



MA Water Resources Research Center

Annual Report 2011-2012

March 1, 2011 – June 30, 2012

Marie-Françoise Hatte
Elizabeth Finn



**Massachusetts Water Resources Research Center
Blaisdell House - 113 Grinnell Way
University of Massachusetts
Amherst MA, 01003**

Tel: 413-545-5531

E-Mail: wrrc@cns.umass.edu

<http://www.wrrc.umass.edu>

Director:

Dr. Paula Rees

rees@ecs.umass.edu

Associate Director:

Marie-Françoise Hatte

mfhatte@cns.umass.edu

Outreach and Education Director:

Jerome Schoen

jschoen@cns.umass.edu

Water Projects Coordinator:

Elizabeth Scotten Finn

esfinn@cns.umass.edu

This report is available on line:
<http://wrrc.umass.edu/about/annual-reports>

*Front cover: The Green River in Greenfield, Mass. after Hurricane Irene of August 2011 which breached the dam, removed the covered bridge footings, and re-routed the stream to obliterate a nearby road.
Photo by MF Hatte*



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Introduction

This report covers the period March 1, 2011 to June 30, 2012¹, the 45th 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.

¹ The USGS reporting year covers March 1 to February 28, while the University of Massachusetts and the Commonwealth of Massachusetts fiscal years run from July 1 to June 30. Projects funded by the State are reported for the period July 1 2011 - June 30, 2012.



Five 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."

Four graduate student projects were also funded: "A remote sensing algal production model to monitor water quality and nonpoint pollution in New England lakes" under PI Dr. Mi-Hyun Park of UMass Amherst; "Monitoring and understanding water quality at three potential Charles River swimming sites" under PI Dr. Ferdi Hellweger of Northeastern University; "Authentic research projects for undergraduates based on groundwater contamination issues related to Arsenic" under PI Julian Tyson of UMass Amherst; and "Assessing human impacts on sediment and contaminant trapping within Oxbow Lake, Northampton, Massachusetts" under PI Jonathan Woodruff of UMass Amherst.

The 104B Program also supported one Technology Transfer projects: the Eighth Annual Water Resources Conference, organized by the Water Center on the University of Massachusetts Amherst campus;

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

The Massachusetts WRRC also administered three 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. The titles of these projects are: "Evaluation of adaptive management of Lake Superior amid climate variability and change," "Climate risk assessment and management," and "Development of a Hydroclimate Synthesis Report for International Upper Great Lakes Study."

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

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

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

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



Research Program

Nine research projects were conducted this fiscal year. One research project was funded through the USGS 104G program, and three research projects received USACE funding through the WRRC. The three research projects funded by the USACE are "Evaluation of Plausible Risk to Lake Superior Regulation and Upper Great Lakes Amid Climate Variability and Change," and Development of a Hydroclimate Synthesis Report for International Upper Great Lakes Study, all led by PI Dr. Casey Brown of UMass Amherst and administered by the Water Center.

Five 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, 2010 – June 30, 2011

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 Misstear (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.

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 388,512 m² in area and provides drinking water to the town of Hudson, Massachusetts. The subwatershed that contributes to Gates Pond is 922,469 m² 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).

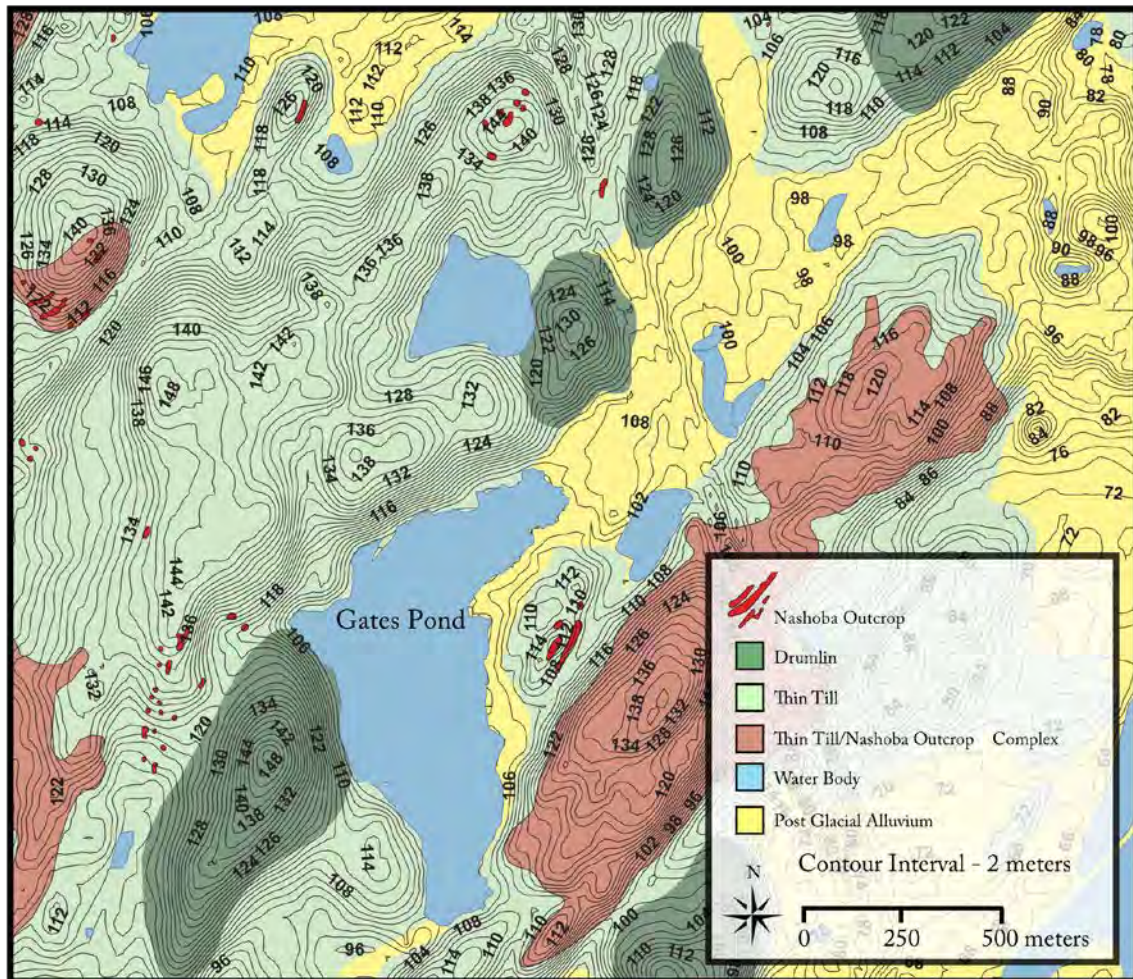


Figure 1 - Surficial geology/topography of the Gates Pond Reservoir field site.

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 Evapotranspiration (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 0.5 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).

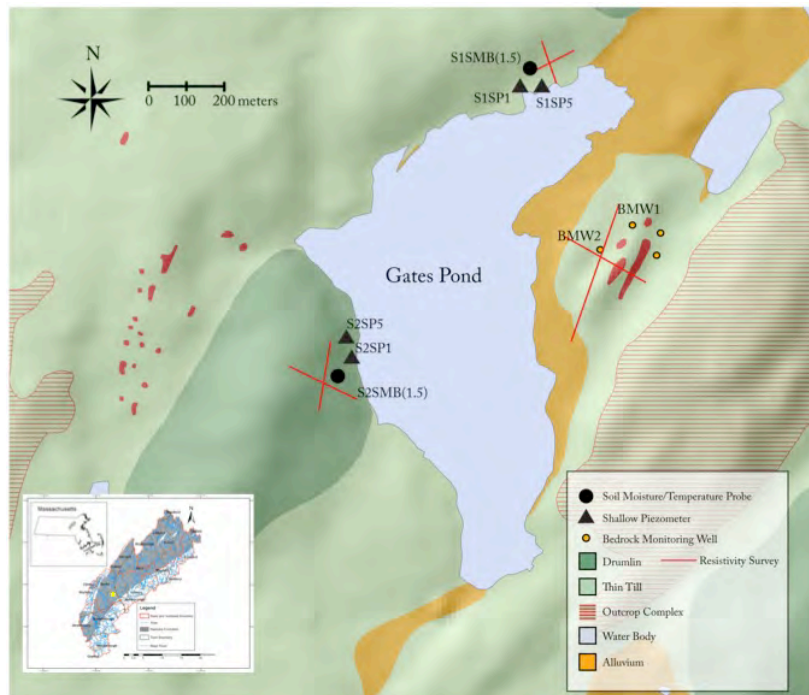


Figure 2. Site map of the Gates Pond Reservoir. In the lower left corner is a site locus showing the location of Gates Pond in relation ship to the Nashoba Formation in Massachusetts.

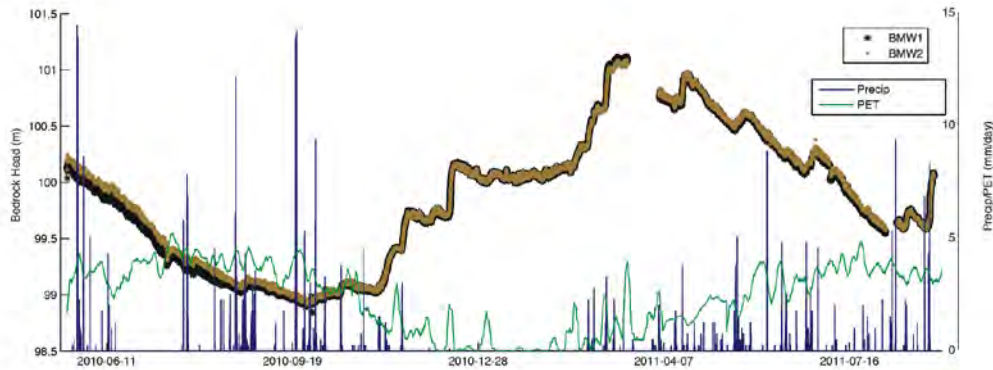


Figure 3. Time series of normalized head from BMW1 and BMW2. Potential evapotranspiration rate as calculated using the Thorthwaite approximation and precipitation rate are also plotted.

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 (Fig. 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 (Fig. 5a and 5b).

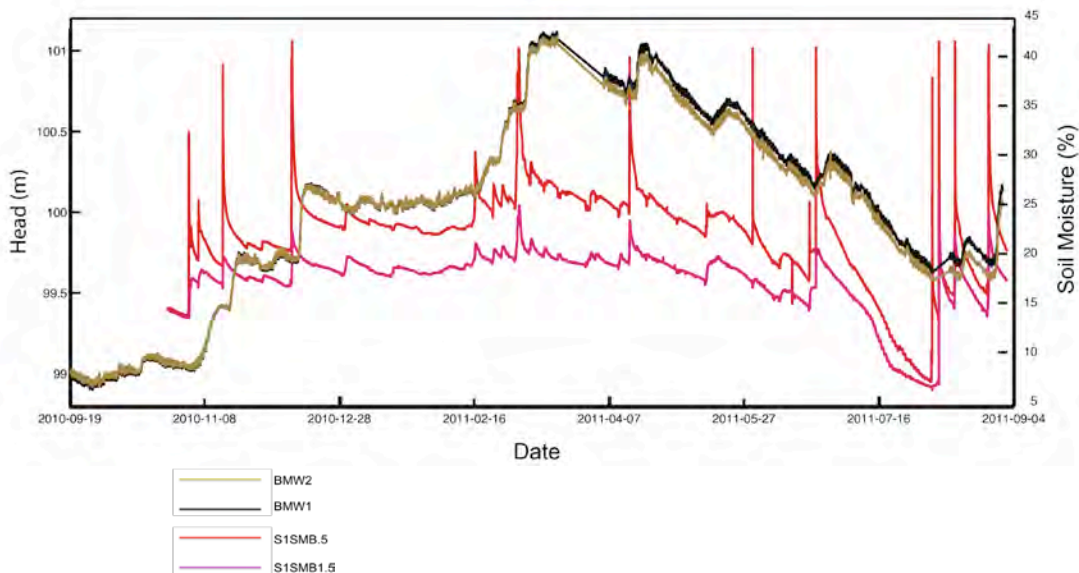


Figure 4. Plot of bedrock head within BMW1 and BMW2 along with the soil moisture gradient within thin till. Thin till is the deposit type that overlies BMW1 and BMW2. Soil moisture probes S1SMB.5 and S1SMB1.5 are collocated within the thin till at 0.5 meters bsl and 1.5 meters bsl respectively.

