable wetlands and aquatic habitats, and are the gateway to commercial fishing areas and shipping lanes. Their urban locations, wide-ranging importance and fragile ecosystem validate our multidisciplinary

research of urban waterways and the environmental issues affecting them. Importantly, our research is relevant to any other urban system in the world.

Of all the tasks RUSS-2 will be capable of, its usefulness lies in the ability to provide a platform for researchers and scholars to make personal observations in previously inaccessible urban waterways. Our ability to directly observe the environment of the Charles River and San Juan Estuary is beneficial to the multiple STEM disciplines operating in our study. We made operation of the submersible [generationally] intuitive by using as its control system the same joystick technology familiar to anyone born after 1980. Our submersible-based research, though still evolving, reveals scientific wonders of underwater ecosystems to nontraditional scholar-explorers as much as it does seasoned field scientists.

### **Student Support**

#### Educational Relevance of this MWRA-funded Project

Educationally, the project develops a replicable model based on project-based learning, which engages scholars who are underrepresented in science with authentic and relevant research that stimulates their interest in environmental science careers. In addition, the proposed project has mechanisms to disseminate the technology, data and educational model to a national community of scientists and faculty.

The educational problem this project addressed is the paucity of underrepresented groups enrolled in field science and marine engineering degree programs and hence engaged in careers in these disciplines. To help remedy this situation MassBay, BFIT and Sagrado utilized this project to link their long-standing, research-based undergraduate degree programs. These degree programs immerse nontraditional scholars in extensive, sophisticated and relevant scientific investigations for the entirety of their undergraduate careers. MassBay's Biotechnology Program, created by the PI in 1993, has produced an unprecedented, for two-year colleges, 19 Goldwater Scholars (America's highest undergraduate science award). Under the mentoring of Co-PI James Giumara, BFIT scholars devise elaborate and effective engineering solutions that enable the research of scientists across multiple disciplines. RUSS-1 demonstrates BFIT's prowess in scientific capacity building through engineering. Since 1993, Co-PI Mayra Rolon has excited scores of Puerto Rican undergraduate scholars from Sagrado for science careers through their participation in her pioneering work on the San Juan Estuary.

This project creates a replicable, national model for interdisciplinary education that stimulates a passion for STEM careers among nontraditional undergraduate scholars at community colleges and minority serving institutions. It also has well-developed dissemination mechanisms reaching a national community of STEM faculty from these institutions. Our MWRA-funded project engages nontraditional scholars in interdisciplinary research that will be useful in studying, monitoring, restoring and sustaining an estuarial ecosystem that is critical to Puerto Rico and pertinent to other urban waterways worldwide. Importantly, our submersible-based research immerses our scholars in early and extensive research experiences at the scientific realms where the biological sciences and marine engineering intersect. The integration of submersible technology into our ongoing research on the Charles River and San Juan Estuary significantly enhances the scientific education of participating scholars in both depth and breadth. The MassBay scholars supported under this Award were:

1. Elias Gilkes (Major: Biotechnology). Mr. Gilkes conducted the culturing of algae collected from the Charles River and San Juan Estuary. He also designed a self-contained *in vitro* system for the large scale culturing of algae in semi-dry conditions. Mr. Gilkes will attend Brandeis University in the Fall as a Biology major;

2. Carolyn Lankron (Major: Biotechnology, Forensic DNA Science). Ms. Lankron's research contributions and scholastic recognition is described above In Section IV," Methodology", and her scholastic recognition stemming from this project below in Section VII, "Notable Achievements and Awards". She will attend MIT as a Biology major in Fall 2013;

3. Geoffrey Reimann (Major: Engineering). Mr. Reimann oversaw the design changes described above for RUSS-2;

4. Kimberly Ramos (Major: Biotechnology), Ms. Ramos is involved in the large-scale production of algae;

5- Alberto Velez (Graduate: Biotechnology, 2001). Mr. Velez designed the RUSS prototype and played a prominent role in the redesign of RUSS-2. He is a 2002 graduate of MassBay's Biotechnology Program and was selected as a recipient of the Barry M. Goldwater Scholarship in the same year. Mr. Velez is Facilities Manager at SBH Scientific in Natick, MA. Like many alumnae of the Biotechnology Program Mr. Velez plays an active role in its research efforts and the mentoring of its students.

### **Notable Achievements and Awards**

1-On March 30, 2013 the Goldwater Foundation released its 2013 Awardees of the Barry M. Goldwater Scholarship, this country's highest undergraduate science award.

See "Massachusetts" at: <http://www.act.org/goldwater/sch-2013.html>

Carolyn Lankron, Biotechnology (Forensic DNA Science) whose project on the genetic basis of water-borne insect host/pathogen interaction was supported, in part, by the WRIP grant was one of the winners. Of importance, Carolyn was the only Goldwater Awardee among the national cohort recipients from a community college. Carolyn is the 19th Goldwater Awardee from MassBay's Biotechnology Program since its inception in 1993.

A newspaper article on Carolyn sums up the prestige she has brought to this WRIP award and program in general. <http://www.metrowestdailynews.com/news/education/x1431009363/MassBay-Biotech-student-wins-Goldwater-Scholarship>

Carolyn will be attending MIT in Fall 2013.

### **Follow-on Funding**

Funding Agency: National Science Foundation

Grant Program: "The MassBay Scholarship for Science, Technology, Engineering and Math (MSTEM) Program,"

Grant Title: MassBay Science Scholars Program

Institution: MassBay Community College

Award Period: 6/1/2012-5/31/17

Award Amount: \$347,000

Cognizant Officer: Dr. Joyce B. Evans ([jevans@nsf.gov](mailto:jevans@nsf.gov))

This 5-year Award allows us to provide full scholarships to 10, Second-year MassBay Community College STEM Scholars who have terminal degree goals in the basic sciences.

### **Publications and Conference Presentations:**

*Development of a "Robotic Underwater Sampling and Surveillance (RUSS)" for the study of Urban Waterways.* Geoffrey Reinman\*, William Bishop\*, and Lindsay Grumbach



Department of Engineering\* and the Department of Biotechnology^, MassBay Community College. Northeastern Science, Technology, Engineering, and Mathematics Talent Expansion (STEP) Conference. April 16, 2013.

*Development of a “Robotic Underwater Sampling and Surveillance (RUSS)” for the study of Urban Waterways.* Geoffrey Reinman\*, William Bishop\*, and Lindsay Grumbach^. Department of Engineering\* and the Department of Biotechnology^, MassBay Community College. Polytechnic Summit, Boston, MA. June 5, 2013.

#### **6. Biopolymer Sorbents for Tungsten Removal (USGS 2012MA346B)**

**Primary Principal Investigator:** Jessica Schiffman, University of Massachusetts Chemical Engineering

**Start Date:** 3/1/2012

**End Date:** 2/28/2013

**Reporting Period:** March 1, 2012 – February 28, 2013

**Funding Source:** USGS (104B)

**Research Category:** Engineering

**Focus Categories:** Treatment, Groundwater, Toxic Substances

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

Since 1999, eighty-eight million “green” tungsten-based bullets have been manufactured to replace the lead-based bullets, which were contaminating Cape Cod’s water supplies. Unfortunately, the inertness of tungsten came into question when it was detected in Massachusetts Military Reservation groundwater. Recent studies support that under certain pH conditions, tungsten will dissolve and leach into underlying aquifers. Tungsten has since been declared an emerging contaminant by the Environmental Protection Agency and the Department of Defense. Thus, our research objective is to develop environmentally benign sorbents capable of irreversibly binding and removing tungsten from our water supplies.

#### **Methodology:**

1. Three molecular weights of chitosans will be characterized using nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy (FTIR), rheology, and for their processability.
2. Sorbents will be made from the most desirable molecular weight of chitosan (identified from Methodology #1). Novel nanostructures including nanoparticles, gels, and films will be synthesized via a combination of solution chemistry, casting, and/or spin-coating.
3. We will characterize the minimum time/temperature required to crosslink the sorbents using two organic agents. Crosslinking will be confirmed by FTIR, visual inspection, and exposing the sorbents to various pHs.

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

1. From characterizing the low, medium, and high molecular weight chitosan it was determined that for our applications the low molecular weight was the best source material and yielded the most reproducible results.
2. We developed processes to fabricate chitosan-based sorbents in numerous modalities: nanoparticles, ultra-thin films, cast-films, nanofiber mats, and hydrogels.
3. Analysis determined the minimum crosslinking time required to create chemically robust sorbents using the organic crosslinking agent, glutaraldehyde. It was determined that cinnamaldehyde is not an efficient crosslinking agent for chitosan films cast from acidic solutions.

From the support provided to us we have established protocols to fabricate a variety of nano- to macro- structured “green” chitosan-based sorbents. From chitosan screening we anticipate these materials to have a high capacity for tungsten removal as will be concluded in future investigations.

**Student Support:**

Number of students supported by grant or matching funds, the degree they are pursuing, and their major.

1. David P. Gamliel, B.S. 2013, Chemical Engineering
2. Annuli N. Princess Okoye, B.S. 2014 (expected), Double Major: Chemical Engineering & Environmental Science
3. Elena P. Pandres, B.S. 2014 (expected), Chemical Engineering
4. Nathaniel Eagan B.S. 2014 (expected), Chemical Engineering

**Notable Achievements and Awards:**

From this project, four undergraduates have gained first-hand lab experience that has enabled them to receive impressive fellowships, awards, and acceptance into summer research programs/graduate school. All four students have been accepted to NSF or DOE sponsored summer research experience engineering materials for water purification or energy generation. Posters prepared on data gathered from this grant received 1<sup>st</sup> and 3<sup>rd</sup> place in the AIChE Regional Student Conference in April 2013.

**Follow-on Funding:**

UMass Amherst Commonwealth Honors College, Honors Research Assistant Fellowship (\$1000 for three undergraduates: Total: \$3000)

**Publications:**

- Rieger, K.A., Birch, N.P., Eagan, N., Schiffman, J.D., “Green Engineering of Antimicrobial Nanofiber Mats” The Fiber Society 2012 Fall Meeting Rediscovering Fibers in the 21st Century, Boston, MA. Full Proceeding.
- Rieger, K.A., Eagan, N.M., Schiffman, J.D., “Nanostructured Chitosan-Cinnamaldehyde Materials Inactivate Microbes” poster presented at the AIChE Northeast Regional Student Conference. April 2013, Amherst, MA.
- Birch, N.P., Pandres, E.P., Schiffman, J.D., “Chitosan:Pectin assemblies: Engineering green nanoparticles and hydrogels” poster presented at the AIChE Northeast Regional Student Conference. April 2013, Amherst, MA.
- Okoye, A.N., Gamliel, D.P., Schiffman, J.D., “Fabricating chemically robust chitosan films for water purification” poster presented at the AIChE Northeast Regional Student Conference. April 2013, Amherst, MA.
- Birch, N.P., Pandres, E.P., Schiffman, J.D., “Chitosan:Pectin assemblies: Engineering green nanoparticles and hydrogels” poster presented at the Tufts University 4th Annual Water: Systems, Science and Society (WSSS) Interdisciplinary Water Symposium; Feeding Ourselves Thirsty: The Future of Water and Food Production. April 2013, Medford, MA.
- Rieger, K.A., Eagan, N.M., Schiffman, J.D., “Nanostructured Chitosan-Cinnamaldehyde Materials Inactivate Microbes” poster presented at the Tufts University 4th Annual Water: Systems, Science and Society (WSSS) Interdisciplinary Water Symposium; Feeding Ourselves Thirsty: The Future of Water and Food Production. April 2013, Medford, MA.
- Okoye, A.N., Gamliel, D.P., Schiffman, J.D., “Fabricating chemically robust chitosan films for water purification” poster presented at the ISPE Student Poster Competition, May 2012, Worcester, MA.
- Okoye, A.N., Gamliel, D.P., Schiffman, J.D., “Fabricating chemically robust chitosan films for water purification” poster presented at the Tufts University 3rd Annual Water: Systems, Science and

**7. Elucidating the impact of upgrading wastewater treatment for nitrogen removal on eutrophication and toxic algal bloom in Long Island Sound (USGS- 2012MA347B)**

**Principal Investigator:** Chul Park, University of Massachusetts Civil & Environmental Engineering

**Start Date:** March 1, 2012

**End Date:** February 28, 2013

**Reporting Period:** March 1, 2012 – February 28, 2013

**Funding Source:** USGS (104B)

**Research Category:** Water Quality

**Focus Categories:** Nutrients, Wastewater, Treatment

**Problem and Research Objectives:**

Long Island Sound (LIS), like many other estuarial and coastal areas in the U.S., has experienced excessive algal blooms and subsequent hypoxia problems each summer. To improve the conditions of LIS, stringent N permits were placed on wastewater effluents discharged to LIS (USEPA, 2011). To comply with the new regulatory permit, the affected wastewater treatment plants (WWTPs) had to upgrade their main treatment systems to biological nutrient removal (BNR) processes, which have resulted in spending more than \$1 billion over the last two decades (O'Shea and Brosnan, 2000). Despite these efforts, it has been reported that the LIS area affected by hypoxia has actually expanded in recent years (O'Shea and Brosnan 2000; Stelloh, 2007).

The objective of this research was to quantify and evaluate the true impact of upgrading WWTP for N removal (i.e., from a conventional activated sludge system to biological nutrient removal processes) on the algal blooms in Long Island Sound.