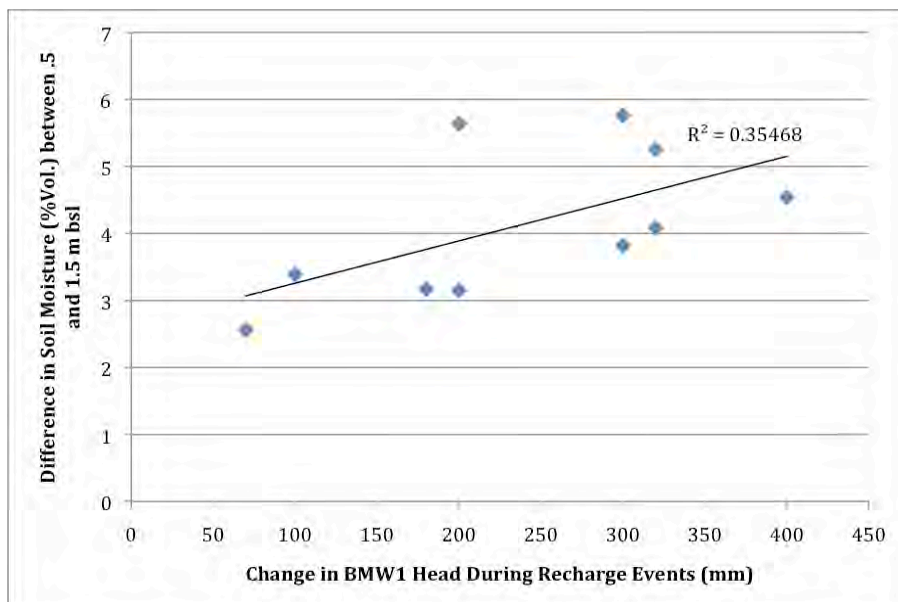


Figure 5a Correlations between soil moisture gradient and magnitude of bedrock recharge event.

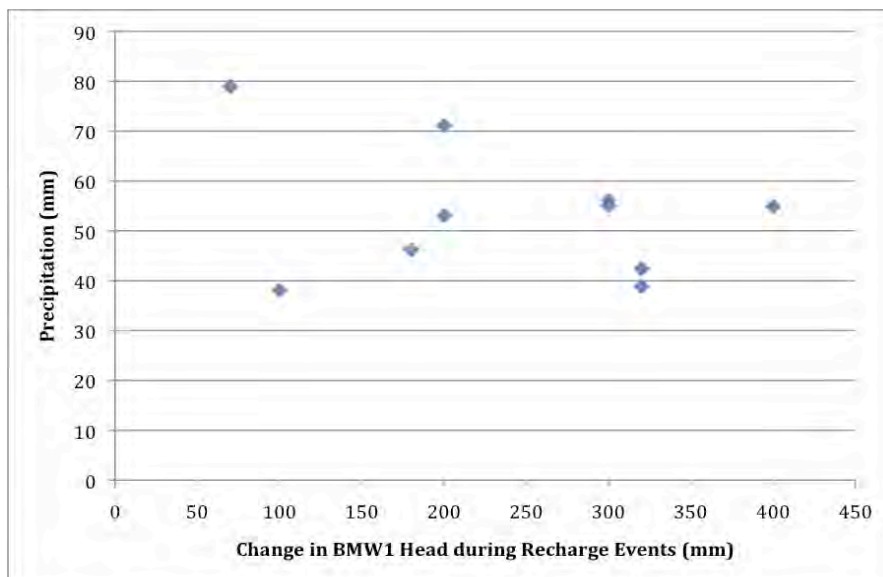


Figure 5b Lack of correlation between magnitude of precipitation event and bedrock recharge event.

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 (Fig. 6a and 6b).

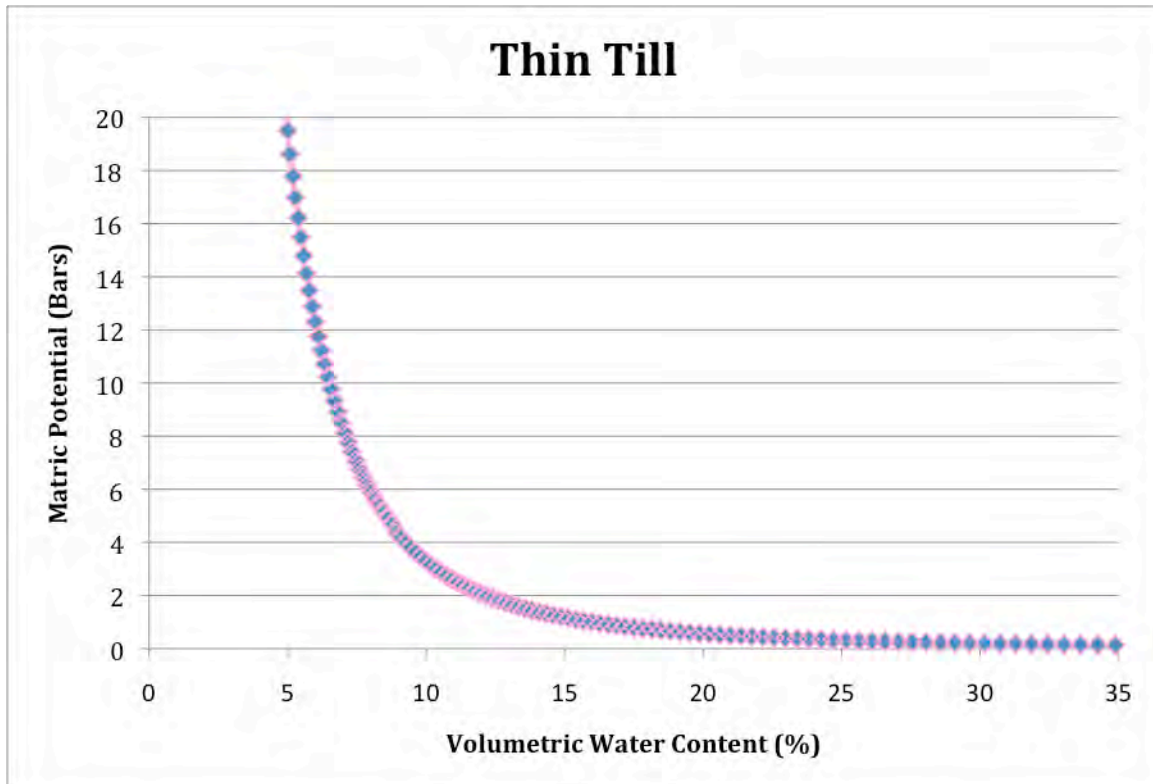


Figure 6a. Soil moisture retention curve for thin till deposits.

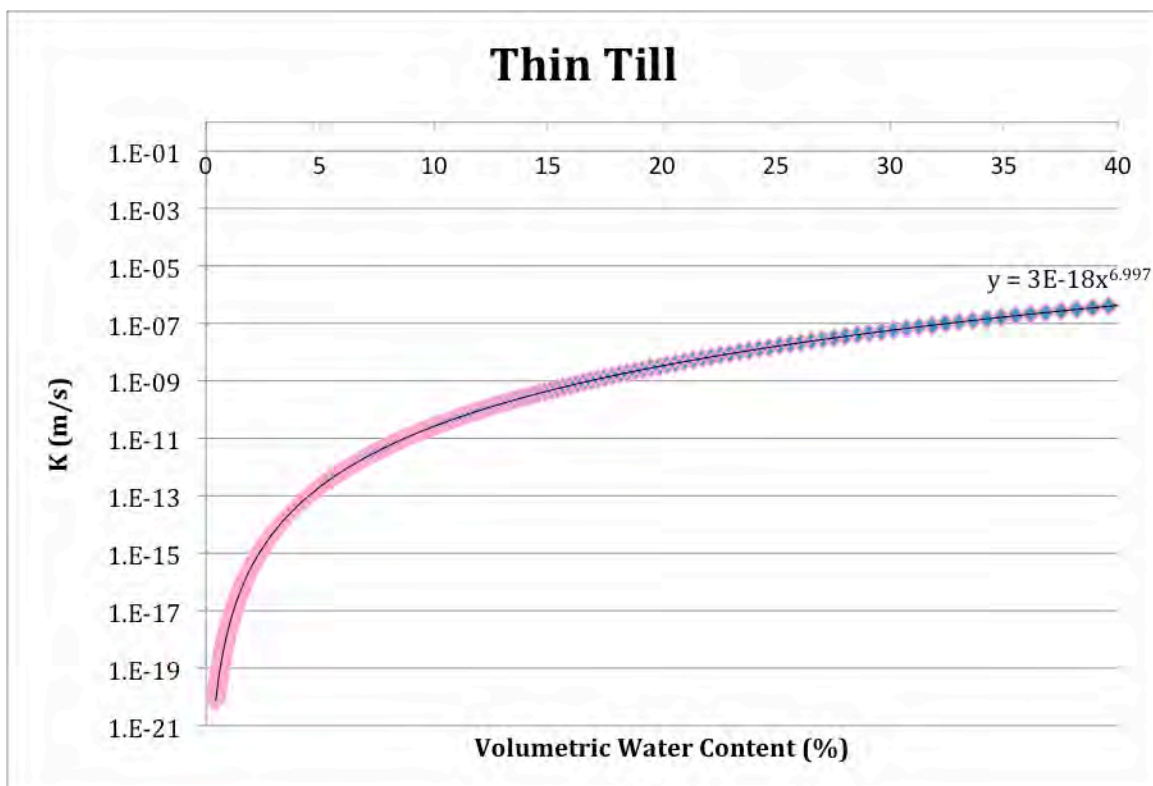


Figure 6b. Unsaturated hydraulic conductivity of the thin till.

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

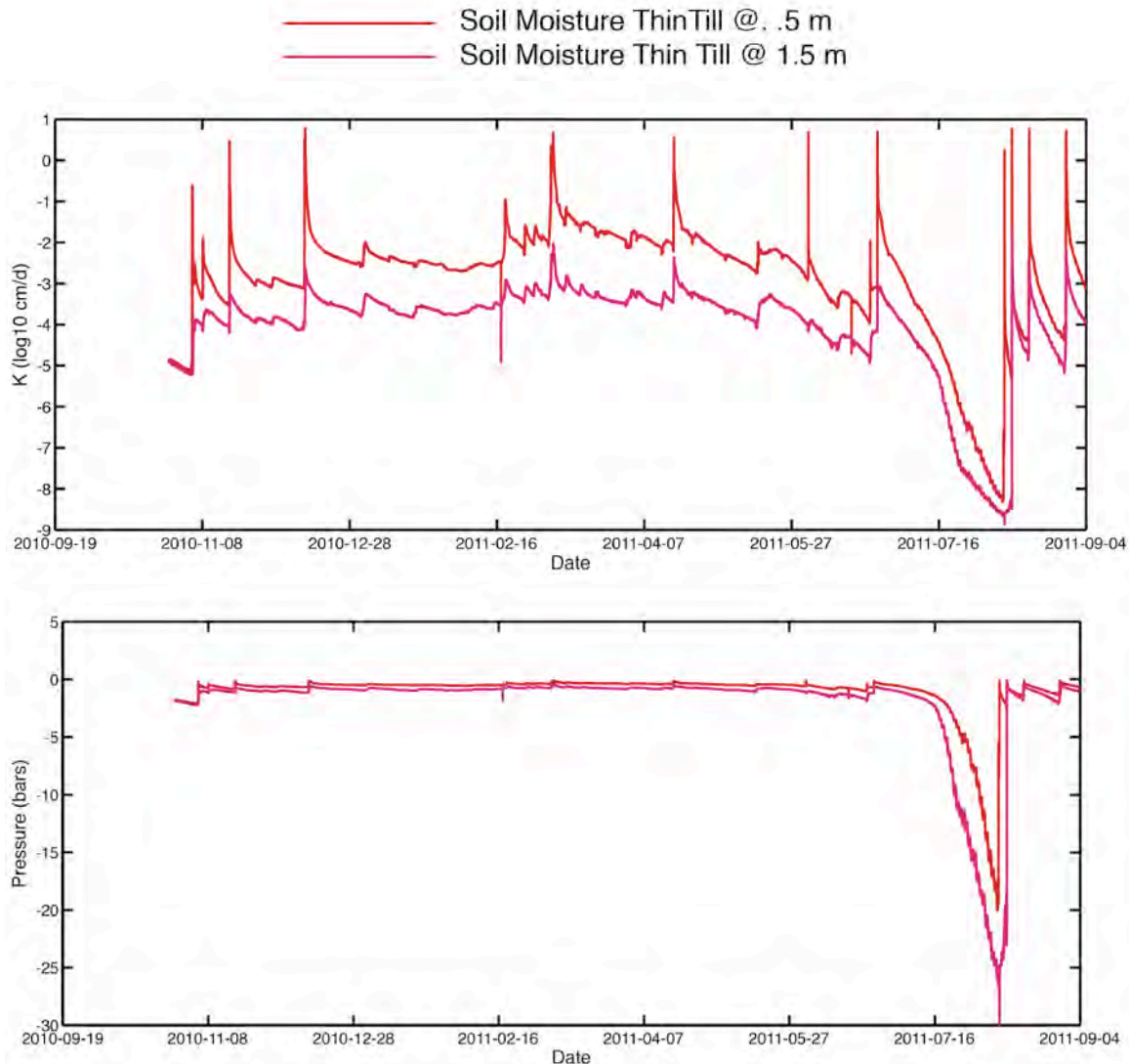


Figure 7. Time series of matric potentials and hydraulic conductivities.

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 σ_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. 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,

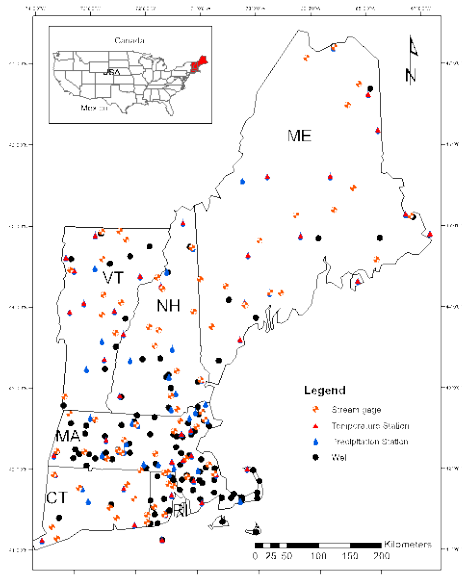


Figure 8: Map displaying location of Weider and Boutt (2010) study sites.

watershed, and climatic environments. Figure 8 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 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. 1960s and 1980s). 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 9 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.

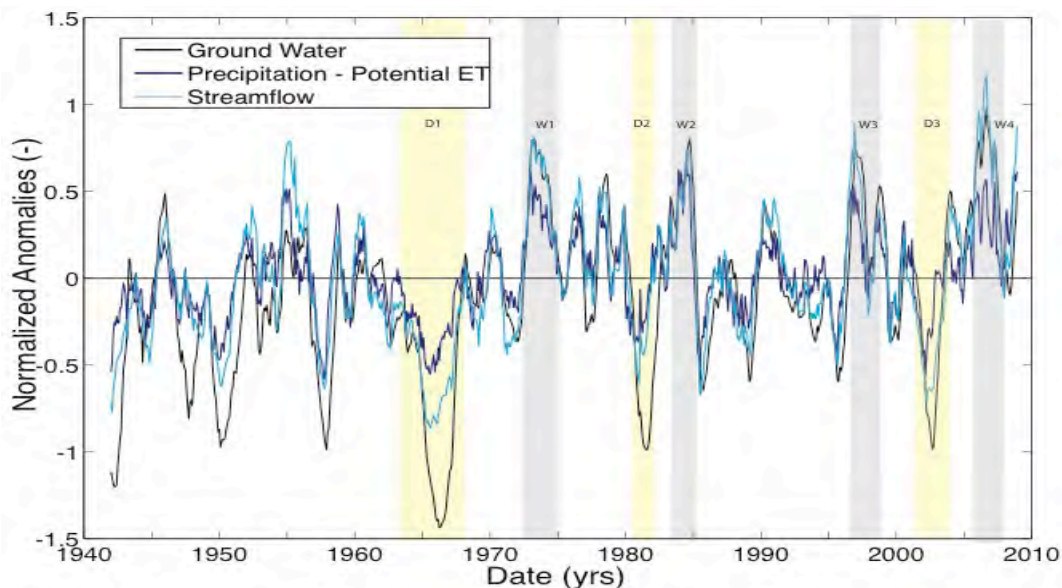
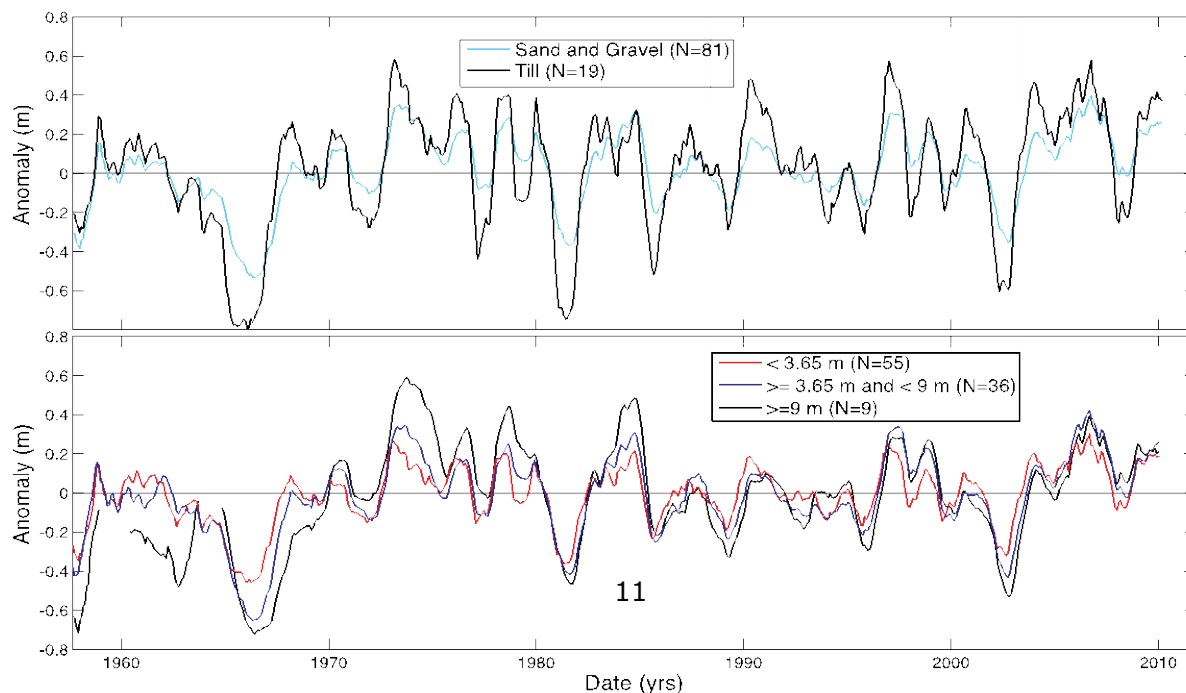


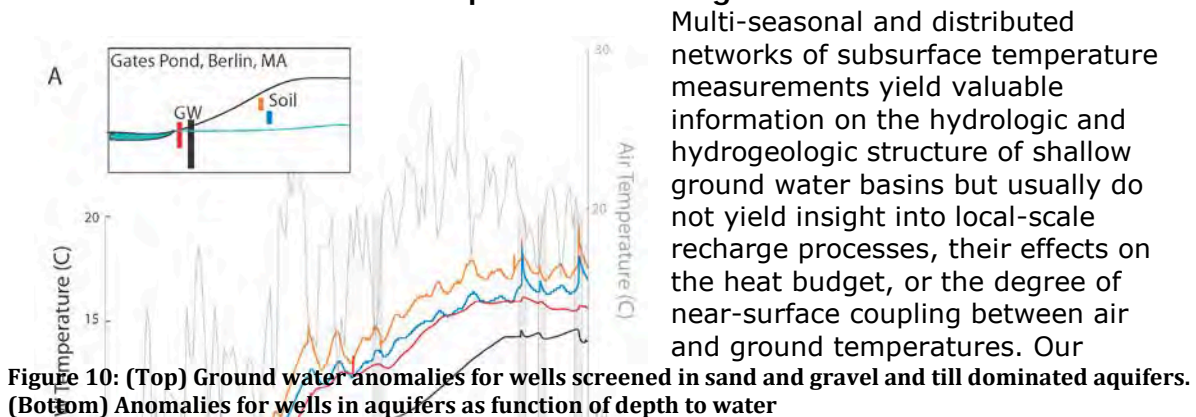
Figure 9: Normalized anomalies for the hydroclimatic data presented in Figure 8. These lines represent the average of all sites and record periods of dry (D) and wet (W) times

The regional water table hydraulic anomalies are controlled by the hydraulic properties of the material that the 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 10 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 10 (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



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 11 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.

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.

Developing a Conceptual Model for Bedrock Recharge in the Glaciated Northeastern US. Bevan, L.B., D.F. Boutt, S.B. Mabee. Novel Methods for Subsurface Characterization Conference. May, 2011. (Poster session). Best-student poster submission.



Student Support, Department of Geosciences

- 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 – Feb 28, 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
 - a. 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.).
 - b. Produce "response surfaces" of Lake System response to climate through simulation using parametrically varied climate forcings.
 - c. Identify dominant climate variables based on the simulated impact of each variable on Lake System performance.
 - d. 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

Articles in Refereed Scientific Journals

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*, 47, 3, doi/10.1111/j.1752-1688.2011.00552.x.

Book Chapter

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.

Other Publications

Hydroclimate Synthesis Report for the International Upper Great Lakes Study. Casey Brown, Paul Moody, Danica Lefever, Jesus Morales. IUGLS.

3. A Remote Sensing Algal Production Model to Monitor Water Quality and Nonpoint Pollution in New England Lakes (USGS 2011MA286B)

Primary Principal Investigator: Mi-Hyun Park University of Massachusetts Amherst

Start Date: March 1, 2011

End Date: Feb 28, 2012

Reporting Period: March 1, 2011 – June 30, 2012

Funding Source: USGS (104B)

Research Category: Water Quality

Focus Categories: Water Quality, Nutrients, Surface Water

Problem and Research Objectives



Many lakes in New England suffer algal blooms because of agricultural and urban runoff and wastewater discharges. Algal blooms deplete oxygen levels and degrade the quality of receiving waters. Algae also cause discoloration and foul taste in drinking water supplies and toxins that are capable of poisoning animals and/or humans. Therefore there is a need for regional algal monitoring programs to manage water resources and protect human health.

Traditional algal bloom monitoring usually requires shipboard field sampling programs accompanied by laboratory analyses to determine *in situ* concentrations of aquatic chlorophyll *a*, a photosynthetic pigment used as a proxy to measure algal biomass (Coskun *et al.*, 2008; Carlson, 1977). The time and resources required to effectively monitor a lake's algal blooms *in situ* limit the spatial and temporal resolution of these datasets. Large algal blooms often shift and change composition dramatically in a short period of time, influenced by rainfall and wind, among other factors, and measured algal concentrations may not be representative of levels throughout the lake (Shafique *et al.*, 2001).

Satellite measurement is especially useful in lakes and inland waters because of the inherent spatial heterogeneity of phytoplankton (Ekstrand, 1992). The unique spectral absorbance/reflectance characteristics of chlorophyll-*a* provide a means to measure blooms over large areas at a temporal and spatial resolution unattainable by field methods (Richardson, 1996; Park and Ruddick, 2007). This study will develop a bio-optical model specific to Lake Champlain using available *in situ* and satellite data. The model will provide for timely and cost-effective monitoring of algal bloom distribution in the lake.

Alternatively, we used satellite remote sensing for regular, synoptic coverage of algal blooms because satellites can scan entire regions of the earth with frequent revisit times. The objectives of this study are to establish an effective satellite algal production model that can be used to remotely monitor the spatial and temporal distributions of algal blooms in Lake Champlain and to evaluate the predictive ability of the satellite model.

Methodology

The study area is Lake Champlain, bordered by New York, Vermont and Quebec, Canada, a good case study for a New England lake because blooms of algae and cyanobacteria (also called blue-green algae, one of the harmful algae) have become an increasing problem in the lake over the past two decades. The models developed in this study are based on *in situ* water quality data for Lake Champlain, obtained from the Vermont Department of Environmental Conservation and the Lake Champlain Basin Program between 2006 and 2009.

We conducted satellite image remote sensing using Landsat Enhanced Thematic Mapper Plus (ETM+) images obtained from the U.S. Geological Survey Earth Resources Observation and Science Center. A satellite overpass time window of ± 1 day was used to establish coincident pairs and processed with ENVI (Ver. 4.7, ITT®) and ArcGIS (Ver. 9.3, ESRI®). All satellite images of coincident pairs from *in situ* sampling data were converted to exoatmospheric reflectance for standardized comparison of data among multiple images.