**Methodology:**

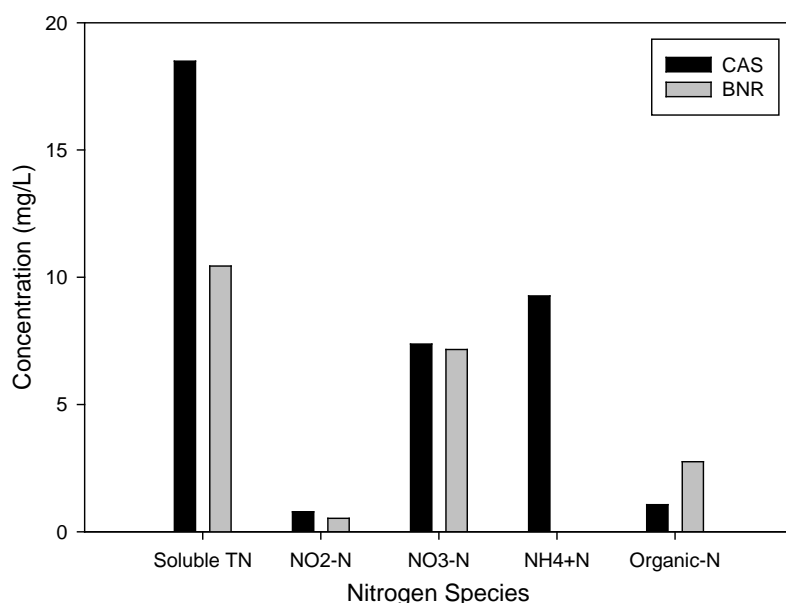
The current research has involved two main study components: operation and study of bench-scale activated sludge systems, and conducting bioassay on effluents using Long Island Sound water. For a lab reactor study, we operated one system in a conventional activated sludge (CAS) process and the other in a biological nutrient removal (BNR) process, both of which were fed the same influent wastewater. This approach was necessary because in this way we could generate effluents with different levels of N from the same source of wastewater (i.e., CAS vs. BNR). This further means that we could control the effect of different influents on the bioassay, which was not feasible for our earlier field bioassay study (Park et al., under review). During the period of the current research the Amherst WWTP underwent retrofitting to BNR processes to comply with a new N permit implemented in fall 2012. This was a great opportunity for our research because we had conducted the bioassay on the Amherst effluents multiple times when the plant was operated in CAS. Consequently, the comparison of recent and old Amherst effluents and subsequent bioassay data were expected to enable us to examine the effect of upgrading a wastewater treatment system to BNR on algal blooms in LIS in a field scale.

The laboratory CAS and BNR reactors were operated in sequencing batch reactors (SBRs) feeding on the primary effluent from the Amherst WWTP. The CAS system was operated in 6 days of SRT and only aerobic condition was available for wastewater treatment. In contrast, the BNR system had about 18 days of SRT with repeating anoxic and aerobic conditions to support nitrification and denitrification. Multiple bioassay experiments were conducted on the lab effluents and field effluents from the Amherst WWTP following the method, described in Park et al. (under review), with slight modification. Briefly, bioassay was performed by incubating 0.5 L of both filtered (0.45 µm) and unfiltered effluents

with 1.5 L of LIS water. Algal blooms were measured by increase in total COD and total suspended solids. Soluble N concentrations were measured at various points along the incubation period by ion chromatography (IC) and total organic carbon/total nitrogen (TOC/TN) analyzer.

#### Principal Findings and Significance:

Figure 1 shows concentrations and composition of N in effluents from lab-scale CAS and BNR reactors. As expected, CAS effluent had higher soluble total N (TN) (18.5 mg/L) with a lower portion of organic N (1.1 mg/L, 5.8%), while the BNR effluent had lower soluble TN (10.4 mg/L) with greater nitrate-N (7.2 mg/L, 68.6%) and organic N (2.8 mg/L, 26.4%). Observing higher concentration and proportion of organic N in BNR effluents is consistent with our earlier study (Westgate and Park, 2010) that showed that BNR effluents contained greater proportion and diversity of organic N (in the form of proteins and enzymes) than CAS effluents, reflecting more complex microbial processes occurring in the BNR process.

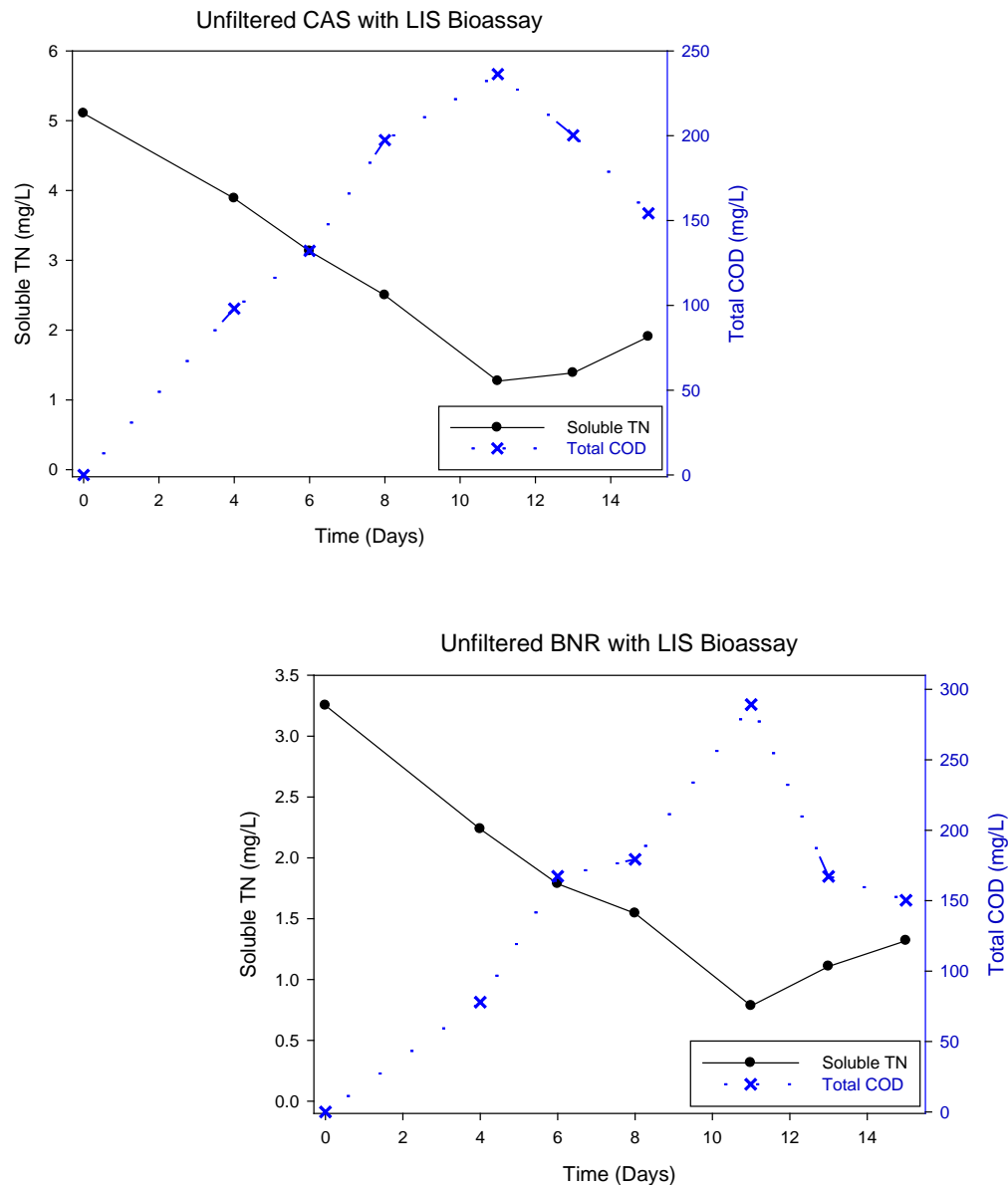


**Figure 1. Concentration of nitrogen species in lab-scale CAS and BNR effluents**

Figure 2 shows the growth of COD and consumption of soluble TN during the laboratory bioassays. The data clearly show that as soluble TN decreased, total COD increased, indicating that algae consumed available nitrogen for their growth. Table 1 presents the maximum COD yield data for bioassay sets with both filtered and unfiltered effluents. Regardless of filtration involved, BNR bioassays led to about 2 times greater yield than CAS bioassays. It is worth noting that not only COD yields (based on N consumption) but the total amount of COD generation was also higher for the BNR bioassay in spite of much lower N available in that bioassay. These results are consistent with our earlier study (Park et al., under review) relying on the field effluent sampling from different WWTPs and subsequent bioassays, which indicates that effluents from BNR process are more productive for algal blooms in the estuarial receiving water.

**Table 1. Maximum COD growth yields in bioassays on lab-scale CAS and BNR effluents (Unit = mg total COD generated/mg soluble TN consumed)**

	CAS	BNR
Unfiltered effluent	62	117
Filtered effluent	74	126



**Figure 2. Changes in total COD and soluble total nitrogen during the bioassay. One part of unfiltered CAS or BNR effluent was incubated with three parts of Long Island Sound water.**

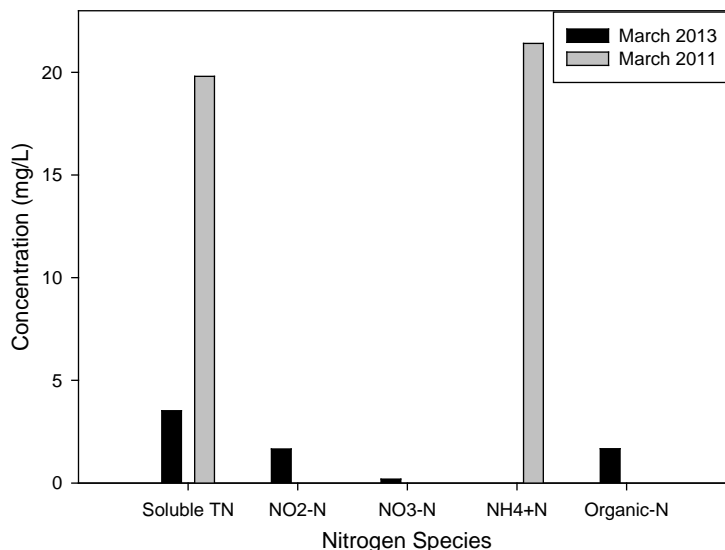
Figure 3 shows that concentration and composition of N in effluents from the Amherst WWTP collected in March 2011 (earlier study) and March 2013 (current research). The 2011 effluent set had much higher soluble TN (19.8 mg/L), because the facility was operated in CAS, while the 2013 effluent showed much lower soluble TN (3.5 mg/L) with high organic N (1.7 mg/L, 47.5%). Table 2 shows a

comparison of maximum COD growth yield between the Amherst effluent bioassays conducted in 2011 and 2013. The 2013 Amherst BNR effluent bioassay led to substantially greater COD yield compared to its old value and even lab-BNR effluent bioassay.

**Table 2. Maximum COD growth yields in bioassays on full-scale Amherst WWTP effluents (Unit = mg total COD generated/mg soluble TN consumed)**

March 2011 (CAS)	March 2013 (BNR)
<b>31</b>	<b>414</b>

In 2011, one part of unfiltered Amherst effluent was incubated with one part of Long Island Sound water (i.e., two time dilution) (Park et al., under review). In 2013, one part of unfiltered Amherst effluent was incubated with three parts of Long Island Sound water (i.e., four time dilution). See Figure 3 for concentration of N values in these two effluents.



**Figure 3. Concentration of nitrogen species from al full-scale Amherst Wastewater Treatment Plant in March 2011 and March 2013. In 2011, the plant was operated in CAS while the plant is currently operated in BNR.**

The importance of this study is that we directly evaluated the effect of changing upstream wastewater treatment processes (i.e., CAS to BNR) on algal blooms in Long Island Sound water. It was found that incubation of low N-laden BNR effluents from both bench and field-scale systems actually brought higher algal growth than did the CAS effluents. These results indicate that reduction of N in wastewater effluents via BNR processes does not bring a positive effect on reducing algal blooms in the estuary. It is currently speculated that special types of organic N included in BNR effluents are responsible for this unexpectedly and undesirably high algal production despite much smaller quantity of N available in that effluent water. Further research is warranted to more carefully evaluate the impact of upgrading a WWTP to a BNR process on the impaired receiving estuary and coastal areas.

#### **Student Support**

Heonseop Eom, PhD student in the Department of Civil and Environmental Engineering, University of Massachusetts Amherst.

### **Notable Achievements and Awards**

Dr. Park presented the study at US EPA Region 1 Science Council.

### **Follow-on Funding**

We have received the Research Grants from Springfield Water and Sewer Commission in two periods as follows:

- 1) June 2012 – May 2013  
The impact of upgrading municipal wastewater treatment facilities for nitrogen removal on Long Island Sound. Springfield Water and Sewer Commission, PI, \$25,000.
- 2) June 2013 – May 2014  
Evaluating the Effect of Upgrading Wastewater Treatment Systems to BNR Processes on Algal Blooms in Long Island Sound. Springfield Water and Sewer Commission, PI, \$20,000.

### **Publications and Conference Presentations:**

Park, C., Sheppard, D., Yu, D., Dolan, S., Eom, H., Brooks, J., and Borgatti, D. (under review) Comparative Assessment on the Influences of Effluents from Conventional Activated Sludge and Biological Nutrient Removal Processes on Algal Bloom in Long Island Sound. Water Research.

Park, C., Sheppard, D., Yu, D., Dolan, S., Eom, H., Brooks, J., and Borgatti, D. (2012) Laboratory investigation on the influences of field BNR and CAS effluents on algal bloom in Connecticut River and Long Island Sound. Oral presentation and conference proceeding, Water Environment Federation 85th Annual Technical Exhibition and Conference (WEFTEC 2012), New Orleans, LA.