The remote sensing chlorophyll *a* algorithms were developed based on step-wise multilinear regression with single-band input and non-reciprocal reflectance band-



ratios. The regression models were calibrated and crossvalidated using coincident pairs from the late summer bloom period (July 20th to September 10th), obtained between 2006 and 2009. The best single band and band-ratio models were then applied to entire satellite scenes to estimate chlorophyll *a* and algal blooms for the entire lake.

Principal Findings and Significance

The regression models provided the most significant band information of satellite imagery for detecting chlorophyll *a* pigments that can be used for estimating algal blooms. The final chlorophyll-*a* models based on the single band model and band ratio model are presented by the following equations:

$$\text{chlorophyll } a (\mu\text{g L}^{-1}) = 14.37 - 685.19(R_{B1}) + 905.94(R_{B2}) \quad (1)$$

$$\text{chlorophyll } a (\mu\text{g L}^{-1}) = -46.51 + 105.30(R_{B2}/R_{B1}) - 40.39(R_{B3}/R_{B1}) \quad (2)$$

where R_{B1} , R_{B2} and R_{B3} are the normalized exoatmospheric reflectance values for Landsat ETM+ bands 1, 2 and 3, respectively. R_{Bi}/R_{Bj} stands for the reflectance ratio of the *i*th band over the *j*th band.

The single band model regression model (Eq.1) showed green band (B2) and blue band (B1) to be the most significant chlorophyll *a* predictors. This is a key difference from other studies. Previous studies had found Landsat's red-sensitive band (B3) useful in single band chlorophyll *a* models because it is least sensitive to atmospheric effects, yet it has the lowest penetration distance in the water column (Richardson, 1996; Sass *et al.*, 2007). The regression model with Band 2 and Band 3 gave similar coefficients of determination (R^2) but higher root mean square errors. The difference is likely due to the collection method of chlorophyll *a* water samples in Lake Champlain. All chlorophyll *a* samples were collected as representative composites of the photic zone, defined as twice the Secchi depth at the time of sampling. The higher water column penetrations achieved by Landsat ETM+ bands 1 and 2 may give better predictions of phytoplankton present in the entire photic zone rather than surficial concentrations collected via grab sampling. It should be noted, however, that ETM+ bands 1 and 2 are more susceptible to atmospheric interference, therefore limiting this single band model to clear sky coincident pairs.

The band ratio model (Eq. 2) slightly outperformed in terms of R^2 the single band model by using the ratio of the chlorophyll *a* green reflectance peak to the blue reflectance minimum, as well as the ratio of the red reflectance trough to the blue reflectance minimum. These two ratios maximize the effects of three distinctive optical features of chlorophyll *a*. The improved performance of the band ratio model over the single band model agrees with the findings of past studies (Vincent *et al.*, 2004) that found more robust results using band ratios. The algal models based on regression analysis also provide similar results.

Table 1. Regression Model Performance

	R_{B1}, R_{B2}	R_{B2}, R_{B3}	$R_{B2/1}, R_{B3/1}$
R^2	0.76	0.85	0.78
RMSE ($\mu\text{g/L}$)	2.11	4.46	2.17

The resulting algal model was applied to satellite imagery to estimate the chlorophyll *a* and algal blooms.

Figure 2 shows a time series of resulting Landsat ETM+ images for chlorophyll *a* and algal blooms in Missisquoi, one of the most eutrophic areas of lake. The results provide the distribution and propagation of chlorophyll *a* and algal blooms. The results of bloom patterns from July 24, August 9 and August 24 show significant concentrations forming in the northeastern side of the Bay, in close proximity to a major tributary (Pike River) while the result on September 10 shows significant concentrations forming in the southern side of the Bay, in close proximity to a major tributary (Missisquoi River). The July and September images show the most intense blooms compared to August. Our approach demonstrates the utility of the satellite based algal models for the purposes of bloom detection and monitoring. The spatial distribution of algal blooms shows similar patterns compared to the distribution of chlorophyll *a*.

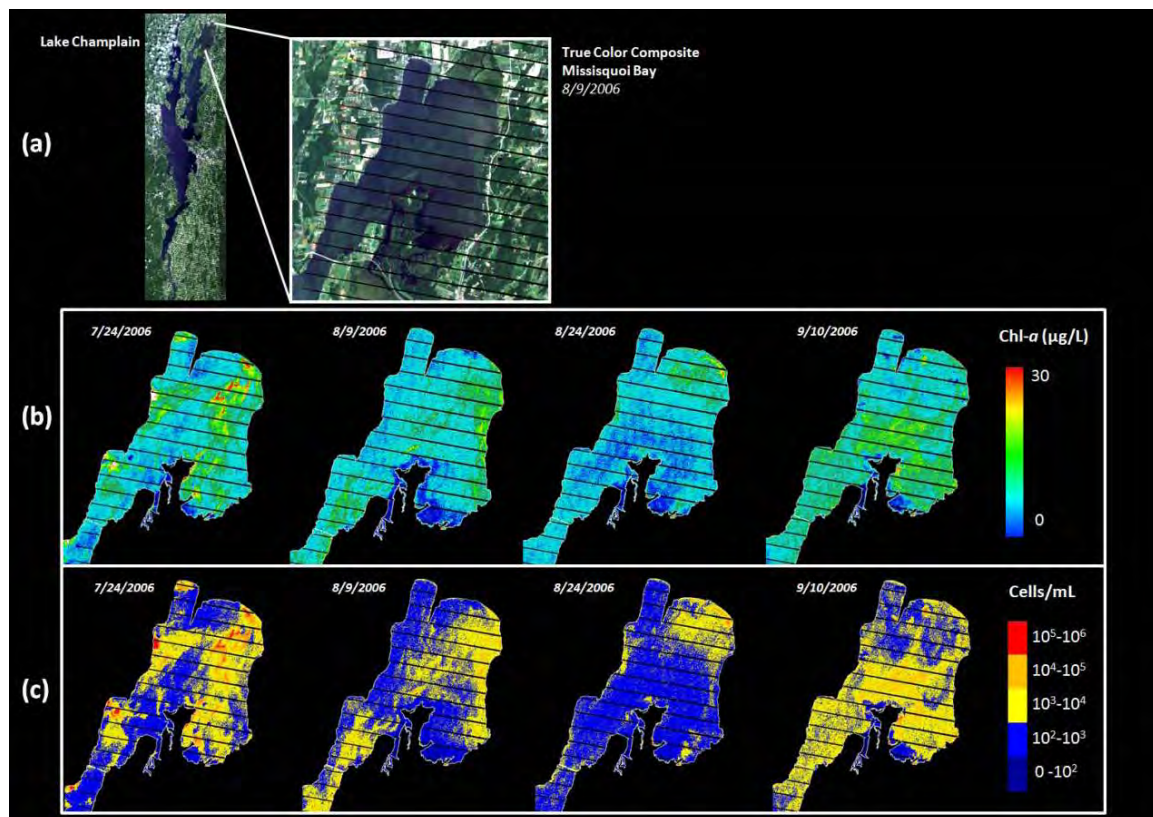


Figure 1. Landsat ETM+ algal prediction model results. (a) True color composites of Lake Champlain and location of Missisquoi Bay cell densities from *in situ* measurements; (b) Chl-*a* concentrations in Missisquoi Bay; (c) Approximate total phytoplankton densities in Missisquoi Bay. The black lines are data gaps due to the sensor's 'SLC-off' condition

The Landsat ETM+ model results were also used to assess how precipitation and river discharge impact bloom formation in Missisquoi Bay. Figure 3 shows daily precipitation data (NOAA NCDC) at Philipsburg station in Canada, located in the vicinity of Missisquoi Bay from July 10 to August 10, 2006 plotted. The data show that the impact of precipitation events on chlorophyll *a* blooms, which are inferred by the model results near the outlets of two major tributaries that discharge to Missisquoi Bay. On July 24, high chlorophyll *a* blooms were detected near the outlet

of the Missisquoi and Pike Rivers whereas on August 9, the areas around the outlets of the Missisquoi and Pike Rivers are very low in cyanobacteria, with higher concentrations forming along the central and eastern portion of the bay. Between the July 24 and August 9 Landsat 7 ETM+ flyovers, a significant precipitation event (0.46 inch) occurred on July 22, just two days before the flyover on July 24. The introduction of nutrients in the stormwater runoff on July 22 likely caused the blooms near the outlets. Between July 31 and August 1, severe precipitation (0.45 inch and 0.90 inch, respectively) occurred about a week before the Landsat flyover on August 9. After the large storm, the distribution of the blooms could shift and subsequent dry days and a small precipitation event (0.07 inch) on the day before the August 9th flyover likely lead to low levels of blooms at the mouths of the two rivers. The bloom initiation and propagation in Lake Champlain could shift within a week. More research should be conducted to confirm this theory, but it demonstrates the power of synoptic coverage of cyanobacteria in determining the drivers of algal blooms.

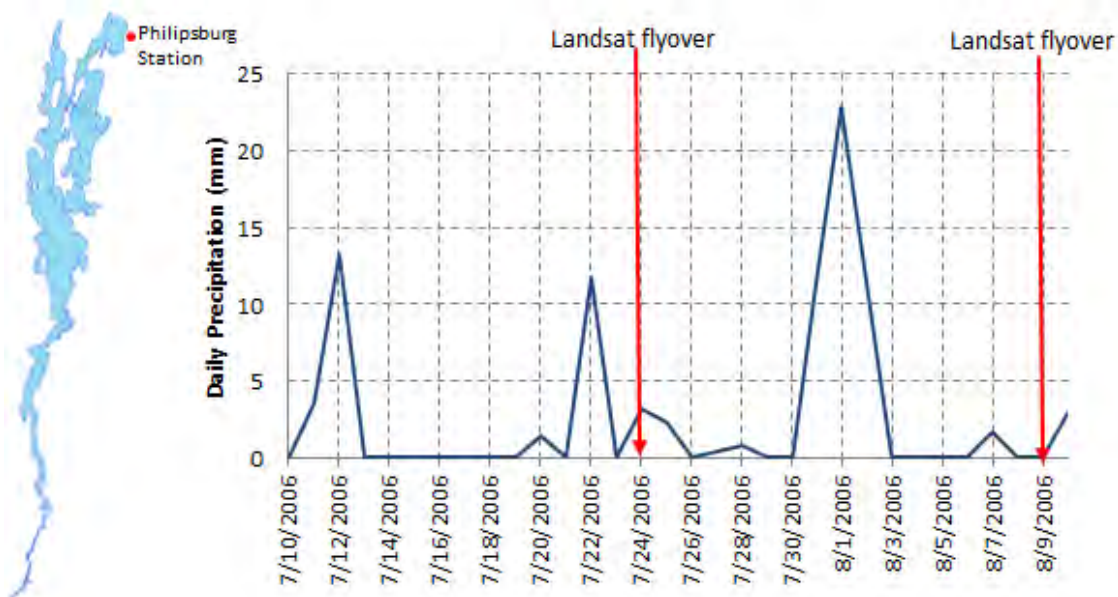


Figure 2. Daily precipitation data recorded at the Enosburg Falls and Burlington Airport weather stations

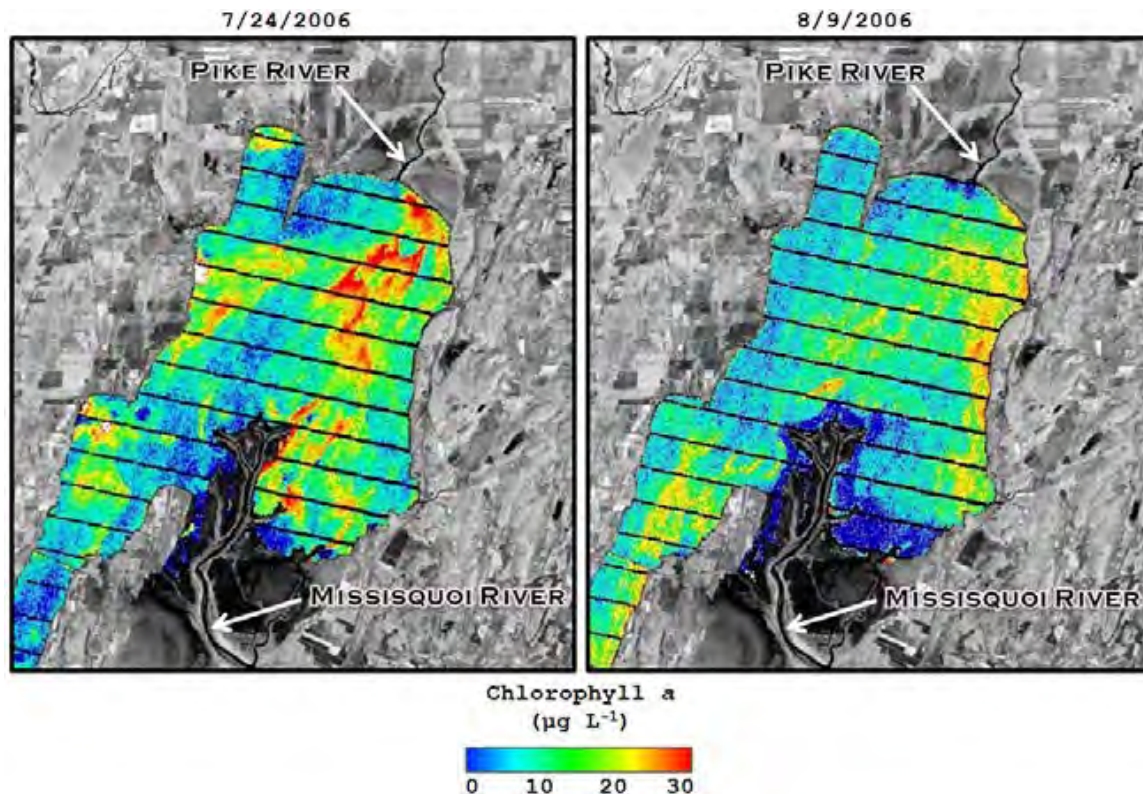


Figure 3. Chlorophyll *a* distribution over Missisquoi Bay on July 24 and August 9, 2006

This study demonstrates how remote sensing models can be developed for lake monitoring programs at relatively low cost. Moreover, our results serve as basis for retrospective study when *in situ* data are not available and provide important information for Lake Champlain resource management. The result can be used for further study to identify the major drivers of algal blooms; and to use it in the early detection of algal blooms.

References

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Student Support

Adam Trescott, Master student, Department of Civil & Environmental Engineering, UMass Amherst

Elizabeth Isenstein, Master candidate, Department of Civil & Environmental Engineering, UMass Amherst

Notable Achievements and Awards

This fund was used to conduct current research and support students. The results in this study have been used to prepare new proposals and will be used to prepare NSF Career Award for preliminary research. The results were also used to present at the workshop for Lake Champlain stakeholders and researchers: "Bay and Basin Missisquoi Bay."

4. Monitoring and Understanding Water Quality at Three Potential Charles River Swimming Sites (USGS 2011MA287B)

Principal Investigator: Dr. Ferdi Hellweger, Northeastern University

Start Date: 3/1/2011

End Date: 2/28/2012

Reporting Period: March 1, 2011 – February 28, 2012

Funding Source: USGS (104B)

Research Category: Water Quality

Focus Categories: Surface Water, Recreation, Water Quality

Problem and Research Objectives

The Charles River has a long and often publicized history of pollution, and has been closed for primary contact (swimming) for about 80 years. In 1995 the US EPA established the Clean Charles River Initiative with the explicit goal of making the river swimmable by 2005. The EPA's prioritization of the Clean Charles River Initiative led to a massive public investment of over \$500 million dollars by the MWRA, BWSC, and other utilities, as well as adjacent municipalities, over the past decade and a half. This clean-up effort has resulted in improved water quality - to the extent that swimming is now a real possibility. In 2009 the Massachusetts legislature established the Charles River Water Quality Commission to study the feasibility of returning public access swimming to the Charles. On a broader scale, opening up a swimming location on the Charles River would make it one of the first urban rivers in the US to be fully reclaimed from pollution to support swimming.

An important task is to determine the water quality at candidate swimming locations. A number of ongoing monitoring efforts (e.g. Charles River Watershed Association,



CRWA) provide data, but only at a relatively coarse spatial and temporal resolution. To determine the water quality at specific swimming locations at a high temporal resolution, we performed water quality monitoring in Summer 2010. That project provided some insight into the water quality, but also identified additional research needs.

Methodology

The Summer 2010 project included monitoring of *E. coli*, turbidity and temperature at 5 potential swimming locations, including Riverside Boat Club (proximity Magazine Beach), MIT Sailing Pavilion, Esplanade Dock, Lee Pool and New Basin. This included daily monitoring by grab sampling as well as hourly monitoring using two ISCO autosamplers.

In Summer 2011, we performed daily sampling of *E. coli*, turbidity, temperature, cyanobacteria cell counts, temperature, turbidity and nutrients at three potential swimming locations from June 1 through August 15. In addition, we deployed an ISCO autosampler for hourly sampling.

The 2010 and 2011 data are being analyzed for relation to long-term monitoring data collected by CRWA and MWRA, and considering dam operation and wind variables.

Principal Findings and Significance

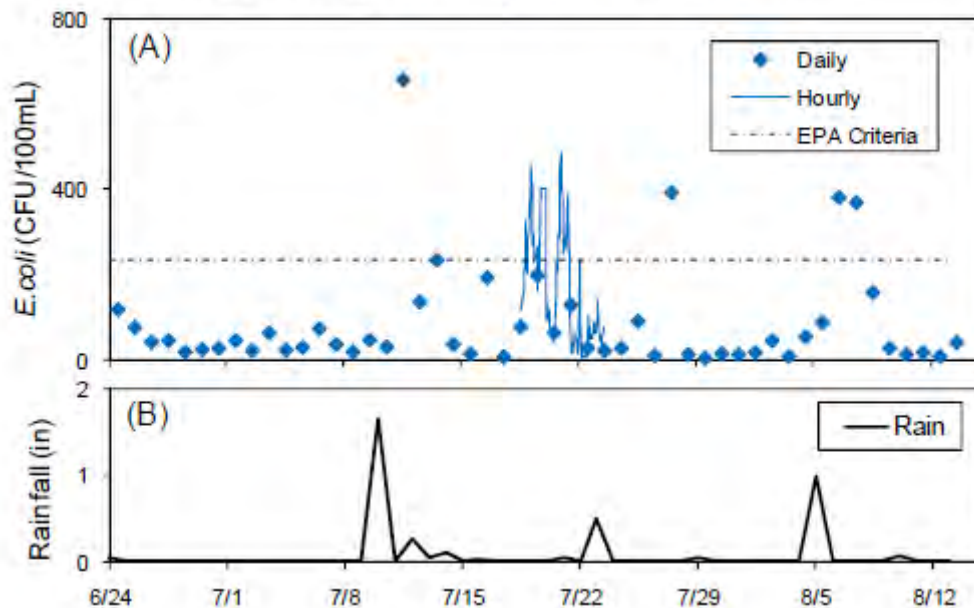
Results from 2010 Monitoring

Some results are presented in Table 1 and Figure 1.

**Table 1. Summary of
Violations of Swimming
Criteria (235 CFU/100mL)**

Site	Daily	Hourly
Riverside	11%	31%
MIT	8%	6%
New Basin	3%	0
Lee Pool	24%	-
Esplanade	8%	1%

Fig. 1. Daily & Hourly *E. coli* at Riverside



Some conclusions from the 2010 sampling include:

1. The water quality at the 5 locations differs significantly (Table 1), which helped narrow down the list of potential swimming locations (e.g. Lee Pool is not a good location).
2. *E. coli* increases after large storms (Figure 1), consistent with past monitoring data.
3. *E. coli* can vary significantly within a 24-h period (Figure 1), so daily data may not be representative.
4. 18-h counts are highly correlated to 24-h counts (R^2 0.96-0.99), so mid-day *E. coli* densities on one day can be available in the morning of the next day.
5. ISCO autosampler results, which exceed the 6-h holding time, are in reasonable agreement with daily grab samples, so this seems to be a feasible monitoring method.

Additional research needs: Monitoring and data analysis

- The 2010 results provide some insight into the water quality at the candidate swimming locations, but more research is needed. Specifically, our sampling period included only a small number of large storms (Figure 1) and no medium storms (0.5-1.0 in). Additional data are needed to characterize the water quality over a wider range of precipitation events.
- Even with an additional summer of monitoring, the database will be limited. One potential solution is to relate the water quality at the candidate swimming locations to those of other longterm monitoring efforts. For example: It may be that the *E. coli* density at MIT is typically twice that of CRWA's Mass Ave location. This would allow for the relation of our data to the long-term record - and the statistical models developed by CRWA.
- Once the best swimming location has been identified and implemented, it has to be managed using a beach closing model. Those models are typically regression equations of *E. coli* density to various meteorological parameters (mostly rain). Our data show that the water quality can change significantly



within a day and previous research (Hellweger and Masopust, 2008) show that this may be due to dam operation and/or wind. The data need to be analyzed considering those variables.

- In addition to *E. coli*, cyanobacteria blooms have been identified as a threat to swimming in the Charles. As with *E. coli*, several monitoring efforts are characterizing cyanobacteria cell densities and toxin concentrations, but no information is available at candidate swimming sites.

The 2011 sampling significantly expanded (doubled) the database of water quality at candidate swimming locations, and helped tie it into other monitoring efforts and contributes to understanding trends. These results are of critical importance to determine the feasibility of swimming, locating the most promising site and developing a management program.

The resulting database consists of about 2,000 *E. coli* data points. The data allowed us to quantify differences in water quality between the potential swimming locations. We also observed that best correlation between *E. coli* and precipitation was found by lagging the precipitation by one or two days. The hourly data can show significant variability within the day, with typically higher concentrations at night. Our cyanobacteria data reveal strong dynamics, including blooms and population crashes, the causes of which are not immediately clear. Unlike for *E. coli*, we don't have a good understanding of what drives the dynamics of cyanobacteria.

We are presently analyzing the data and are preparing a manuscript for publication in a peer-reviewed journal.

We co-organized workshop entitled "Swimming-related water quality in the Charles River " at EPA/NE, Chelmsford, MA.

Student Support

- One graduate student pursuing PhD in Civil Engineering at Northeastern University.
- Two high school students.
- Two high school teachers.

Notable Achievements and Awards

- PI Hellweger was awarded the 2012 Environmental Merit Award by the EPA, for his research on the water quality of the Charles River.
<http://www.northeastern.edu/news/2012/04/swimming-in-that-dirty-water/>
- PI Hellweger submitted a proposal to NSF/CMMI entitled "Collaborative Research: Identification and Model (in)Validation of a Class of Switched Nonlinear Systems with Applications to Urban Water Quality". The proposal is pending.
- PI Hellweger and graduate student Ruan were awarded the 2011 Volunteer Recognition Award by the Charles River Conservancy, for their research on the water quality of the Charles River.

Publications and Conference Presentations

Articles in Refereed Scientific Journals

Ruan, X. and others. Paper documenting results of Charles River water quality research conducted in 2010 and 2011. In preparation.



Hellweger, F. L., Ruan, X., Cherchia, E., Sanchez, S. 2012. Applicability of Standard Antibiotic Toxicity Tests to the Ambient Aquatic Environment. *Annals of Environmental Science* 5(1), 8.

Other Publications

Xiaodan Ruan, Sarah Sanchez, Kellie Burtch, Diana Cost, Rebecca Powers, Julia Leung, Robert Cost, Ferdi Hellweger. 2012. Swimming in Urban Rivers in the US is no longer an Imagination— a two-year case study of Charles river. RISE 2012: Research and Scholarship Expo, Northeastern University, Boston, MA (Poster). <http://www.northeastern.edu/rise/?presentations=swimming-inurban-rivers-in-the-us-is-no-longer-an-imagination-a-two-year-case-study-of-charles-river>

Xiaodan Ruan, Diana Cost, Kellie Burtch, Julia Leung, Rebecca Powers, Robert Cost, Ferdi Hellweger. 2011. Are You Going to Jump in the Charles in 2012?!. Charles River Water Quality Workshop. EPA New England Lab, Chelmsford, MA.

Hellweger, F. L. 2011. Boston's Charles River: E. coli, models, satellites, cyanobacteria, economics and mutants. Research Seminar. Camp, Dresser & McKee University (CDMU), Cambridge, MA.

Hellweger, F. L., Ruan, X., Cherchia, E., Sanchez, S., 2011. Applicability of standard antibiotic toxicity tests to the ambient aquatic environment. SETAC Annual Conference, Boston, MA (poster).

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

Principal Investigator: Dr. Andrew Ramsburg, Tufts University

Start Date: 6/7/2011

End Date: 2/28/2013

Reporting Period: June 7, 2011 – February 29, 2012

Funding Source: USGS (104B)

Research Category: Water Quality

Focus Categories: Hydrology; Water Quality; Water Quantity

Descriptors: Pharmaceuticals, emerging contaminants, nitrification

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 strict 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 suggested 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 (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 human and 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 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 survey on Cape Cod detected 43 microconstituents among 14 sampling sites that included wastewater influents and drinking water supplies (Zimmerman, 2005).