### **8. Land Use, Land Cover and Stormwater Management in Massachusetts under Conditions of Climate Change: Modeling the Linkages (USGS- 2012MA352B)**

**Principal Investigator:** Elizabeth Brabec, UMass Landscape Architecture and Regional Planning

**Start Date:** 5/27/2012

**End Date:** 1/5/2013

**Reporting Period:** March 1, 2012 – February 28, 2013

**Funding Source:** USGS 104B

**Research Category:** Climate and Hydrologic Processes

**Focus Categories:** Management and Planning, Floods, Water Quantity

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

One of the major impacts of impervious surfaces associated with urbanization is the alteration of hydrologic cycles resulting in excessive runoff, lack of infiltration, and insufficient aquifer recharge (Booth and Jackson 1997; Brabec, Schulte, and Richards 2002). Consequently, human-induced flooding at various scales is a problem in urbanized areas, particularly under the increased intensity and duration of storm events promised by climate change in the New England Region (IPCC 2007; Rock et al. 2001). Past research has focused on the relationship between stormwater runoff and land cover associated with land use and density either at the overall watershed scale or at the neighborhood scale. Current research has focused on the connection between the effectiveness of stormwater best management practices (BMPs) such as porous paving, infiltration trenches, bioswales, and greenroofs, from the neighborhood scale to the watershed scale. However, this research has not been incorporated into models that test the interactions of three variables: (1) projected climate change precipitation levels, (2) varying development patterns (land use and land cover), and (3) flooding impacts. Therefore, further research is needed to understand the relationship between effective impervious area (EIA),

stormwater infiltration BMPs, and land use and land cover (Brabec 2009) under various storm events. In addition, understanding whether such relationships at the neighborhood scale can be effectively aggregated at a watershed scale is crucial for policy-making in implementing BMPs across scales.

#### **Nature, Scope, and Objectives of the Research:**

This study is part of a larger scope of research that aims to answer the following questions: (1) to what degree does installing stormwater BMPs at the neighborhood scale effectively reduce stormwater runoff and minimize flooding? (2) to what degree does the effectiveness of stormwater BMPs at the neighborhood scale translate to effects at the watershed scale? (3) what is the implication of additional non-structural stormwater BMPs such as land use planning and open space preservation on stormwater management at the watershed scale when limited structural stormwater BMPs exceed their capacity for infiltration and retention of stormwater onsite at the neighborhood scale?

#### **Methodology:**

This study employed SWAT (Soil and Water Assessment Tool) for hydrological modeling. The long-term flooding hazard index (HI) was constructed based on the SWAT output of streamflow and was defined as the probability of the number of days in 45 years when a stream flows overbank. Detention was identified as a key tool for mitigating flooding and was selected for testing in the model. Growth scenarios were developed under the Boston ULTRA-ex project. Four land use scenarios varying by distribution of projected population growth in the watershed were created and tested in the model. Climate change assessment was incorporated into SWAT modeling along with detention and land use scenarios input in separate procedures. First, climate sensitivity tests were conducted using 150 combinations (+0, 1, 2, 3, 4, 5°C in mean temperature; 0,  $\pm 10\%$ ,  $\pm 20\%$  in mean precipitation; 0,  $\pm 10\%$ ,  $\pm 20\%$  in precipitation variation) under current land use. The results from climate sensitivity tests were compared with GCM models projected for climate change trends in the Northeast region—increased precipitation and temperature. Therefore, only positive increase in precipitation and temperature up to 3°C were selected for testing the effect of detention with a total of 36 combinations (+0, 1, 2, 3°C in mean temperature; 0, +10%, +20% in mean precipitation; 0, +10%, +20% in precipitation variation). Finally, three climate change scenarios were selected to test urban growth scenarios. Low Impact climate change scenario was the combination of +3°C, +10% in mean precipitation and 0% in precipitation variation; Medium Impact climate change scenario was the combination of +2°C, +10% in mean precipitation and +10% in precipitation variation; High Impact climate change scenario was the combination of +1°C, +20% in mean precipitation and +20% in precipitation variation. Linear regression analysis was used to investigate the relationship between the percentage of land areas used for detention and the HI value under each climate sensitivity tests in current land use.

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

1. Under the definition of long-term flooding hazards defined in this study, the Charles River watershed was the most flood-prone at the lower basin with increasing flooding hazards toward upstream when the climate change impact becomes greater. Therefore, the long-term climate change-induced flooding hazards are more severe in the suburban communities of Boston.
2. Detention alone as a long-term climate change-induced flooding hazard mitigation strategy was effective (1% increase in detention may reduce HI by 0.06% to 0.28%) yet weak (R square ranges from 0.07 to 0.15). Therefore, it is critical to integrate multiple BMPs and incorporate land use planning into hazard mitigation.
3. Current Trend growth scenario encountered the most land change converting agricultural and forest lands to urban development and resulted in higher HI than other growth scenarios that were focusing on densifying or redeveloping currently built areas. In addition, the climate change impacts showed a greater variance in HI than the impacts from growth scenarios.



4. The findings suggested that suburban communities along the main stem of the Charles River watershed would be exposed to a greater probability of long term climate change-induced flooding hazards. Climate change adaptation is critical since the impacts from climate change are greater than land use impacts on streamflow. Finally, green infrastructure incorporating multiple structural and non-structural BMPs plays an important role in serving as flooding mitigation and climate change adaptation strategy.

#### **Student Support**

Chingwen Cheng, PhD expected, August 2013

#### **Notable Achievements and Awards**

Chingwen Cheng was among 20 PhD students selected to an international workshop on social vulnerability and risk reduction organized by the United Nations University Institute for Environment and Human Security (UNU-EHS) and funded by the Munich Re Foundation (MRF) in Germany from July 1 to 7 in 2012. The name of the workshop was “Summer Academy on Social Vulnerability: *From Social Vulnerability to Resilience: Measuring Progress toward Disaster Risk Reduction.*” The chair of the workshop was Professor Susan Cutter at the South Carolina University.

#### **Publications and Conference Presentations:**

- Cheng, C. 2013. Social Vulnerability, Green Infrastructure, Urbanization and Climate Change-Induced Flooding: A Risk Assessment for the Charles River Watershed, Massachusetts, USA.
- Cheng, C., E. Brabec, R. L. Ryan, Y. E. Yang, C. Nicolson, and P. S. Warren. 2013. Future Flooding Risk Assessment under Growth Scenarios and Climate Change Impacts for the Charles River Watershed in the Boston Metropolitan Area. *Proceedings of Joint Association of European Schools of Planning (AESOP) and The Association of Collegiate Schools of Planning (ACSP) Annual Congress*. July 15-19, 2013, Dublin, Ireland (in preparation).
- Cheng, C., E. Brabec, Y. E. Yang, and R. L. Ryan. 2013. Effects of detention for flooding mitigation under climate change scenarios: Implications for landscape planning in the Charles River Watershed, Massachusetts, USA. *Fábos Conference on Landscape and Greenway Planning 2013*. University of Massachusetts Amherst. April 12-13, 2013, Amherst, Massachusetts.
- Cheng, C., E. Brabec, Y. E. Yang, and R. L. Ryan. 2013. Rethinking stormwater management in a changing world: Effects of detention for flooding mitigation under climate change scenarios in the Charles River Watershed. *Council of Educators in Landscape Architecture (CELA) Annual Conference*, March 27-30, Austin, Texas.
- Cheng, C., E. Brabec, R. L. Ryan, P. Warren, and C. Nicolson. 2012. Green infrastructure planning for climate change adaptation: Integrate social vulnerability flooding risk assessment for the Boston Metropolitan Area future scenarios. *The Association of Collegiate Schools of Planning (ACSP) 53rd Annual Conference*. November 1-3, Cincinnati, Ohio.

#### **9. Modeling of Road Salt Contamination and Transport in Ground Water (USGS- 2012MA376B)**

**Principal Investigator:** Rudolph Hon, Boston College Earth and Environmental Sciences

**Start Date:** 3/1/2012

**End Date:** 2/28/2013

**Reporting Period:** March 1, 2012 – February 28, 2013

**Funding Source:** USGS 104B

**Research Category:** Water Quality

**Focus Categories:** Water Quantity, Non Point Pollution, Water Supply

**Problem and Research Objectives:**

Winter de-icing chemicals are undeniably beneficial by helping to mitigate the inherent transportation hazards during the snow and ice storm seasons. On the other hand these chemicals tend to accumulate in local aquifers leading to a gradual increase of Na and Cl in the impacted aquifer systems. The current effort under this program is to determine a set of realistic boundary conditions in an aquifer exposed to high road salt loading conditions and correlate the impact with increasing sodium and chloride concentrations in the public drinking water supply and in the local drainage system (aquatic life). The observed parameters will be used as inputs into a computer model to simulate the de-icing chemicals pathways between their sources and the discharge points along the local drainage systems. The study is carried out on the Old Pond Meadows aquifer in Norwell, Massachusetts.

**Methodology:**

For the purpose of monitoring we set up 5 separate sites: 3 for spatial monitoring and 2 for temporal long term monitoring. The spatial monitoring plan includes two 2-D vertical cross-sections and one 1-D track along a stream for baseflow discharge characterization. During this effort we collected a total of 170 representative water samples from 23 monitoring wells located near a public water supply pumping well for the Town of Norwell. All samples were analyzed by ion chromatography for ionic species and by Inductively Coupled Plasma Spectrometry for 15 metals.

Long term monitoring is achieved by installing AquaTroll 200 sensors in a cluster of 3 monitoring wells each reaching a different depth within the aquifer and by distributing 6 similar sensors at selected sites in the stream that is the principal drainage of the same aquifer. The sensors are deployed for long term (month to years) monitoring of temperature, water column depth, and specific conductance at 15 minute intervals. Specific conductance data were calibrated to yield concentrations of chlorides for monitoring dissolved levels of chloride de-icers.

**Principal Findings and Significance:**

To this date not all data have been yet fully evaluated and at this moment more data are still being acquired. However several important findings can be identified as critical to our understanding of how dissolved de-icers move inside an aquifer. Perhaps most revealing is the scale and extent of observed heterogeneities of dissolved de-icers within the aquifer due to preferential pathways in both the lateral and vertical directions. A better understanding of these pathways will help to better constrain our future effort to simulate de-icers migration paths and consequently to design better management practices of both the de-icer application rates and the preservation of drinking water resources for the future. A final report will be submitted to WRRRC in the Fall 2013.

**Student Support**

Jacob Anderson – M.Sc., Geoscience

Andrew Basler – B.Sc., Environmental Geoscience

**Publications and Conference Presentations:**

Anderson, Jacob (M.Sc. summer 2013): Geochemical Tracers of Road Salt Contamination in Surface Waters and Groundwater

Anderson, J., Hon, R., Dillon, P., Besancon, J., and McInnis, J.R., 2012. Assessment of vertical profiles of dissolved road salt in suburban aquifers of eastern Massachusetts; Geological Society of America Abstracts with Programs, Vol. 44, No. 7, p. 356

Anderson, J., Hon, R., Dillon, P., Besancon, J., and McInnis, J.R., 2012. Continuous monitoring of increasing road salt concentration in ground water in an active pumping field in Massachusetts; Geological Society of America Abstracts with Programs, Vol. 44, No. 7, p. 580

- Besancon, J., Hon, R., and Anderson, J. 2012. Comparison of impacts of winter de-icing chemicals in several glacial basins in eastern Massachusetts; Geological Society of America Abstracts with Programs, Vol. 44, No. 7, p. 580
- Anderson, J., Hon, R., Dillon, P., Besancon, J., and McInnis, J.R., 2013. Assessment of vertical profiles of dissolved road salt in suburban aquifers of eastern Massachusetts; Geological Society of America Abstracts with Programs. Vol. 45, No. 1, p.117
- Besancon, J. and Hon, R., 2013. Sodium chloride as an environmental tracer in a glacial aquifer system, eastern Massachusetts; Geological Society of America Abstracts with Programs. Vol. 45, No. 1, p.97
- Hon, R., Besancon, J. and Dillon, P., 2013. Future directions of research on road salt contamination in aquatic systems; Geological Society of America Abstracts with Programs. Vol. 45, No. 1, p.68

## **10. Acid Rain Monitoring Project**

**Principal Investigator:** Marie-Françoise Hatte, MA Water Resources Research Center, UMass Amherst

**Start Date:** January 1, 2013

**End Date:** June 30, 2013

**Reporting Period:** January 1, 2013– June 30, 2013

**Funding Source:** USGS (104B) and MassDEP

**Descriptors:** Acid Deposition; Surface Water Quality; Volunteer Monitoring

### **Problem and Research Objectives**

This report covers the period July 1, 2012 to June 30, 2013, the twelfth year of Phase IV of the Acid Rain Monitoring Project. Phase I began in 1983 when about one thousand citizen volunteers were recruited to collect and help analyze samples from nearly half the state's surface waters. In 1985, Phase II aimed to do the same for the rest of the streams and ponds<sup>3</sup> in Massachusetts. The third phase spanned the years 1986-1993 and concentrated on a subsample of streams and ponds to document the effects of acid deposition to surface waters in the state. Over 800 sites were followed in Phase III, with 300 citizen volunteers collecting samples and doing pH and ANC analyses. In 2001, the project was resumed on a smaller scale: about 60 volunteers are now involved to collect samples from approximately 150 sites, 26 of which are long-term sites with ion and color data dating back to Phase I. In the first years of Phase IV (2001-2003), 161 ponds were monitored for 3 years. Between Fall 2003 and Spring 2010, the project monitored 151 sites twice a year, mostly streams, except for the 26 long-term sites that are predominantly ponds. Since 2011, reduced funding eliminated our October sampling and monitoring now occurs in April only. In 2011, we also stopped monitoring some of the streams in order to add and revisit ponds that were monitored in 2001-2003. This year is the third year of monitoring for those added ponds.

### **Goals**

The goals of this project are to determine the overall trend of sensitivity to acidification in Massachusetts surface waters and whether the 1990 Clean Air Act Amendment has resulted in improved water quality.

### **Methods**

The sampling design was changed in 2011 to monitor both streams and ponds, and that design was continued in 2012 and 2013. In 2001-2003 mostly ponds were monitored. In Fall 2003 the sampling scheme switched to streams to evaluate their response to air pollution reductions. In 2011 the site list was modified to include both ponds and streams. Half of the streams monitored since 2003 were kept,

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<sup>3</sup> Note: The term stream in this report refers to lotic waters (from creeks to rivers) and the term ponds refers to lentic waters (lakes and ponds, but not marshes)

and half of the ponds monitored in 2001-2003 were added back. The streams that were removed were chosen randomly within each county. Ponds that were reinstated on the sampling list were chosen at random within those counties, by ease of accessibility, to replace the removed streams. Because those sites were not chosen with a preconceived plan, they can be considered picked at random.

One collection took place this year, on April 7, 2013.

Methods were unchanged from previous years: Volunteer collectors were contacted six weeks before the collection to confirm participation. Clean sample bottles were sent to them in the mail, along with sampling directions, a field sheet/chain of custody form, and directions including GPS coordinates and maps to the sampling sites. Volunteers collected a surface water sample at their sampling sites either from the bank or wading a short distance into the water body. They collected water one foot below the surface, upstream of their body, after rinsing their sample bottle three times with pond or stream water. If collecting by a bridge, they collected upstream of the bridge unless safety and access did not allow it. They filled in their field data sheet with date, time, and site code information, placed their samples on ice in a cooler and delivered the samples to their local laboratory right away. They were instructed to collect their samples as close to the lab analysis time as possible. In a few cases, samples were 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 were sent any needed supplies (sulfuric acid titrating cartridge, electrode, buffers), two quality control (QC) samples, aliquot containers for long-term site samples, and a lab sheet one week to ten days before the collection. They analyzed the first QC sample (an unknown) in the week prior to the collection and called in their results to the Statewide Coordinator. If QC results were not acceptable, the volunteer analyst discussed possible reasons with the Statewide Coordinator and made modifications until the QC sample analysis gave acceptable results. On collection day or the day after, volunteer labs analyzed the second QC sample before and after the regular samples, and reported the results on their lab sheet along with the regular samples. Analyses were done on their pH-meters with KCl-filled combination pH electrodes. Acid neutralizing capacity (ANC) was measured with a double end-point titration to pH 4.5 and 4.2. Most labs used a Hach digital titrator for the ANC determination, but some used traditional pipette titration equipment. Aliquots were taken from the 26 long-term sites to fill two 60mL bottles and one 50mL tube per site for later analysis of ions and color. These aliquots were kept refrigerated until retrieval by UMass staff.

Aliquots, empty bottles, and results were collected by the ARM Statewide Coordinator between one and three days after the collection. The Cape Cod National Seashore lab mailed those in, with aliquot samples refrigerated in a cooler with dry ice.

The Statewide Coordinator reviewed the QC results for all labs and flagged data for any lab results that did not pass Data Quality Objectives (within 0.3 units for pH and within 3mg/L for ANC). pH and ANC data were entered by one ARM staff and proofread by another. Data were entered in a MS excel spreadsheet and uploaded into the web-based database at <http://63.135.115.71/acidrainmonitoring/>. Data were also posted on the ARM web page at <http://wrrc.umass.edu/research/acid-rain-monitoring-project>. Note that ARM data is also available on the national CUAHSI database, via Hydro Desktop (<http://cuahsi.org/HIS.aspx>).

Water Resources Research Center's Elizabeth Finn managed the Environmental Analysis Lab (EAL) and provided the QC samples for pH and ANC to all of the volunteer labs. EAL also provided analysis for pH and ANC for samples from Hampshire and Franklin Counties, and color analysis for the long-term site

samples. New this year, the UMass Extension Soils Laboratory, under the direction of Dr. John Spargo, analyzed the samples from the long-term sites for cations, and University of New Hampshire's Water Quality Analysis Laboratory, under the direction of Jody Potter, analyzed the samples from the long-term sites for anions.

Aliquots for 25 long-term sites (one sample was accidentally emptied by the volunteer lab staff before taking aliquots for ion analyses) were analyzed for color on a spectrophotometer within one day; anions within one month on an Ion Chromatograph; and cations within two months on an ICP at the UMass Extension Soils Laboratory on the UMass Amherst campus. The data was sent via MS Excel spreadsheet to the Statewide Coordinator who uploaded it into the web-based database.

The Statewide Coordinator and the Project Principal Investigator plotted the data to check for data inconsistencies and gaps. They then analyzed the April data from 1983 through 2013, using the statistical software JMP (<http://www.jmp.com/software/>) to run bivariate analyses of pH, ANC, ions, and color against date. This yielded trends analyses with a fitted X Y line, using a 95% confidence interval.

## Results

1. There were 150 sites to be monitored, 77 ponds and 73 streams. Of those, 19 ponds and 7 streams are "long-term" sites that are sampled every year and analyzed for color and a suite of ions in addition to pH and ANC.
2. Sampling was completed for 147 sites (77 ponds and 70 streams) including 25 of our long-term sites.
3. The only quality control problem this year was the UMass Boston laboratory not passing our quality control samples. The data from those samples is considered to be unreliable and is therefore removed from the statistical analysis. We had valid pH and ANC data for 134 sites. One long term site sample was accidentally emptied before taking aliquots, resulting in valid data for only 25 sites for color and ions.
4. The network of volunteers was maintained and kept well informed on the condition of Massachusetts surface waters so that they would be able to participate effectively in the public debate. This was accomplished by e-mail and telephone communications, as well as through updates via an internet list-serv. 53 volunteers participated in this year's collection. Several new volunteer collectors were recruited to replace ill or retiring volunteers via several internet listservs and by word of mouth.  
There were 10 volunteer labs across the state, in addition to the EAL at UMass Amherst, in charge of pH and ANC analyses (Table 1).

**Table 1: Volunteer Laboratories**

Analyst Name	Affiliation	Town
Joseph Ciccotelli	Ipswich Water Treatment Dept	Ipswich
Nicole Henderson	UMass Boston Environmental Studies Program	Boston
Sherrie Sunter	MDC Quabbin Lab	Belchertown
Dave Bennett	Cushing Academy	Ashburnham
Holly Bayley	Cape Cod National Seashore	South Wellfleet
Robert Caron	Bristol Community College	Fall River

<b>Analyst Name</b>	<b>Affiliation</b>	<b>Town</b>
Bob Bentley	Analytical Balance Labs	Carver
David Christensen	Biology Dept. Wilson Hall WSC	Westfield
Jim Bonofiglio	City of Worcester Water Lab	Holden
Carmen DeFillippo	Pepperell Waste Water Treatment Plant	Pepperell
Beckie Finn, Brooke Andrew	University of Massachusetts Environmental Analysis Lab	Amherst

5. The ARM web site and searchable database were maintained and updated. 2013 pH, ANC, ions and color data that met data quality objectives were added to the web database via the uploading tool created in previous years. The database was evaluated for quality control and uploading errors were corrected. Note that our website is migrating to a new address ([www.wrrc.umass.edu](http://www.wrrc.umass.edu)).
6. The data collected was analyzed for trends in pH and ANC in April months (134 sites) and for color and ions (25 sites), using the JMP® Statistical Discovery Software (<http://www.jmp.com/software/>). Trend analyses (scatter plots, regression, and correlation) were run on pH, ANC, each ion, and color separately, predicting concentration vs. time.

## Data Analysis Results

### Trend analysis for pH and ANC

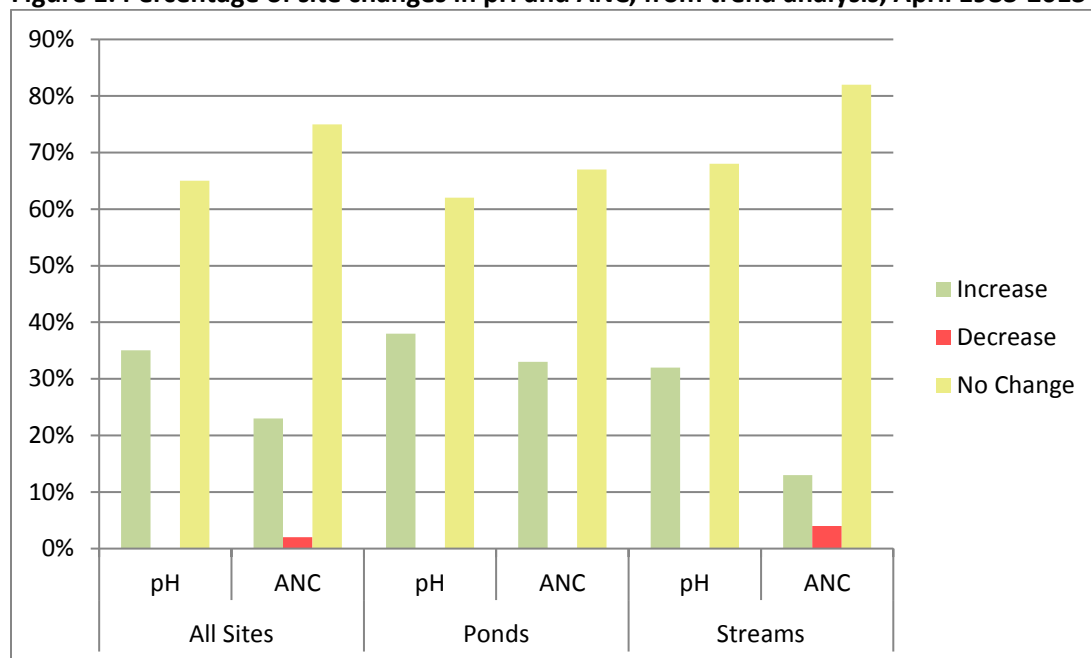
Table 2 displays the number of sites out of a maximum of 136 that show a significant change over time for pH or ANC. If the difference was not statistically significant ( $p > 0.05$ ), the sites are tabulated in the 'No Change' category.

**Table 2: Trend analysis results for pH and ANC, April 1983 – April 2013**

	<b>All Sites</b>		<b>Ponds</b>		<b>Streams</b>	
	<b>pH</b>	<b>ANC</b>	<b>pH</b>	<b>ANC</b>	<b>pH</b>	<b>ANC</b>
Increased	47	31	25	22	22	9
Decreased	0	3	0	0	0	3
No Change	87	100	41	44	46	56
Total	134	134	66	66	68	68

Those results are also graphed in Figure 1.

**Figure 1. Percentage of site changes in pH and ANC, from trend analysis, April 1983-2013**



This trend analysis indicates that for most sites, neither pH nor ANC changed significantly over time. However, for those sites that show a significant change, many more show an increase than a decrease in value: 35% of the sites saw an increase in pH and 23% had an increase in ANC. We again note a difference between ponds and streams. More ponds (38%) than streams (32%) saw an increase in pH, and for ANC the difference is very noticeable: 33% of ponds increased in ANC while only 13% of streams did, while no ponds decreased in ANC but 4% of streams did.

Now in our third year of monitoring both ponds and streams, we continue to see a positive trend in ponds, which seem to be improving a little more each year. Streams show a lesser improvement, particularly for ANC. This year for the first time in many years, we had a lingering snowpack and our sampling date of April 7 likely caught the snowmelt acid pulse that we try to document by sampling in early spring. It is possible that the acid pulse is more noticeable in streams than ponds due to the more rapid reaction of moving water to precipitation in streams than in ponds.

**Table 3: Comparison of percent of sites showing changes in pH and ANC, 2011-2013**

<b>2011</b>	<b>All Sites</b>		<b>Ponds</b>		<b>Streams</b>	
	<b>pH</b>	<b>ANC</b>	<b>pH</b>	<b>ANC</b>	<b>pH</b>	<b>ANC</b>
Increased	28%	19%	22%	17%	35%	22%
Decreased	2%	1%	1%	0%	3%	3%
No Change	70%	79%	76%	83%	62%	75%
<b>2012</b>	<b>All Sites</b>		<b>Ponds</b>		<b>Streams</b>	
	<b>pH</b>	<b>ANC</b>	<b>pH</b>	<b>ANC</b>	<b>pH</b>	<b>ANC</b>
Increased	29%	21%	28%	33%	34%	23%
Decreased	2%	2%	1%	0%	4%	3%
No Change	69%	78%	71%	67%	62%	75%
<b>2013</b>	<b>All Sites</b>		<b>Ponds</b>		<b>Streams</b>	
	<b>pH</b>	<b>ANC</b>	<b>pH</b>	<b>ANC</b>	<b>pH</b>	<b>ANC</b>
Increase	35%	23%	38%	33%	32%	13%
Decrease	0%	2%	0%	0%	0%	4%
No Change	65%	75%	62%	67%	68%	82%

**Ions and Color**

Trend analyses were run for the 25 long-term sites that were analyzed for thirteen ions and color.