Pharmaceutically active compounds 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) pharmaceuticals 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 pharmaceuticals may be better removed where wastewater treatment is 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 pharmaceutical 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 is to fill key data gaps related to whether or not nitrifying bacteria are partially responsible for observations of pharmaceutical degradation in treatments designed for enhanced removal of nutrients. This overall objective will be met by focusing on three specific objectives: (i) elucidation of the rates of pharmaceutical attenuation by nitrifying organisms, (ii) identification of the metabolites produced during the nitrification process, and (iii) development of modeling tools for prediction of pharmaceutical degradation within the context of enhanced nutrient removal.

Methodology

A series of batch experiments is being conducted to evaluate the sorption and biodegradation of five selected pharmaceuticals (atenolol, diazepam, metoprolol, naproxen and sotalol) in nitrification activated sludge systems. Note that topiramate was replaced by sotalol (a beta-blocker) as the latter is more relevant to this project. Evaluation of sotalol, along with atenolol, and metoprolol will enable us to assess attenuation within a family of beta blockers that differ by one-to-two functional groups, which our initial experiments suggest has an important influence on the degradation (see results below).

Pharmaceutical sorption is being evaluated using batch experiments setup in 30 ml foil covered glass vials with teflon caps. Each vial contains mixed liquor from our



nitrification sequencing batch reactor (SBR) and the target pharmaceutical at concentrations in the range of 500 ng/L to 50 µg/L. Sorption of the pharmaceutical at each concentration is assessed in triplicate. Homogenous samples are collected every six to eight hours. Samples are centrifuged and the pharmaceutical concentration in the aqueous phase is measured. The sorbed pharmaceutical concentration (µg /g-suspended solids) is calculated. Equilibrium is considered to have been achieved when the measured aqueous pharmaceutical concentration of three successive samples is 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) is calculated for each pharmaceutical.

Experimental protocols for our degradation experiments include controls (in the absence of pharmaceutical) for (i) nitrification (i.e., ammonia + nitrite oxidation), (ii) ammonia oxidation, and (iii) nitrite oxidation. These controls characterize the microbial consortia obtained from our nitrification sequencing batch reactor before each experiment. Nitrification experiments that contain pharmaceutical are conducted in duplicate and include controls for pharmaceutical degradation during (i) ammonia oxidation when nitrite oxidation is inhibited by low concentration of sodium azide (<20 µM, (Ginestet et al., 1998)) (nitration control), (ii) nitrite oxidation when $\text{NO}_2\text{-N}$ is added rather than $\text{NH}_4\text{-N}$, and (iii) inhibition of ammonia oxidation using allylthiourea (ATU). Time course samples are collected to quantify pertinent solutes during the experiment. Samples are analyzed for the pharmaceutical (HPLC), pharmaceutical metabolites (HPLC), ammonia (Hach test), nitrite (IC), and nitrate (IC). Biomass for all experiments is taken from a nitrification enrichment sequencing batch reactor (Nit-SBR) maintained in the PI's laboratory. The Nit-SBR is continuously operated with a feed with ammonia and without the any exogenous organic carbon. Pharmaceutical degradation data will be fit using kinetic models for each pharmaceutical that incorporate the relevant modules from the Activated Sludge Model framework (Henze et al., 2000).

Principal Findings and Significance

Research in this reporting period focused on evaluating the sorption and degradation of three beta-blockers: atenolol (ATN), metoprolol (MET) and sotalol (SOT) during nitrification. Results from the batch sorption experiments suggest that sorption to biomass holds limited potential for attenuating these pharmaceuticals during wastewater treatment. 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 ± 0.03 and 0.09 ± 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) sorption data for pharmaceuticals - a total of 309 measured sorption coefficients that include 65 pharmaceuticals. Since the full details of the study are available in a manuscript submitted for publication in *Water Research*, focus here will be placed on the key findings. One of the aspects we wanted to explore was the role of experimental protocols (experiment type, inactivation method, etc) on the assessment of pharmaceutical sorption. It turns out that data for this type of assessment are limited by a lack of diversity in the way these experiments are conducted. Most protocols employ batch experiments with no inactivation (or the study does not report inactivation). The available data are, in

many cases, characterized by a high degree of variability. This variability masks any effect related to the protocol (Figure 1 and Figure 2) (i.e., no statistically significant difference can be attributed to experimental protocols).

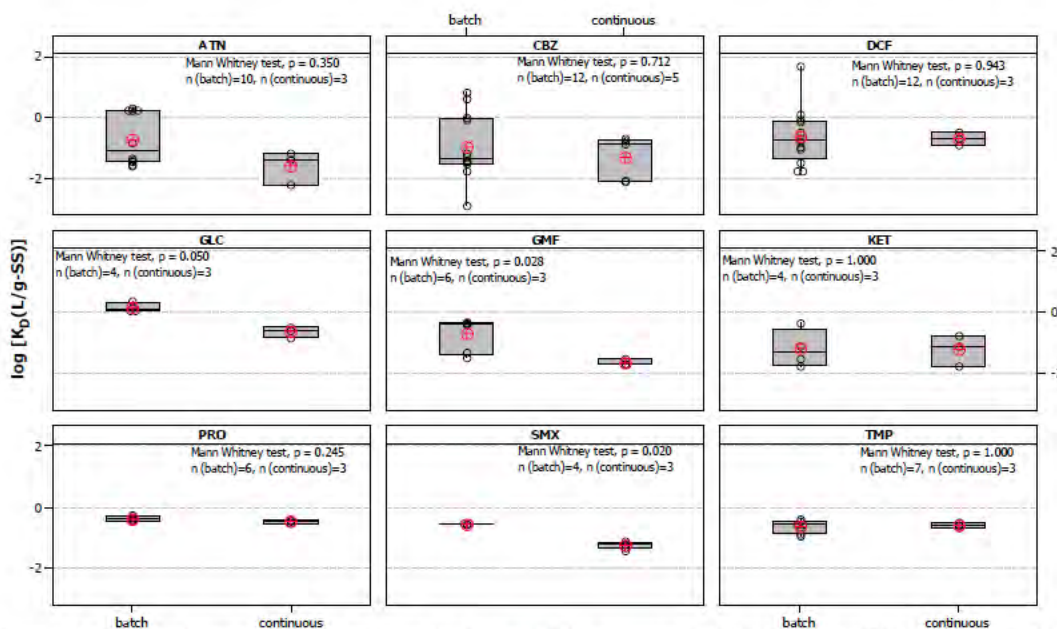


Figure 1. Comparison of measured sorption coefficients for atenolol (ATN), carbamazepine (CBZ), diclofenac (DCF), glibenclamide (GLC), gemfibrozil (GMF), ketoprofen (KET), propranolol (PRO), sulfamethaxazole (SMX) and trimethoprim (TMP) from batch and continuous experiments. Individual data points shown 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.

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 (as described by a linear distribution coefficient, KD) to the octanol-water distribution coefficient for the Equations (1) and (2) illustrate how KOW values can be corrected to produce distribution coefficients (D) for monoprotic acidic and basic compounds, respectively (Sangster, 1989).

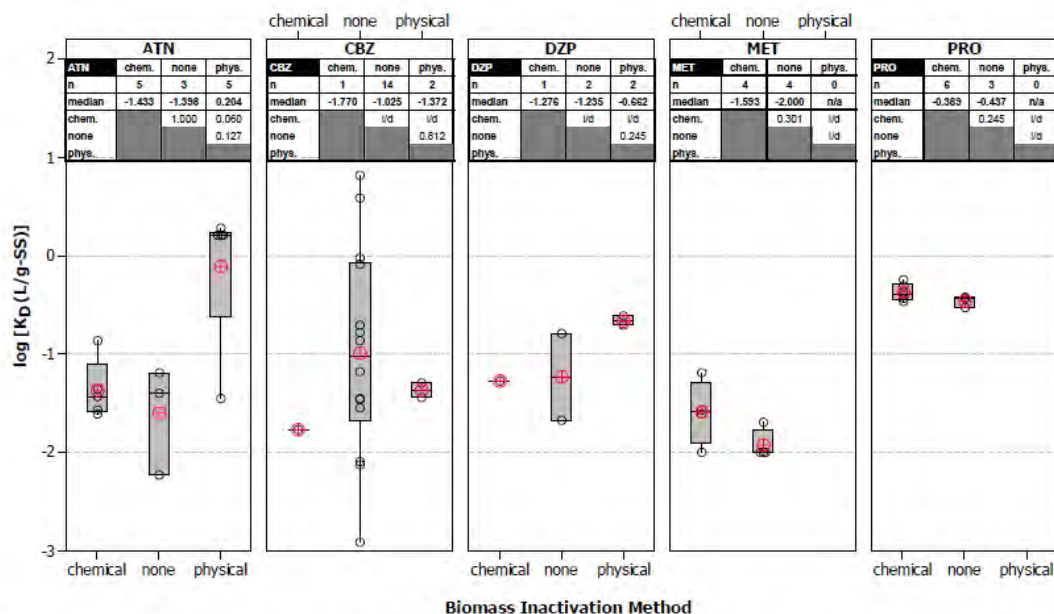


Figure 2. Measured Sorption Coefficients for atenolol (far left), carbamazepine, diazepam (middle), metoprolol and propranolol (far right) from batch and continuous experiments using chemical inactivation (e.g., NaN_3) no biomass inactivation, and physical inactivation (e.g., lyophilization). Individual 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 $\log[K_D(\text{L/g-SS})]$ 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).

For multiprotic systems, where multiple species may exist in solution simultaneously, $\log D$ was calculated using Marvin 5.6.0.4, 2011, ChemAxon (<http://www.chemaxon.com>).

$$D_{\text{Acidic-PhAC}} = K_{\text{OW,Acidic-PhAC}} \left[1 + 10^{pH - pK_A} \right] \quad (1)$$

$$D_{\text{Basic-PhAC}} = K_{\text{OW,Basic-PhAC}} \left[1 + 10^{pK_A - pH} \right] \quad (2)$$

Despite the importance of accounting for pH when assessing pharmaceutical sorption, only four studies report the pH at which the experiments were conducted (Urase and Kikuta, 2005; Abegglen et al., 2009; Horsing et al., 2011; Stevens-Garmon et al., 2011). The influence of pH can be seen in Figure 3 which shows data from these four studies. Note that attempts to correlate KD to KOW results in poor predictive power as assessed by adjusted R^2 and the Nash-Sutcliffe Efficiency (NSE) of the best fit correlations. Moreover, the pH correction fails to improve the correlations to a level that is meaningful for the prediction of pharmaceutical sorption to biomass.

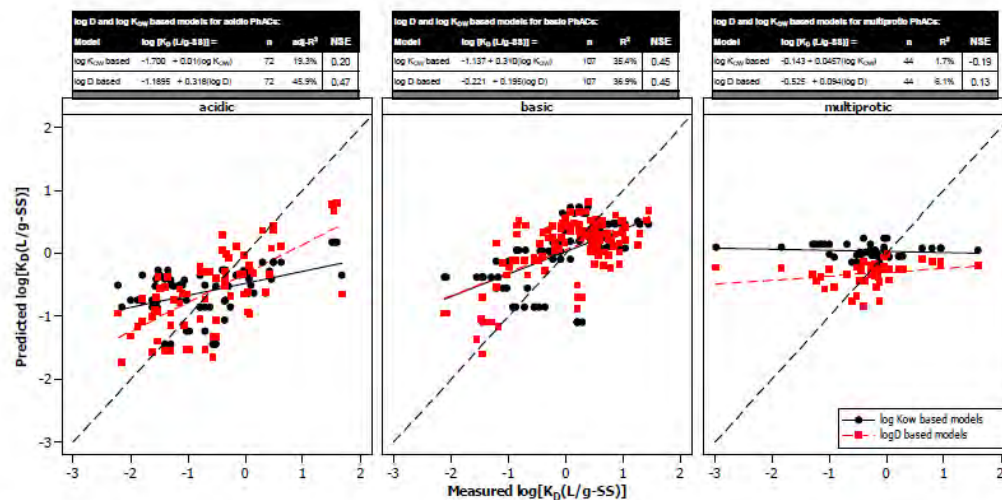


Figure 3. Reported log K_D values with predictions using one parameter models based on log K_{ow} (top panels) and pH corrected octanol-water partitioning coefficient (log D) (bottom panels) for acidic (left), basic (middle), and multiprotic (right) PhACs using data from available sorption studies.