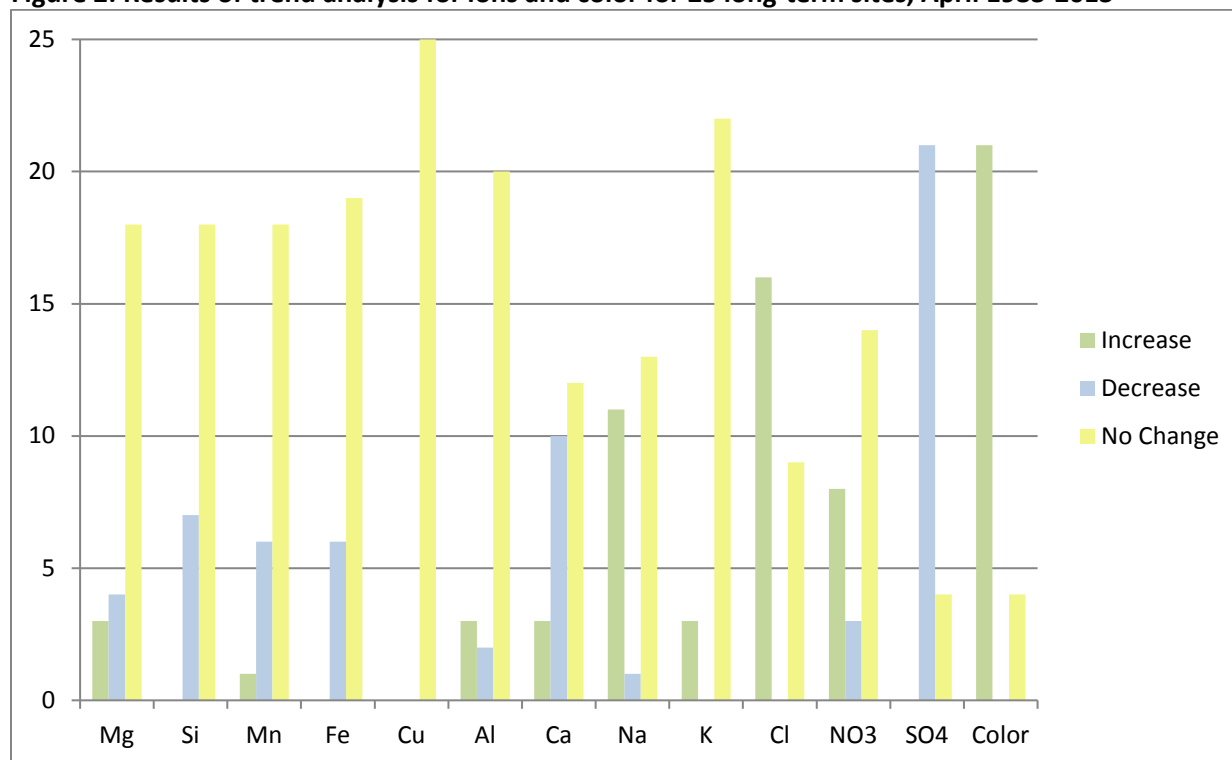
Table 4 and Figure 2 show the results of the trend analysis for all parameters.

**Table 4: Trend analysis results for ions and color April 1983 – April 2013**

	<b>Increase</b>	<b>Decrease</b>	<b>No Change</b>
<b>Mg</b>	3	4	18
<b>Si</b>	0	7	18
<b>Mn</b>	1	6	18
<b>Fe</b>	0	6	19
<b>Cu</b>	0	0	25
<b>Al</b>	3	2	20
<b>Ca</b>	3	10	12
<b>Na</b>	11	1	13
<b>K</b>	3	0	22
<b>Cl</b>	16	0	9
<b>NO3</b>	8	3	14
<b>SO4</b>	0	21	4
<b>Color</b>	21	0	4



**Figure 2: Results of trend analysis for ions and color for 25 long-term sites, April 1983-2013**



Results are similar to previous years, with most cations showing no significant change over the years, or if they do, the change is a decrease more often than an increase, except for Sodium where half the sites show an increase. This is probably tied to the increase of Chloride, due to road salting practices in Massachusetts. A minor change this year is some increase in Aluminum and Potassium. We continue to see a very significant downward trend in Sulfate. More sites now show an increase in nitrate, so we reiterate the observation that now that sulfate emissions have been curbed, attention should be paid to decreasing NOx emissions

### Discussion

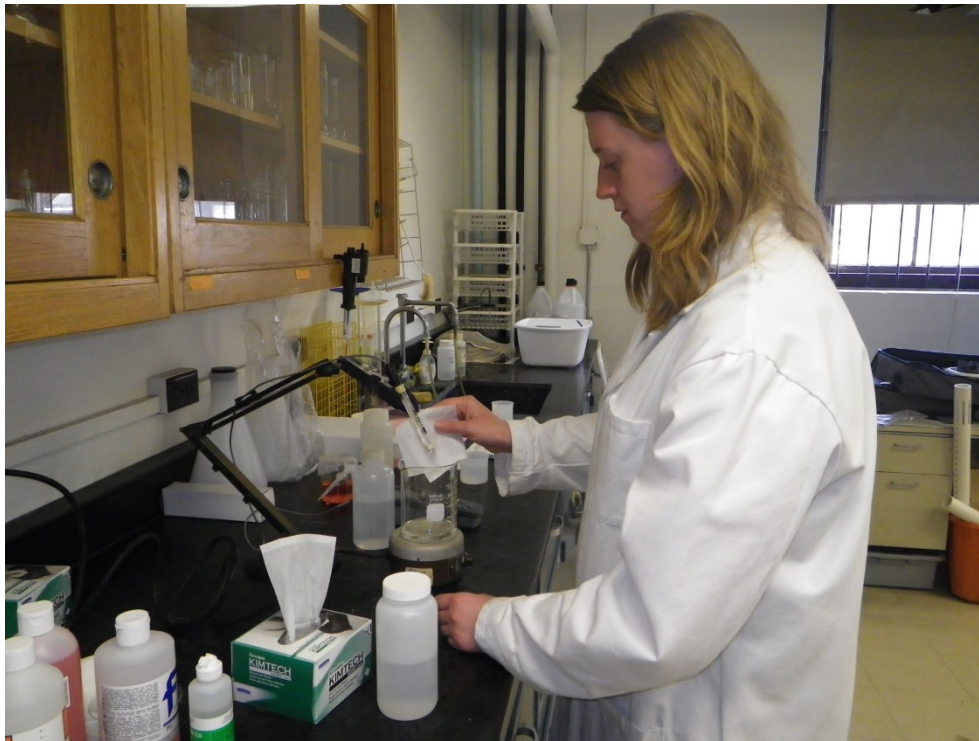
This year we sampled immediately after a major snowmelt event, when we would expect a pulse of acidity to reach our surface waters. While pH did not seem affected overall, stream alkalinity decreased and could be a result of increased acidity in melt water “consuming” acid neutralizing capacity. Likewise, more sites showed an increase in nitrate this year than in the past. A note of caution: we switched to new laboratories for ions this year. Sulfate results are much lower than previous years, and it is possible that the analytical methods differ enough between the two laboratories that it would explain this marked decrease. We will endeavor to continue using these two laboratories in the future to confirm current trends.

### Acknowledgements

Thank you to all of the project’s volunteers who make this project possible by collecting samples all over the state under any weather conditions, and who spend many hours in the lab analyzing samples. A special thought to our first organizing volunteer Leon Ogrodnik, a key figure in the early years of the Acid Rain Monitoring Project, who passed away in May of this year.

### Student Support

1 BS, Natural Resources Conservation



Brooke Andrew, WRRC student employee, analyzing pH and ANC at the Environmental Analysis Laboratory at the University of Massachusetts

## 11. 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, 2012 – June 30, 2013

**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

### Research Objectives

The Upper Blackstone Water Pollution Abatement District (UBWPAD, the District) sponsors a water-quality monitoring program to track river quality in the Blackstone River and to study the impacts of the wastewater treatment plant on the river. In 2012, UMass conducted a water quality-monitoring program along the main stem of the Blackstone River. The objective of the program was to collect data to continue to assess the response of the river to reduced nutrient concentrations in the District wastewater treatment plant effluent.

The District provides wastewater treatment to the City of Worcester and surrounding communities including Auburn, Cherry Valley Sewer District, Holden, Millbury, Rutland, and West Boylston. The District's advanced biological nutrient removal (BNR) process, constructed as part of a \$180 million facility upgrade, produces a high quality effluent that has helped to improve the water quality of the Blackstone River. The BNR process at the facility reduces the amount of phosphorus in the District's discharge; excess phosphorus can contribute to excessive growth of algae in the river. The treatment

process also provides nitrogen removal. Too much nitrogen can stimulate excessive algae growth in Narragansett Bay, the water body into which the Blackstone River ultimately flows.

Since the BNR process became operational in late 2009, there have been dramatic decreases in the amounts of phosphorus and nitrogen that enter the Blackstone River and Narragansett Bay from the District treatment facility. Calendar year 2012 data show that phosphorus has been reduced by 78% compared to previous levels (2006-2008) and nitrogen has been reduced by 62% (Figure 1). Additionally, the total nitrogen load to Narragansett Bay from the District and the seven largest wastewater treatment facilities (WWTFs) in Rhode Island has also been significantly reduced (Figure 2).

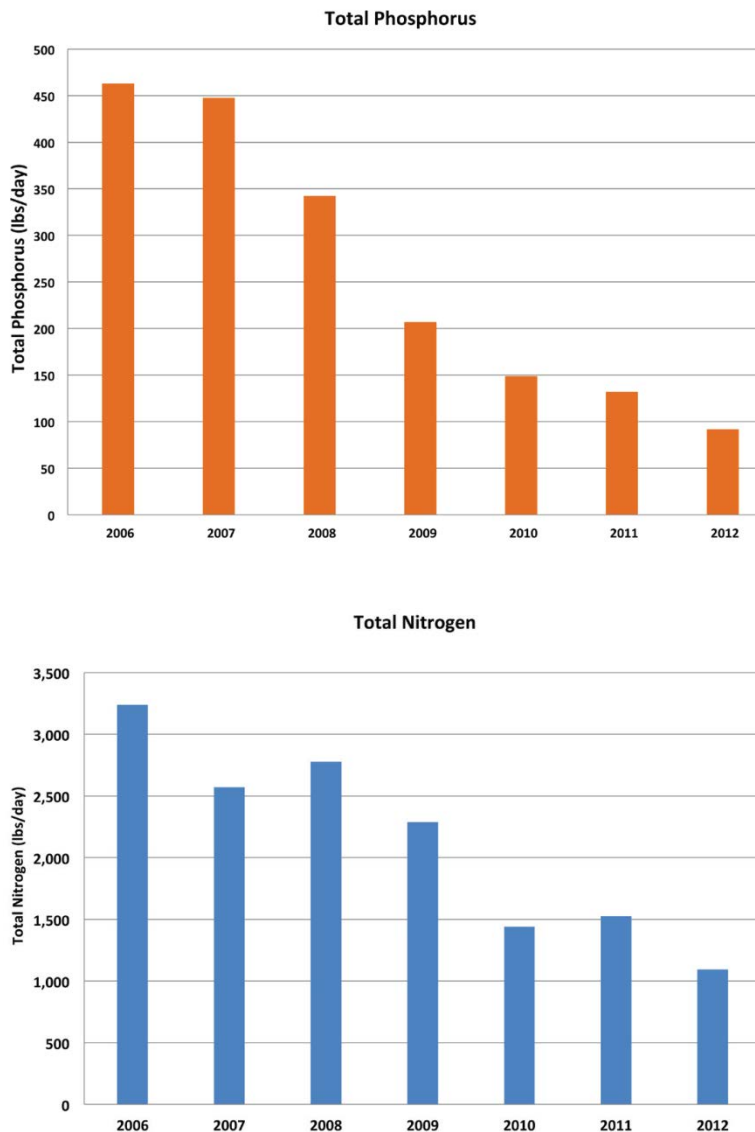


Figure 1. Effluent loading of Total Phosphorus and Total Nitrogen have been reduced by 78% and 62% from previous levels (2006-2008), respectively.

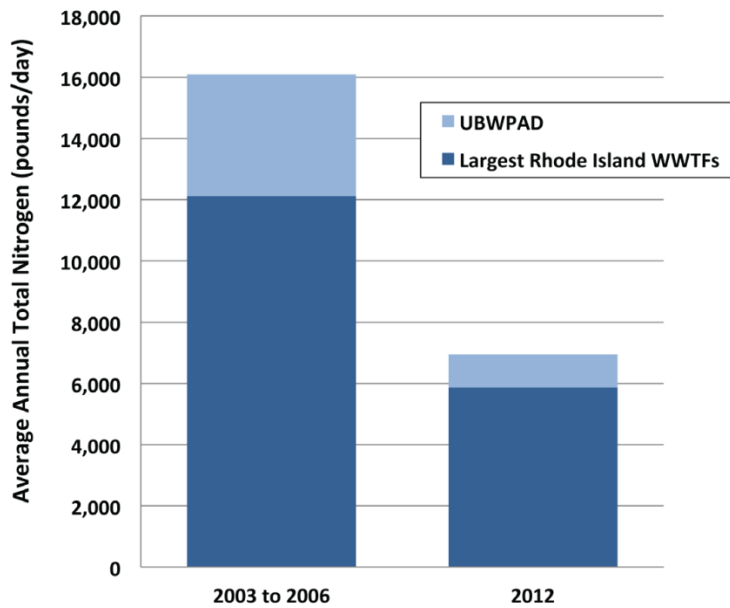


Figure 2. Over the past six years, the Total Nitrogen load to Narragansett Bay from the largest WWTFs has been reduced by more than half.

### 2012 Sampling program Overview

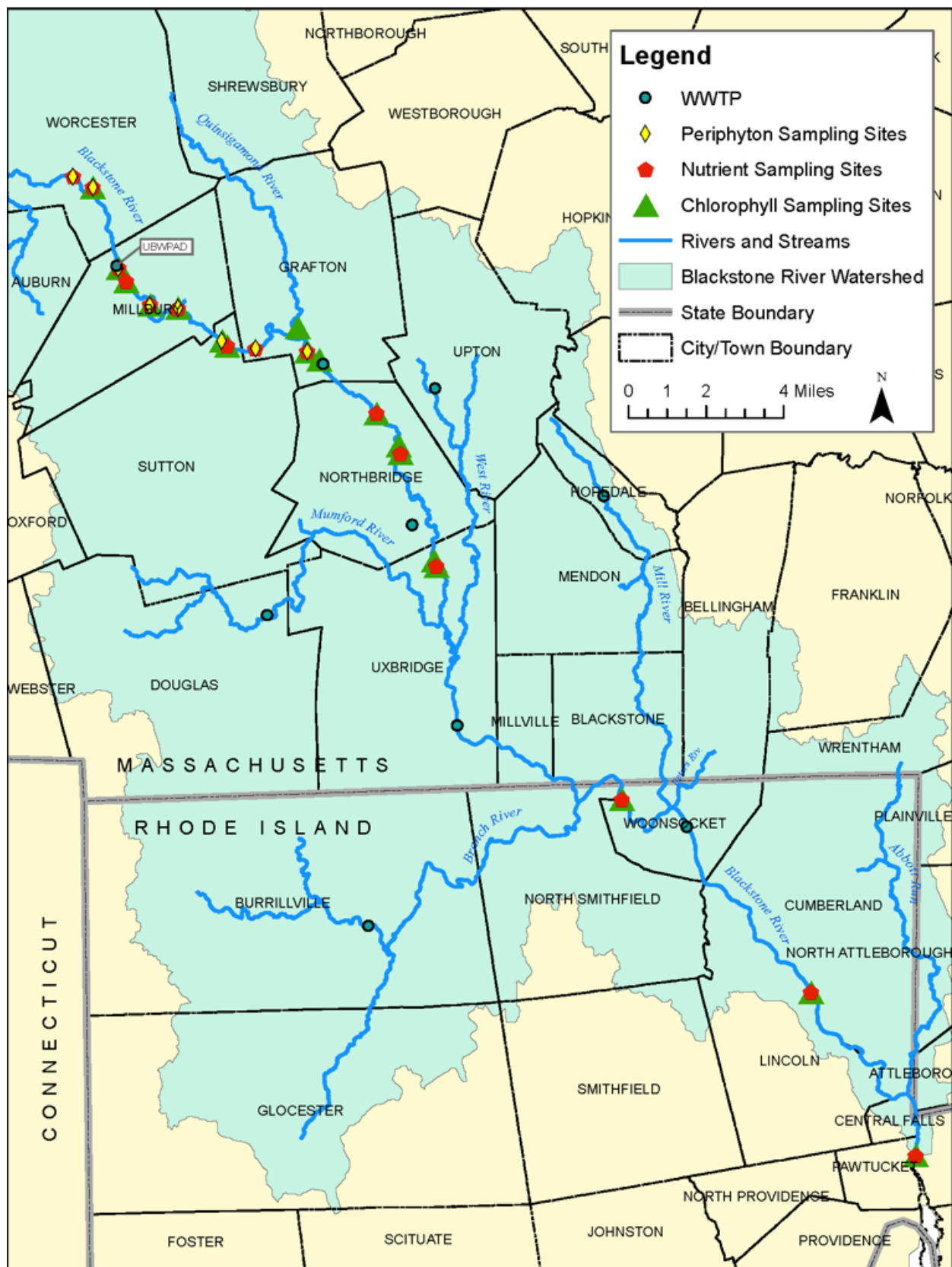
In 2012, sampling was conducted from April through November at multiple Blackstone River main stem sites located in Massachusetts and Rhode Island, as shown on the accompanying map. The study included monthly water quality sampling for nutrients, bi-weekly monitoring for chlorophyll-a, and a visual assessment of algal blooms and rooted plants, or macrophyte, growth in the river. The three Rhode Island sites were co-sampled with the Narragansett Bay Commission's (NBC) ongoing monitoring program ([snapshot.narrabay.com](http://snapshot.narrabay.com)). The 2012 data were compared to historical river data collected as part of the District's study and other sampling programs.

In 2012, the District added periphyton sampling surveys to its monitoring program. Periphyton are algae that are attached to submerged rock and river bottom surfaces. While some periphyton growth is to be expected in natural water systems, and can form a part of a healthy ecosystem, too much periphyton growth is not desirable for aesthetic reasons and because it could be an indication of river impairment. The objective of the 2012 periphyton survey was to provide more comprehensive monitoring of river biological conditions. The 2012 periphyton surveys added to a very limited set of data collected by Massachusetts Department of Environmental Protection (MassDEP) in 2008, and will serve as a basis for future periphyton surveys and monitoring in the river.

### 2012 River Sampling Results

In 2012, Blackstone River streamflow was lower than historical average conditions, driven in large part by the relatively mild and dry 2011-2012 winter, followed by a dry spring. Precipitation in July 2012 was also below average, contributing to the low streamflow conditions. Figure 3 compares 2012 and historical mean daily streamflow in the Blackstone River at the United States Geological Survey (USGS) gage in Woonsocket, RI.

During the relatively dry 2012 summer, stormwater run-off impacts on river water quality were expected to be reduced because of reduced rainfall, and impacts from wastewater treatment facilities were expected to potentially be more pronounced because of less dilution by high river flows.



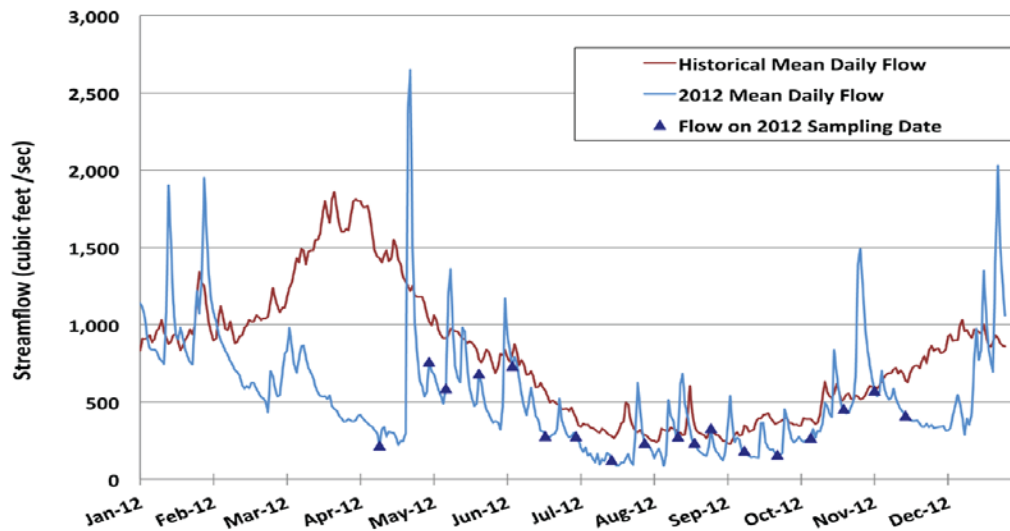


Figure 3. 2012 Mean Daily Streamflows at USGS Blackstone River Gage, Woonsocket, RI were lower than historical stream flows.

### Phosphorous and Nitrogen

The 2012 river sampling results were compared with historical data collected during similar conditions prior to 2009 to evaluate the changes in river water quality following the District's facility upgrades. The historical data set was comprised of data collected between 1997 and 2008 by the District, Massachusetts Department of Environmental Protection, the United States Geological Survey (USGS), the Army Corps of Engineers (ACOE), Rhode Island Department of Environmental Management (RIDEM) and others. The comparison shows that phosphorous and nitrogen loads in the river were 66% and 38% lower, respectively, in 2012 than in previous dry years (Figure 4).

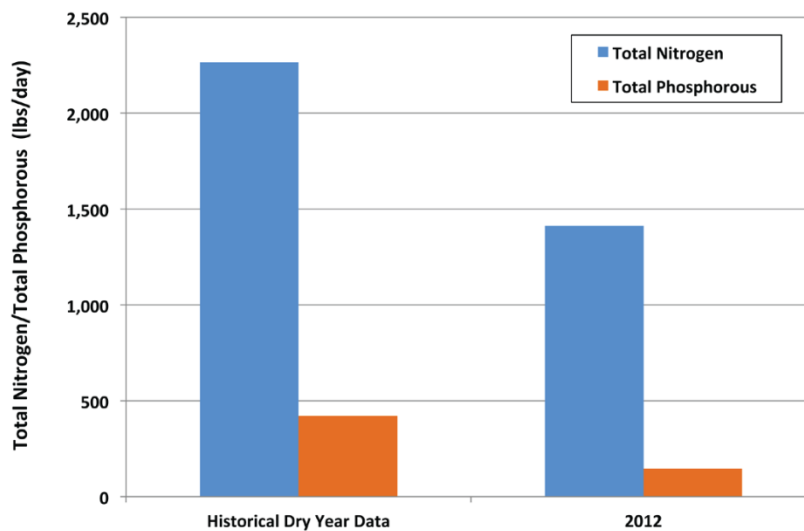


Figure 4. Total Phosphorous and Total Nitrogen load in the River in Millbury, MA downstream of District's discharge has decreased 66% and 38%, respectively.



## Chlorophyll-*a*

Nutrients in the river, from both point and non-point sources, can contribute to increased algal growth, which is expressed in chlorophyll-*a* concentrations. Point sources are discharges from wastewater treatment facilities. Non-point sources include pollutant loads from stormwater that find their way into rivers and streams. The rate of river flow is an important factor influencing algal growth. On the Blackstone River, increased algal growth tends to occur in stagnant or low flowing stretches of the river, frequently located behind old industrial era dams.

Chlorophyll-*a* measurements collected in 2012 were compared with historical chlorophyll-*a* concentrations collected during low river flow conditions to evaluate whether there is evidence of less algal growth in the river. Figure 5 shows maximum chlorophyll-*a* concentrations measured in 2012 and historically along the river from upstream of the District in Millbury, MA (left side of graph) to the river outlet at Slater Mill in Pawtucket, RI (right side of graph). This comparison indicates that maximum algal growth in portions of the river has decreased. Visual surveys of algal growth over the past few years suggest that there was also less macrophyte growth (rooted plants) in the river in 2012 than in previous years.

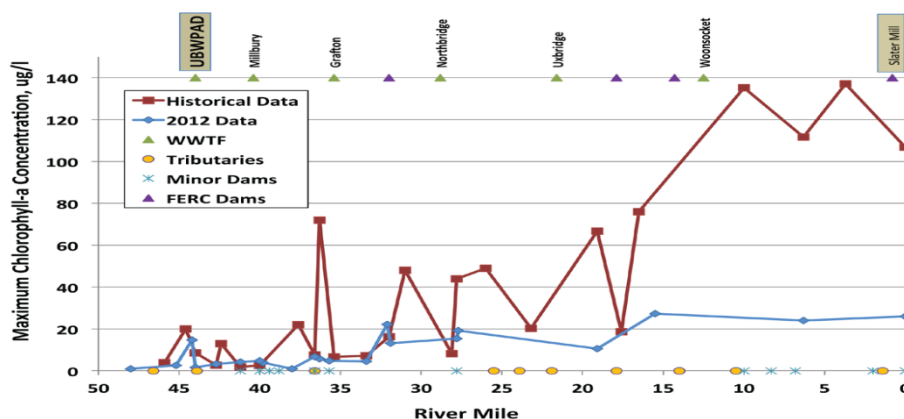


Figure 5. Sharp reductions in chlorophyll-*a*, an indicator of algal growth, have been observed in the River.

## Periphyton

The periphyton-sampling program conducted in 2012 included visual assessments of periphyton cover and actual periphyton sample collection at eight river locations including three sites sampled by MassDEP in 2008. Periphyton sampling did not extend downstream of river mile 35, because south of this location the river generally becomes deeper, resulting in less light penetration and conditions that are not favorable for periphyton growth. In 2012, periphyton was detected at all the sampling locations, including those upstream of the confluence of the District's effluent channel. Sampling program results indicate increased periphyton growth downstream of the District compared to conditions upstream of the treatment facility discharge; however, concentrations were below 100 mg/m<sup>2</sup>, what MassDEP has described as "nuisance levels" (MassDEP, 2009) based on a literature review. The 2012 periphyton chlorophyll-*a* concentrations suggest a potential decrease in periphyton at the locations sampled earlier by MassDEP, Figure 6, but more data are needed to confirm these results.

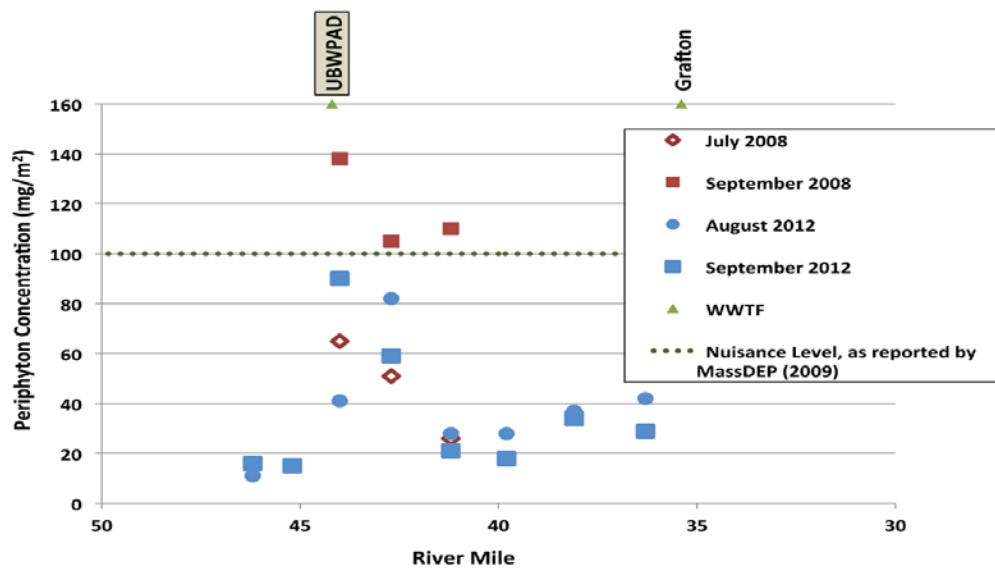


Figure 6. 2012 Periphyton concentrations are below nuisance levels and decrease significantly 3 miles downstream of UBWPAD.