These results suggest that reliance upon K_{ow} and D alone may be inappropriate when considering pharmaceutical sorption. Thus, we attempted to correlate the observed sorption (as described by KD) to molecular descriptors of the solute including molecular weight (MW), molecular volume (MV), aromaticity, number of rotatable bonds (n.RB), hydrogen bonding capacity (hydrogen bond donors- n.HBD and acceptors- n.HBA) 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 (adj- R^2) and predicted r-square (pred- R^2). Model residuals were checked for homoscedasticity; multicollinearity between model variables was evaluated.

Interestingly the correlation and predictive capability for these types of models was found to plateau at approximately 60% for both acidic and basic pharmaceuticals (Figure 4). Also, the approach was ineffective for multiprotic pharmaceuticals (no models with statistically-significant parameters were found to characterize the data set). The NSEs of the best fit four parameter models are 0.622 (acidic pharmaceutical correlation) and 0.603 (basic pharmaceutical correlation), which suggests that while the best polyparameter models offer improvement over previously establish correlations, none can be characterized as having strong predictive power (i.e., $NSE > 0.7$, McCuen et al., 2006). We hypothesize that the performance plateau results from only including solute-based descriptors, and suggest greater emphasis be placed on characterization of the sorbent in studies examining pharmaceutical sorption to suspended solids present in biological treatment units.

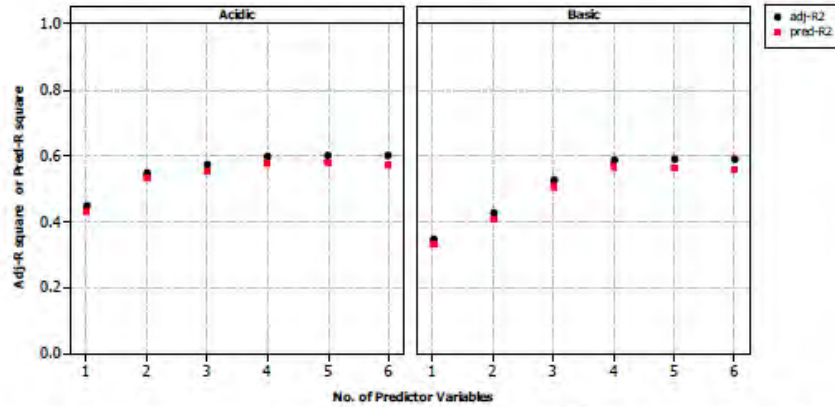


Figure 4. Evaluation of model correlation (adj-R^2) and predictive (pred-R^2) capabilities for log D based models for K_D for acidic (left panel) and basic (right panel) PhACs.

To assess whether or not sorption to biomass is an important attenuation mechanism for pharmaceuticals during biological waste treatment, we examined pharmaceutical removal as a function of operational conditions (specifically SRT, MLSS and HRT) assuming a priori knowledge of K_D (since our research, as described above, suggests predictive models require greater refinement). The fraction of pharmaceutical mass removal via sludge wasting ($f_{\text{PhAC-WAS}}$) was calculated as a function of K_D using Equation 3.

$$f_{\text{PhAC-WAS}} = \frac{\left(X \cdot \frac{\text{HRT}}{\text{SRT}} \right) \cdot K_D}{1 + \left(X \cdot \frac{\text{HRT}}{\text{SRT}} \right) \cdot K_D} \quad (3)$$

Where X is the biomass concentration, HRT is the hydraulic retention time and SRT is the solids retention time. As can be seen in Figure 5, sludge wasting is most relevant for PhACs having K_D greater than 1.00 L/g-SS. Note that a $K_D=1.00$ L/g-SS corresponds to the 70th percentile of all available data for pharmaceutical sorption on biomass.

Consider that sludge wasting even in an activated sludge processes having a 6-hour HRT and operated at a 1-day SRT with 2 g/L MLSS (i.e., $X \cdot \text{HRT}/\text{SRT} = 0.5$ gMLSS/L) for BOD removal (e.g., Deer Island Treatment Plant), accounts for no greater than 25% of the mass of most pharmaceuticals entering the treatment unit. Removal of pharmaceuticals through sorption alone (via WAS) in the high-rate system is greater than 50% only if $K_D > 2.00$ L/gMLSS - a K_D value which corresponds to the 77th percentile of reported values for K_D . Removal via WAS will be even less relevant for the majority of pharmaceuticals as the growth of activated sludge WWTPs operated at longer SRTs to achieve nutrient removal continues as WWTPs in the Northeast move towards more stringent nutrient removal targets. One option for meeting nutrient targets is through the use of MBRs. Although the high mixed liquor concentration of MBRs may be advantageous for sorption of pharmaceuticals having relatively higher K_D , MBRs are often used in process configurations with a long SRT

(e.g., Ng and Hermanowicz, 2005). Thus, the benefit of sorption as potential pathway for pharmaceutical removal is often times offset by limited sludge wasting. For example, in an MBR operating under typical nitrifying conditions (SRT = 15 d, HRT = 8 h, MLSS = 10 g/L - i.e., $X \cdot \text{HRT} / \text{SRT} = 0.22$ gMLSS/L), less than 10% of the mass of most pharmaceutical is removed through sorption to WAS. Results from these calculations suggest that pharmaceutical attenuation via sorption and wasting has only limited relevance in most biological treatment systems.

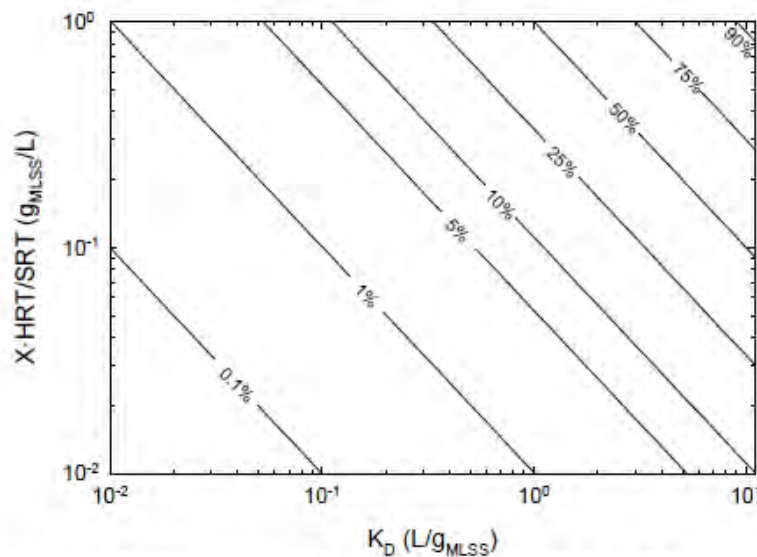
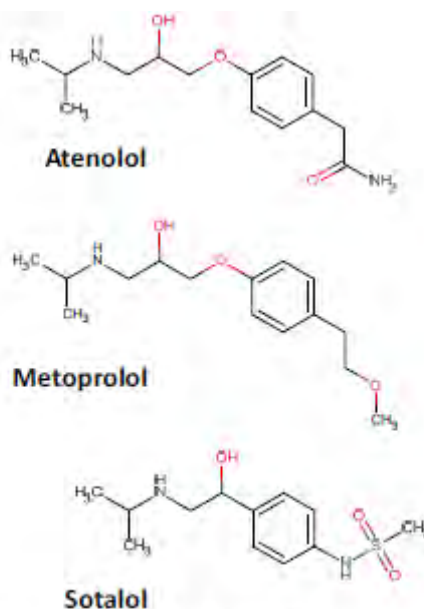


Figure 5. Contour plot showing fraction of PhAC removed from a biological reactor in waste activated sludge (WAS) based on PhAC K_D (x-axis) and operating conditions – MLSS(X), HRT and SRT (y-axis).

Research during this reporting period also examined the biodegradation of ATN, MET and SOT during nitrification. Experiments were conducted in fully aerated, 3 L borosilicate glass, batch reactors containing 400 mg/L VSS and a feedstock consisting of ammonium sulfate, potassium phosphate, and micronutrients. The initial ammonia-nitrogen concentration in each batch reactor is between 15-20 mg-N/L. Initial pharmaceutical concentration in each reactor was 20 $\mu\text{g/L}$ (each pharmaceutical was evaluated separately). Concentrations of ammonia, nitrite, nitrate, biomass, and pharmaceutical were quantified over the course of a 12-hour period as described in the method section. Data were then used to model the kinetics of the nitrification process and pharmaceutical degradation in systems where ammonia oxidation was uninhibited and inhibited. Relevant data for each of these three pharmaceuticals is shown in Table 1 and the molecular structures are shown in Figure 6.

Table 1. Pharmaceuticals studied in this reporting period.

pharmaceutical (class)	MW (g/mol)	Log K _{ow}	TPSA (Å ²)	rot. bonds	% aromatic carbons	numb. H-bond sites	typical trade names	typical concentrations in wastewater influent (ug/L)
Atenolol (β blocker)	266.34	0.16	84.60	8	43%	7	Tenormin, Atenolol	— 2.3 (Ternes et al., 2007; Miege et al., 2008)
Metoprolol (β blocker)	259.34	3.48	41.49	6	40%	6	Lopressor	0.21-0.25 1.80-2.60 (Siemens et al., 2008)
Sotalol (β blocker)	272.4	0.24	78.4	6	50%	8	Betapace	0.4 – 2.0 0.64-0.83 (Gabet-Giraud et al., 2010) (Vieno et al., 2006)


Figure 6: Chemical structures of atenolol, metoprolol and sotalol.

To explore whether or not the presence of the pharmaceutical influences the rate of nitrification, we fit nitrification rates for the reactors on containing (~20 µg/L) pharmaceutical and those for reactors serving as the nitrification control (no pharmaceutical). For atenolol, the average nitrification rate in the control was 3.97 ± 0.42 (mg-N/g-VSS.h). In each of the reactors containing the pharmaceutical, these rates were 4.00 ± 0.43 , and 3.95 ± 0.53 (mg-N/g-VSS.h). Therefore, it appears that atenolol has no statistically significant influence on the nitrification process at low concentration. Similar results were found in systems containing metoprolol or sotalol –pharmaceuticals have no apparent influence on the rate of nitrification (Table 2).

Note that these experiments were conducted several months apart, resulting in differences in nitrification rates between experiments for the three pharmaceuticals. An important aspect of our experimental protocol is maintaining low nitrite concentration in the batch reactors. It has recently been suggested that nitration may be responsible for some of the observed pharmaceutical biodegradation in lab studies (Gaulke et al., 2008; Gaulke et al., 2009). Nitration reactions are rarely relevant in natural or engineered environmental systems where nitrite concentrations



are low. Nitrite concentrations in all batch experiments never exceeded 5 mg-N/L, permitting a single step nitrification model to be employed in this phase of the research.

Table 2. Nitrification Rates (mg-Ng-VSS⁻¹h⁻¹) in Pharmaceutical Degradation Experiments

pharmaceutical	control (no pharmaceutical)	replicate A	replicate B
Atenolol	3.97 ± 0.42	4.00 ± 0.43	3.95 ± 0.53
Metoprolol	5.62 ± 0.44	5.70 ± 0.47	5.49 ± 0.42
Sotalol	2.88 ± 0.39	2.83 ± 0.39	2.95 ± 0.40

The batch experiments were also designed to assess the potential of the nitrifiers to degrade the selected pharmaceuticals. Results indicate that atenolol was degraded during nitrification whereas no degradation was observed for metoprolol or sotalol. Interestingly, atenolol biodegradation was also noted in the nitrification inhibition control reactor (275 µM ATU for nitrification inhibition). Atenolol degradation was modeled using pseudo first order kinetics. The VSS normalized, pseudo first-order rate coefficients for the two replicate reactors containing atenolol were 2.33 ± 0.45 Lg-VSS⁻¹d⁻¹ and 2.65 ± 0.92 Lg-VSS⁻¹d⁻¹. The rate coefficient for the reactor in which nitrification was inhibited was 0.577 ± 0.45 Lg-VSS⁻¹d⁻¹. The degradation rate of atenolol in the presence of nitrification in these experiments is more than four times faster than the rate when nitrification is inhibited. We suspect that the degradation in the inhibited system is the result of some heterotrophic degradation.

Work in the coming period will assess this through a series of additional experiments, some of which will be focused on elucidating biomass populations. Specifically, the degradation of atenolol during nitrite oxidation will be assessed to evaluate whether the observed degradation of atenolol in the nitrification inhibition experiment is a result of the activity of nitrite oxidizing bacteria. In addition, we anticipate completing DNA extraction for the samples from experiments conducting and analyzing the DNA using quantitative real time PCR (qPCR) to elucidate the relative concentrations of ammonia oxidizing, nitrite oxidizing, and heterotrophic bacteria. Data from experiments evaluating degradation of atenolol and naproxen during nitrification (note that experiments with naproxen were completed prior to the reporting period) will be modeled within the framework of the Activated Sludge Model framework (Henze et al., 2000).