### Next Steps

The District plans to continue annual water quality monitoring of the Blackstone River to maintain a basis for evaluating changes in river quality and to continue to refine the scientific understanding of river conditions. In support of making data available to all interested parties, UMass has submitted the Blackstone River data collected from 2010 through 2012 to the Consortium of Universities for the Advancement of Hydrologic Science, Inc. (CUAHSI) database, which is sponsored by the National Science Foundation ([www.cuahsi.org](http://www.cuahsi.org)). CUAHSI will be publishing these data this summer, and the data will be publicly available for download through the CUAHSI Hydrologic Information System (HIS) databases and servers ([his.cuahsi.org](http://his.cuahsi.org)).

See <http://www.ubwpad.org> for the detailed results of 2012 sampling program described in *Blackstone River Water Quality Monitoring Program Report – 2012 Field Season* (UMass, 2013).

### Student Support

- 1 Undergraduate, College of Natural Sciences
- 1 MS Geosciences

## Information Transfer and Outreach

Four meetings were held this year as part of our Information Transfer Program. The combined number of participants for the four events amounted to 285. Three of the workshops took place in Amherst, and the symposium was held in Medford, Massachusetts.

The Fluvial Geomorphology workshop sought input from Massachusetts environmental agencies, professional experts, and planners on whether it would be a good idea to establish a statewide program of fluvial geomorphological assessments in Massachusetts.

The Symposium on the Value of Water, on the Tufts University campus, gathered academics, water professionals and state agency personnel to synthesize the state of knowledge on how society currently



values water quality, water quantity, and environmental flows. It also helped train the future generation of water experts by hosting a student poster presentation competition.

Growing Your Green Infrastructure Program was held on the campus of UMass Amherst to help New England municipalities implement or consider a green infrastructure program to reach their stormwater and water quality improvement goals.

The River's Calendar Symposium convened academia, state and federal agencies, and nonprofit organizations to understand phenology as an indicator of climate change.

### **1. Fluvial Geomorphology Workshop (USGS- 2012MA337B)**

**Principal Investigator:** Paula Sturdevant Rees, Christine Hatch, Marie-Francoise Hatte

**Start Date:** 3/1/2012

**End Date:** 2/28/2013

**Reporting Period:** July 1, 2011 – June 30, 2012

**Funding Source:** USGS 104B

**Focus Category:** Geomorphological Processes, Floods, Sediments

#### **Problem Statement:**

Recent extreme flooding in Massachusetts and neighboring states has resulted in devastating erosion of stream banks, causing catastrophic damage to roads and bridges, agricultural fields, and riparian ecosystems. Yet in Massachusetts no standardized tools exist to assess the geomorphological health of streams, particularly with regard to identifying areas of high erosion hazard, high quality aquatic habitats and areas affected by changes induced by humans.

There is also an ecological need for fluvial geomorphic assessment in Massachusetts. The 2001 Massachusetts Water Resources Commission (WRC) Stressed Basins report identified that habitat factors are important indicators of river aquatic biological integrity, but there is a lack of consistent fluvial geomorphic data in the state. As a result, fluvial morphology has not been included in some recent USGS studies in the state cooperative program, including "Indicators of Streamflow Alteration, Habitat Fragmentation, Impervious Cover, and Water Quality for Massachusetts Stream Basins" (2010, Weiskel et al., USGS Scientific Investigations Report 2009-5272) and "Factors Influencing Riverine Fish Assemblages in Massachusetts" (2011, Armstrong et al., USGS Scientific Investigations Report 2011-5193). Geomorphology assessments occur in specific river restoration projects, but there is not a consistent methodology applied or specified by the state. There is an opportunity to incorporate fluvial geomorphic assessments into the statewide water quality assessments performed by DEP and reported to the EPA.

We proposed to hold a fluvial geomorphology (FGM) workshop to provide input on an appropriate methodology for assessments that could be used consistently statewide and produce data that could be used in both public safety and environmental programs. The purpose of this workshop was to gather experts, concerned scientists, and environmental agencies to explore the need and feasibility of using fluvial geomorphology to assess and restore streams in Massachusetts. The ultimate goal was to identify or create tools useful to decision makers and local practitioners to protect sensitive areas and restore river corridors.

#### **Methodology:**

We established a steering committee to plan the workshop. The committee consisted of the following people:

University of Massachusetts:

Paula Rees, Marie-Françoise Hatte, Jerry Schoen, WRRRC

Steve Mabee, Office of the State Geologist  
Christine Hatch, UMass Geosciences  
Massachusetts Department of Fish & Game, Division of Ecological Restoration:  
Beth Lambert, Carrie Banks  
Massachusetts Department of Conservation and Recreation:  
Linda Hutchins  
Massachusetts Department of Environmental Protection:  
Gerry Szal, Jane Peirce, Heidi Davis  
Vermont DNR:  
Mike Kline

The Workshop's hosts were the Massachusetts Geological Survey, Extension and Water Resources Research Center/UMass Amherst, and primary funding came from a USGS Water Research Institutes Program grant of \$6,738. Massachusetts Department of Ecological Restoration provided match funds in the amount of \$2,519. Another co-sponsor included the Mass. Department of Environmental Protection.

### **Project Description**

The workshop was held on the campus of the University of Massachusetts Amherst on October 25, 2012. Forty-seven people attended. In the morning Mike Kline of the Vermont ANR, which runs a successful program of fluvial geomorphic assessment, presented the basics of geomorphology and the advantages of conducting such assessments. Next, various agencies and individuals listed their needs that would be filled by FGM assessments. In the afternoon, nine participants spoke about the type of assessment they conduct, and the day concluded with a facilitated discussion to outline GFM goals for Massachusetts, what techniques would fit our goals, and what next steps ought to be. One recommendation was to form a Geomorphic Assessment Task Force to oversee those next steps, and the Task Force was started.

### **Outcomes**

A Workshop outcomes summary was drafted after the meeting and sent to all participants, outlining Management Objectives, Approach Needed, and Next Steps.

Some funding options were outlined during the workshop, and the Workshop hosts Stephen Mabee and Marie-Françoise Hatte subsequently wrote a proposal in response to a RFP from the Massachusetts Emergency Management Agency (MEMA) and Department of Conservation and Recreation (DCR) for the availability of Federal Emergency Management Agency (FEMA) Hazard Mitigation Grant Program (HMGP) funding. The proposal was submitted on March 15, 2013 for the HMGP 5% Initiative, and we expect a response by Fall 2013.

## **2. Symposium on the Value of Water (USGS- 2012MA380B)**

**Principal Investigator:** Paula Sturdevant Rees, MA Water Resources Research Center, UMass Amherst

**Start Date:** 3/1/2012

**End Date:** 2/28/2013

**Reporting Period:** March 1, 2012 – June 30, 2013

**Funding Source:** USGS 104B

**Focus Category:** Water Use, Economics, Management and Planning

### **Objectives:**

Our objectives for this Symposium were (1) to create a working relationship with Tufts University's Water: Systems, Science and Society; (2) give several UMass Amherst graduate students experience in collaborating with Tufts University students to plan a day-long conference; and (3) provide an

opportunity for Massachusetts Environmental Agencies staff in Boston to participate in a water themed conference.

**Methodology:**

WRRC Director and Associate Director and three to four UMass Amherst graduate students met every other week from January through April and participated in conference calls with the Tufts University Symposium team of students and advisor. The UMass students took charge of one of the panel sessions (The Value of Environmental Flows) and helped recruit sponsors for the event. WRRC staff also recruited sponsors, organized a student poster competition, recruited poster judges and secured the participation of a dozen Agency staff, in addition to helping with symposium logistics.

**Principal Findings and Significance:**

165 people attended the Symposium, entitled “The Glass Half Full: Valuing Water in the 21<sup>st</sup> Century,” took place on April 27, 2012 on the campus of Tufts University in Medford, Mass. The day-long event featured the following Agenda:

- Opening Remarks: Rich Vogel (Tufts University) and Paula Rees (MA WRRC)
- Morning Keynote Address: Jerome Delli Priscoli (USACE Institute for Water Resources)
- Panel 1: Value of Clean Water - Challenges of Water Sanitation in the Developed and Developing World. Jerry Griffiths (Tufts University); Daniele Lantagne (Harvard Kennedy School of Government); Elena Naumova (Tufts University); Janine Selendy (Horizon International)
- Panel 2: Scarcity & Floods – Managing the Extremes. Casey Brown (UMass Amherst); Stephen Estes-Smargiassi (Mass. Water Resources Authority); Katherine Meirdiercks (Siena College); Peter Weiskel (USGS)
- Poster Session (29 posters)
- Panel 3: The Value of Environmental Flows. Kathy Baskin (Mass. Executive Office of Energy and Environmental Affairs); Sharon Davis (Murray-Darling Basin Authority and Harvard University); Robert Johnston (Clark University); Mark Smith (The Nature Conservancy)
- Closing Remarks: President Anthony Monaco, Tufts University.

**Student Support**

1 Undergraduate, Mathematics

**Graduate students participating from UMass:**

June Hart, MS Environmental Conservation  
Scott Steinschneider, PhD Civil & Environmental Engineering  
Zachary Smith, MS Geosciences  
Jessica Pica, MS Civil & Environmental Engineering

**3. Growing your Green Infrastructure Workshop (2012MA386B)**

**Principal Investigators:** Dr. Paula Rees, MA Water Resources Research Center

**Start Date:** 3/1/2012

**End Date:** 2/28/2013

**Reporting Period:** March 1, 2012 – February 28, 2013

**Funding Source:** USGS 104B

**Focus Categories:** Management and Planning, Water Supply, Water Use

**Problem and Research Objectives:**

The original plan was to hold a workshop focused on identifying data and analysis requirements for assessing future water needs and availability across the Commonwealth. Potential topics of discussion

included translation of existing data to water managers in a useful format, how best to address sustainability and resilience questions for various service areas, development of integrated water resources management plans, and identification of potential solutions to future water availability, sustainability, and resilience issues. However, plans for this workshop were put on hold until after release of the Commonwealth's Sustainable Water Management Initiative (SWMI) framework, which was delayed until late 2012, in order to better align with state and local needs. A workshop related to this is planned for 2013.

Regional partners suggested that we instead focus on a workshop to help communities grow green infrastructure programs. On December 6, 2012, the WRRRC in collaboration with the Water Infrastructure Capacity Building Team, HUD Capacity Building for Sustainable Communities, hosted "Growing Your Green Infrastructure (GI) Program," a skill-building workshop for HUD/EPA/DOT Sustainable Communities grantees and others in New England. This one-day workshop was designed to equip participants to implement successful green infrastructure programs and practices in their communities. Specifically, our goal was for participants to:

- Learn regulatory, technical, outreach, and financial strategies that will help overcome challenges to implementing a successful GI program, specific to New England
- Be inspired by and get new ideas from case studies in and close to the region
- Have opportunities to learn from each other's experiences.

#### **Methodology:**

The workshop was by invitation only, and was designed for New England municipalities implementing or considering a green infrastructure program to reach their stormwater management and/or water quality improvement goals. It was also designed to be relevant to regional planning entities and state agencies whose constituent municipalities are considering green infrastructure approaches. The workshop consisted of a mixture of expert presentations, case studies and peer networking opportunities. Regulatory, technical, financial and outreach strategies to implement successful green infrastructure programs and practices were covered. The agenda for the day is shown on the next page.

#### **4. Growing Your Green Infrastructure Program**

The day-long workshop featured the following agenda:

Welcoming remarks (Paula Rees, WRRRC); Loading up the bandwagon: Generating buy-in for your green infrastructure program (Khristopher Dodson, Syracuse University Environmental Finance Center); Green infrastructure and the regulatory framework (Gina Snyder, EPA Region 1); Right practice, right place: Green infrastructure technologies that work in New England (Robert Roseen, Geosyntec); Financing strategies for green infrastructure programs (Jennifer Cotting, University of Maryland Environmental Finance Center); Consensus-building strategies that lead to sustainable funding (Josh Secunda, EPA Region 1); Stories from the field: Implementing green infrastructure (Simsbury, CT – Hiram Peck, Town of Simsbury; Jonathan Ford, Morris Beacon Design. Cincinnati, OH – Allison Roy, University of Massachusetts. Pittsfield, MA – Kathleen Ogden, Vanasse Hangen Brustlin, Inc.);

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

Thirty-three individuals participated, in addition to the planning committee. Eleven of the attendees represented the Sustainable Communities grant organizations. The conference included participants from all six New England states. An overview of the breadth of organizations represented by the participants is provided in Table 1. Evaluations from the event were positive. One hundred percent of respondents reported they received practical guidance that applies to their existing or planned green infrastructure program, 94% were satisfied or very satisfied with the event overall, and 88% said the event met their expectations.

Table 1: Overview of Participants

Capitol Region Council of Governments	Hartford	CT
Connecticut Department of Economic and Community Development	Hartford	CT
Town of Mansfield CT	Mansfield	CT
Greater Portland Council of Governments (City of Portland)	Portland	ME
Franklin Regional Council of Governments	Greenfield	MA
Pioneer Valley Planning Commission	Springfield	MA
Lakes Region Planning Commission	Meredith	NH
Upper Valley Lake Sunapee Regional Planning Commission	Lebanon	NH
State of Rhode Island	Providence	RI
Two Rivers-Ottawquechee Regional Commission	Woodstock	VT
CT NEMO	--	CT
City of Worcester	Worcester	MA
City of Chicopee	Chicopee	MA
City of Northampton	Northampton	MA
Town of South Hadley	S. Hadley	MA
New Hampshire Housing Finance Authority	--	NH
US EPA Region 1	--	--
City of Holyoke	Holyoke	MA
City of Portland	Portland	ME
NH Dept. of Environmental Services, Planning, Prevention, & Assistance Unit	--	NH
Metropolitan Area Planning Commission	Boston	MA

Several issues were suggested for future events or technical assistance needs. These included:

- Effectiveness of LID strategies – like last presentation
- More examples similar to Simsbury, CT – integrating GI into land use ordinances
- Implementation – how-to guidance, examples (like the Simsbury case)
- Working with elected officials
- Green infrastructure and resilience / adaptation in rural areas
- Always interested in more green infrastructure and how to pay for it
- Re-writing zoning / regs for BMPs
- More technical design guidance (like hands on)
- More about technologies themselves and failed / bad examples along with the ones that worked well
- Further specifics on financing and funding
- Green infrastructure and liability issues that result
- Rural areas actual green infrastructure technologies
- More on the technologies, lessons learned (case studies from engineers)

Participants from communities suggested several areas where assistance would help them attain their goals, including:

- Collaborations / grant writing / funding
- Simplified guidance for financing and regulatory requirements / science
- Monetary resources

- Education / training for local volunteers and officials
- Stormwater sampling
- Information sharing and updates
- Grant writing, consensus-building, help with the establishment of a stormwater fee
- Collaborations

#### **Follow-on Funding**

We submitted a pre-proposal to the Dorris Duke Foundation for a student-training program related to Green Infrastructure. While this proposal was declined, we continue to explore other funding opportunities in the Green Infrastructure and stormwater areas. Over the summer we will be convening a variety of meetings to identify collaborative research and education opportunities in the area of stormwater. In particular, colleagues in Extension are working with the state to develop a stormwater certification program for the workforce. We will be discussing how the water center can help support these efforts.

#### **4. The River's Calendar symposium: effects of climate change on phenology of riparian systems. (2012MA388B)**

**Principal Investigators:** Jerry Schoen, MA Water Resources Research Center

**Start Date:** 3/1/2012

**End Date:** 2/28/2013

**Reporting Period:** March 1, 2012 – February 28, 2013

**Funding Source:** USGS 104B

**Focus Categories:** Ecology, Climatological Processes, Methods

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

*Problem:* Climate change is a known threat to river systems, but knowledge on specific impacts is limited. Riparian areas are known to be valuable, yet vulnerable refuges in a changing climate.

*Phenology* shifts are a concern; *asynchrony*, or mismatches in these shifts for different species, may wreak havoc in the balance between aquatic, terrestrial and airborne organisms that share these zones. Understanding asynchrony is critical to developing adaptation strategies for both human and natural communities along rivers - programs that will help them survive in coming changes. However, phenological datasets that might inform adaptation strategies are sparse, particularly for aquatic invertebrates. *Research Objectives:* to bring together scientists and recreational interests (fly fishermen) to discuss these issues and provide input on strategies to develop a citizen science program to track aquatic insect phenology in order to provide data that might help to provide better understanding of these questions.

#### **Methodology:**

Convene symposium, attended by representatives of academia, state and federal agencies, and nonprofit organizations.

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

Symposium successfully conducted, 40 representatives of academia, state and federal agencies, and nonprofit organizations attended. Proceedings link provided below.

#### **5. Stream Continuity Project**

**Principal Investigator:** Scott Jackson, Environmental Conservation, UMass Amherst

**Start Date:** Spring 2000

**End Date:** Ongoing

**Reporting Period:** July 1, 2012 – June 30, 2013

**Funding Source:** UMass Extension

**Descriptors:** Stream Crossings; Water Quality; Fish Passage

Under a memorandum of understanding with UMass extension, WRRRC staff worked to 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, WRRRC staff served as the database coordinator and quality assurance officer.

## **Environmental Analysis Laboratory**

**Reporting Period:** July 1, 2012 – June 30, 2013

The Environmental Analysis Laboratory (EAL) was created in 1984 by WRRRC 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 currently conducts analysis of pH, alkalinity, dissolved oxygen, total phosphorus and chlorophyll *a* to support environmental research, management, and monitoring activities.

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. The quality-control program for volunteer-monitoring groups continued for pH, alkalinity and dissolved oxygen. EAL also provided Total Phosphorus and Chlorophyll *a* analyses to watershed groups through the MA DEP funded “Water Quality Analyses Support for Massachusetts Volunteer Monitors” (see report below).

EAL also continued to provide Chlorophyll *a* analysis for the Upper Blackstone Pollution Abatement District (UBWPAD) and will continue to do so for another year.

### **Student Support**

1 Undergraduate, Natural Resource Conservation.

## **1. Water Quality Analyses Support for Massachusetts Volunteer Monitors (SECTION 319 NPS PROJECT 11-12/319)**

**Principal Investigators:** Marie-Françoise Hatte, MA Water Resources Research Center

**Start Date:** 1/1/2012

**End Date:** 6/30/2013

**Reporting Period:** 7/1/2012 / 6/30/2013

**Funding Source:** Massachusetts Department of Environmental Protection

**Descriptors:** Water Quality, Laboratory Analyses, Volunteer Monitoring

### **Description:**

This project reinstated UMass Environmental Analysis Laboratory (EAL) analysis services to volunteers and others in the Commonwealth and provided free analysis of chlorophyll *a* and total phosphorus to citizen groups.

After a couple of decades providing support to citizen groups who monitor their local surface water bodies, the (EAL) ceased this service due to staff departure, equipment failure, and lack of funding. Citizen groups were left with no option to have their samples analyzed for Total Phosphorus to the low level of detection prescribed by their Quality Assurance Project Plans (QAPP), and with less optimal options for their chlorophyll determinations.

With funding from DEP's 319 Program, the Water Resources Research Center—who runs the EAL—purchased a new spectrophotometer (Shimadzu UV-1800) and trained two staff (Elizabeth Finn and Marie-Françoise Hatte) to use this instrument for the analysis of chlorophyll *a*. Our staff spent several months refining the chlorophyll analysis method, and started offering free analyses in 2012 to volunteer groups who responded to our advertising of this service. We updated the analysis protocol for chlorophyll *a* and submitted it to DEP for formal approval, which was granted July 2, 2013.

We also advertised our availability to help volunteer groups write a QAPP for their monitoring project. No group needed this service the first year of the project, and three groups requested help with their QAPP the second year. We are currently in communications with the Herring Ponds Watershed Association in Plymouth to update their QAPP for chlorophyll *a* monitoring, Farm Pond Advisory Committee for total phosphorus monitoring, and Friends of Lake Quannapowitt for chlorophyll *a* and total phosphorus monitoring.

Next we turned our attention to total phosphorus and got training for Elizabeth Finn on the analytical method. We revised the method in accordance with DEP's Quality Control team, and submitted it for approval, which was granted on 02/20/2013.

In 2012, we performed 30 analyses for 3 volunteer groups, (14 chlorophyll and 16 TP analyses) (see Table 1) and also started running chlorophyll analyses for the Upper Blackstone Project. One group, Citizens Restoring Congamond in Southwick, MA, requested 30 TP sample bottles in 2012, but never returned any samples.

**Table 1: Volunteer Group Samples Analyzed in 2012**

<b>Date</b>	<b>Group</b>	<b>TP</b>	<b>Chlorophyll</b>	<b>Total</b>
6/5/2012	FOLQ		2	
6/5/2012	LSWA		1	
8/10/2012	FOLQ		4	
8/10/2012	LSWA		2	
10/5/2012	FOLQ		2	



10/5/2012	LSWA		1	
11/16/2012	LSWA	2		
11/16/2012	LSWA	4		
11/16/2012	NRWA	10		
11/16/2012	FOLQ		2	
	<b>Total</b>	<b>16</b>	<b>14</b>	<b>30</b>

FOLQ = Friends of Lake Quannapowitt, Wakefield, MA

LSWA = Lake Singletary Association, Sutton, MA

NRWA = Nashua River Watershed Association, Groton, MA

In 2103, we received responses from 8 volunteer groups to our offer sent to 50 groups regarding free TP and chlorophyll analyses and QAPP assistance (see Table 2). Webster Lake Association decided that they would be unable to do the testing this year, so withdrew their request for analyses, making the count down to 7 groups for 2013. We will offer them a total of 70 analyses, 10 samples each for each group. It has not been determined as of this writing how many TP analyses vs. chlorophyll analyses will be performed.

**Table 2: Volunteer Groups Requesting EAL Analyses in 2013**

Charles River Watershed Association, Weston, MA
Farm Pond Advisory Committee, Sherborn, MA
Friends of Lake Quannapowitt, Wakefield, MA
Herring Ponds Watershed Association, Sagamore Beach, MA
Lake Singletary Association, Sutton, MA
Lake Wyola Association, Shutesbury, MA
Nashua River Watershed Association, Groton, MA
Webster Lake Association, Webster, MA

Once our TP method was finalized, we prepared our application to DEP for official certification of our laboratory for the analysis of Total Phosphorus. The application went to the Director, Laboratory Approval Program, Massachusetts Department of Environmental Protection on May 29th with payment of \$920.00. On July 8, 2013 we received the administrative review, which pointed out a couple of minor problems which we will address immediately and resubmit once the issues are resolved. There will then be a technical review (can take up to 48 days), contingent upon passing the analysis of at least two Performance Test samples (at least one month apart). We therefore do not anticipate receiving official certification before 2014, but plan to continue working on this deliverable after the end date of this project until certification is obtained.

We also re-wrote a QAP for the EAL and submitted it for approval to MassDEP, which was granted on July 8, 2013.

#### **D. Lessons Learned**

Many of the established watershed groups already have an approved QAPP in place for total phosphorus. Chlorophyll *a* was not commonly included in many QAPPs. Because the chlorophyll samples are essentially pre-filtered water samples – the lab receives only the filters – more care and explanation of the chlorophyll sampling process was needed, and thus provided.

Richard Chase of the DEP Central Regional Office was extremely helpful by providing guidance on the updating of the SOPs and by providing quality control samples to test the accuracy of the total

phosphorus method. We also have a plan to run chlorophyll samples this summer in conjunction with MassDEP to compare our results.

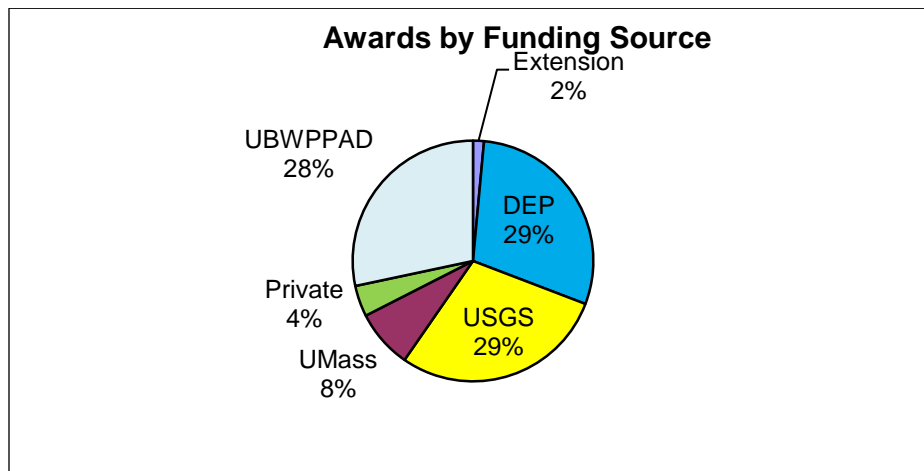
The lab certification process is a lengthy one, but we anticipate improving our lab services as a result of our effort to become certified for TP analyses.

## Financial Overview

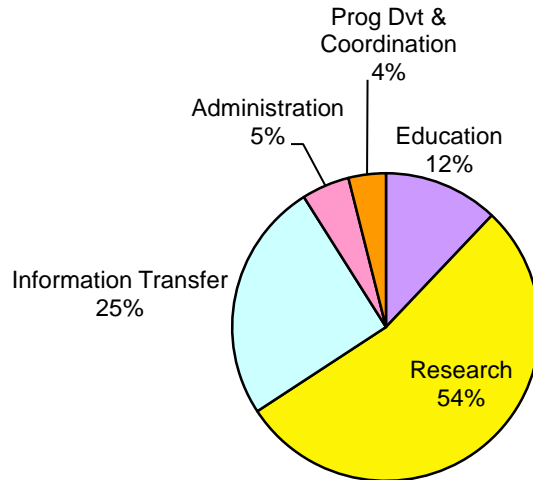
Center revenues come strictly from grants and contracts. The University of Massachusetts contributes 20% of the salary for a half-time Director and also provides physical facilities for the WRRRC.

Total revenues amounted to \$320,319 (Brown pass-through projects not included)

USGS 104B:	\$ 92,335 broken down as follows:
	\$30,000 Jackson research project
	\$26,210 Workshops
	\$16,125 Administration
	\$5,000 Schiffman research Project
	\$5,000 Brabec research project
	\$5,000 Park research project
	\$5,000 Hon research project
UMass (Director)	\$ 25,180
Extension	\$ 4,700
ARM Project	\$ 30,000
MASTEP	\$ 49,994
Blackstone River	\$ 90,756
EAL	\$ 13,355
Lab Analyses Support	\$ 14,000



### Awards by Category



### Awards by Sponsor Type