Work in the coming period will also focus on evaluating the degradation of diazepam, and possibly some structurally similar pharmaceuticals, during nitrification. Diazepam is a Schedule IV controlled substance which requires State and Federal registration before research can commence. State registration was obtained on 27 Feb 2012, and we are in the final stages of the Federal registration process.

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Publications and Conference Presentations

Sathyamoorthy, S. and Ramsburg C. A., Sorption of Pharmaceuticals during Biological Wastewater Treatment: A Critical Review and Assessment, Water Research, in review

Sathyamoorthy S. and Ramsburg C.A., 2012, Degradation of selected pharmaceuticals during nitrification, In Proceeding of WEFTEC 2012, New Orleans, LA, accepted.

Student Support

1. Sandeep Sathyamoorthy, PhD Candidate, Environmental and Water Resources Engineering program, Department of Civil and Environmental Engineering, Tufts University
2. Catherine Hoar, BS Environmental Engineering student, Department of Civil and Environmental Engineering, Tufts University

6. Assessing Human Impacts on Sediment and Contaminant Trapping within Oxbow Lake, Northampton, Massachusetts (USGS 2011MA298B)

Primary Principal Investigator: Dr. Jonathan Woodruff, UMass Amherst Geosciences

Start Date: 4/1/2011

End Date: 3/31/2012

Reporting Period: March 1, 2011 – February 29, 2012

Funding Source: USGS (104B)

Research Category: Climate and Hydrologic Processes

Focus Categories: Floods, sediments, toxic substances

Problem and Research Objectives

To assess deposition rates and associated contaminant inventories within Connecticut River floodplain lakes and ponds and how they have changed through time in response to both natural processes and man-made disturbances.

Methodology

Evaluates changes in sediment and heavy metal accumulation from Oxbow Lake in Northampton, MA as a case study using a combination of sediment cores and geophysical surveys.

Principal Findings and Significance

The magnitude of deposition in Oxbow Lake over the last hundred years was observed to be roughly equivalent to maximum water depths in the lake and point to the rapid infilling in recent centuries. The timing for the onset of rapid infilling occurs contemporaneous with the documented creation and beginning of routine maintenance of the tie-channel connecting the lake to the main river, followed shortly after by a rapid rise in heavy metal concentrations related to industrial activity along the river. Mercury concentrations are particularly high in recent sediments, with peak concentrations reaching ~500 ppb. Results point to the



creation and routine maintenance of inlets increasing the connectivity of off-river waterbodies to the main river in recent centuries, and the enhanced sediment trapping along the floodplain at an optimal time for capturing legacy contaminants introduced during the industrial era.

The effects of Hurricane Irene on the Connecticut River during the project provide rare insight into the depositional response of backwater floodplain environments like Oxbow Lake to an extreme precipitation event. Torrential rains from the Irene event resulted in flash-flooding within the uplands of the Connecticut River. Here excessive channel erosion and landscape disturbance provided widespread access to glaciolacustrine sediments common to the uplands of many Atlantic draining rivers. Once mobilized, these fine grained sediments were rapidly transported to downstream, diluting particulate organics, and capping contaminated industrial depocenters like Oxbow Lake with a relatively clean, inorganic, clay/silt layer.

Publications

Woodruff, J.D. and Martini, A.M., 2012. Post-Colonial Inlets and the Rapid Infilling of Floodplain Lakes and Coves: Connecticut River, U.S.A, Paper No. 2-9, Northeastern Section, GSA, 47th Annual Meeting, Durham, USA

Woodruff, J.D., Naughton, T.N., Elzidani, E.Z., Martini, A.M., in preparation, Sediment trapping and human impacts on off-river waterbodies, U.S.A., Geomorphology

Woodruff, J.D., Kratz, L.N., Mabee, S.B., Morrison, J., Martini, A.M., in review, Tropical Cyclone Impacts on Western North Atlantic Rivers: Insights from Hurricane Irene. Geology

Kratz, L.N., Woodruff, J.D., Martini, A.M., and Morrison, J., 2012. Resultant Sedimentation from Tropical Storm Irene in the Lower Connecticut River, Paper No. 2-10, Northeastern Section, GSA, 47th Annual Meeting, Durham, USA

Bouberhan, H., Martini, A.M., and Woodruff, J.D., 2012. Controls on Methylmercury Production in Two Connecticut River Embayments, Paper No. 53-3, Northeastern Section, GSA, 47th Annual Meeting, Durham, USA

Student Support

Two students pursuing Master of Science degrees in Geosciences were supported with funds and matching funds associated with this grant.

7. Authentic Research Projects for Undergraduates based on Groundwater Contamination Issues Related to Arsenic (USGS-2011MA306B)

Principal Investigator: Julian Tyson, Department of Chemistry, UMass Amherst

Start Date: March 1, 2011

End Date: February 29, 2012

Reporting Period: March 1, 2011 – February 29, 2012

Funding Source: USGS (104B)

Focus Categories: Groundwater, Toxic Substances, Water Quality



Problem and Research Objectives

The goal was to devise authentic research projects for undergraduates based on groundwater contamination issues related to arsenic. In particular, the possibility of examining both (a) the mechanisms by which arsenic is dissolved in the shallow aquifers in countries like Bangladesh, and (b) some strategies for remediation of contaminated water by low-cost, readily available materials.

Methodology

Some preliminary experiments were conducted by a graduate student over the summer under the direction of Professor Tyson, who also worked on the project, and who enlisted the help of some high school teachers, present for a week's workshop.

Professor Tyson then created projects for groups of undergraduate students from the honors first-year class to work on in both the fall and the spring semester. Each project team was led by a graduate student (including the student funded by the grant) or by an experienced upper-level undergraduate.

Principal Findings and Significance

In the fall, the relevant group themes consisted of (1) dissolution of arsenic sulfide minerals, (2) removal of arsenic from contaminated water by moldy biomass, and (3) removal of arsenic from contaminated water by coffee grounds (a form of biochar). In the spring, relevant themes were (1) removal of arsenic from contaminated water by wood biochar, and (2) coffee grounds. Over the two semesters there were 10 projects in total. It proved difficult to obtain arsenic sulfide minerals. Initial, promising results with the coffee grounds was mitigated by the discovery that an extracted chemical (or chemicals) interfered with the measurement. Biochar containing iron is very promising. All of the projects were sufficiently challenging to engage the students fully during the semester, and the self-reported satisfaction was very high. The biologically mediated remediation was less convincing, and although the students were challenged, this may not be a promising line of investigation. Part of the problem is that food spoilage molds are quite difficult to culture on food that contains preservatives.

Student Support

One graduate student was supported. She is pursuing a doctoral degree in analytical chemistry.

Notable Achievements and Awards

This was a relatively modest project, but has opened up a new area of investigation for the undergraduate arsenic groups, namely the potential of remediation of contaminated water by biochar materials. During the period of the award, Professor Tyson was awarded a small grant by the Analytical Division of the American Chemical Society to create a public lecture/demonstration concerning the impact of arsenic compounds in the environment, which was delivered in December 2011. He has also been invited to contribute a book, in the John Wiley Analytical Chemistry Series, on much the same topic. The book will include a chapter on engaging undergraduate students in authentic research experiences.

8. Development of a Hydroclimate Synthesis Report for International Upper Great Lakes Study (USGS-2011MA315S)



Principal Investigator: Dr. Casey Brown, UMass Amherst Civil & Environmental Engineering

Start Date: September 16, 2011

End Date: December 31, 2011

Reporting Period: March 1, 2011 – February 29, 2012

Funding Source: Supplemental

Research Category: Climate and Hydrologic Processes

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

Problem and Research Objectives

The fundamental goal of this Synthesis was to prepare a comprehensive report on the conceptual underpinnings of the strategy that the IUGLS took with respect to climate change impact analysis, and its relationship to the development of Lake Superior regulation plan options.

Methodology

Current findings of the IUGLS as well as relevant findings in the peer reviewed literature were reviewed and synthesized to produce a single document to guide decision making in the selection of a new regulation plan for the Upper Great Lakes.

Principal Findings and Significance

The report led to the adoption of an adaptive management strategy in order to address uncertainty on the Upper Great Lakes.

Publications and Conference Presentations

Hydroclimate Synthesis Report for the International Upper Great Lakes Study. Casey Brown, Paul Moody, Danica Lefever, Jesus Morales. IUGLS.

Student Support

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

9. Climate Risk Assessment and Management (USGS- 2011MA316S)

Principal Investigator: Dr. Casey Brown, UMass Amherst Civil & Environmental Engineering

Start Date: 9/16/2011

End Date: 9/15/2012

Reporting Period: March 1, 2011 – February 29, 2012

Funding Source: Supplemental

Research Category: Climate and Hydrologic Processes

Focus Categories: Climatological Processes, Management and Planning

Problem and Research Objectives:

The overarching objective of this effort is to develop methods for vulnerability assessment and risk evaluation that can be applied to assist in water management risk-informed decision making. The U.S. Army Corps of Engineers (USACE) is contributing toward the development of a risk management framework for incorporating the uncertainty of future climate change into decision making. The



framework is intended to be applied across a project's entire lifecycle, since climate change uncertainty may require making sequential decisions over time and updating design and plans as more is learned.

One of the critical next steps is to develop approaches that can be applied to water management. Water management decisions require trading off conflicting objectives that affect many groups of stakeholders. The work effort is developing procedures to assess the vulnerabilities of a water resources project or system of projects to climate change and variability. The information can then be used for risk evaluation of the water management system under future climate conditions. The methods developed in this study should support the development of guidance for incorporating climate change considerations into water management. The methods should be useful for revising water management operating plans and reservoir reallocation studies.

Methodology

1. Vulnerability Assessment. The goal of this step is to develop "bottom-up" vulnerability assessment methods for multi-objective water management. The vulnerability assessment will identify what type of climate changes or variability causes problems for the system. The process can identify the potential thresholds where system performance begins to degrade and other conditions that cause severe problems for the system. 2. Risk Assessment and Evaluation. Risk is defined by the consequences and likelihood of an event. The results of the vulnerability assessment can be used to determine consequences from potential climate events. The likelihood of an event may be based on a wide range of climate information including historical information, climate model projections, stochastic simulations, and paleo-climatological information. 3. Risk Informed Decision Making and Adaptive Management Strategies. The overall aim of the risk evaluation is to better inform water management decisions. This step will support the development of risk management strategies for water management. Given the uncertainties associated with future climate, adaptive management strategies may perform better for a wider range of future climate conditions and be more responsive to changing conditions. The process is being applied to a case study of the Coralville Reservoir in Iowa.

Principal Findings and Significance

The work is ongoing but the framework shows promise and USACE is considering for broad application to federal water projects.

Student Support

The funding provides partial support for 1 MS student.

10. Acid Rain Monitoring Project

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

Start Date: January 1, 2012

End Date: June 30, 2012

Reporting Period: January 1, 2012– June 30, 2012

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, 2011 to June 30, 2012, the eleventh 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 ponds² 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 50 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 second year of monitoring for those newly added ponds.

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.

Methodology

The sampling design was changed in 2011 to monitor both streams and ponds, and that design was continued in 2012. 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, 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 15, 2012.

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 there were safety and access concerns. 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

² 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)



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. The Statewide Coordinator also made visits to two of the labs with newer analysts to go over procedures and quality control. 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. Unfortunately they sent the samples too late and cation analysis could not be done on those samples due to sample holding time violation.

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 proofed by another. Data were entered in a MS excel spreadsheet and uploaded into the web-based database at <http://umatei.tei.umass.edu/ColdFusionProjects/AcidRainMonitoring>. Data were also posted on the ARM web page at <http://www.umass.edu/tei/wrrc/arm/>.

Water Resources Research Center's Elizabeth Finn ran 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. UMass Chemistry Department's Dr. Julian Tyson and his laboratory team of graduate students analyzed the samples from the long-term sites for anions and cations.

Aliquots for 26 long-term sites 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 Environmental Analysis Lab (EAL) 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 2012, 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 143 sites (72 ponds and 71 streams) including 25 of our long-term sites. Two of our long-term sites were not analyzed for anions due to unmet holding times, and in the cation analysis, the lab was unable to analyze for K due to equipment failure.
3. The only quality control problem this year was the UMass Boston laboratory not passing our quality control samples, so we picked up all of their samples and analyzed them at EAL.
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. 54 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.
5. The ARM web site and searchable database were maintained and updated. 2012 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).
6. The data collected was analyzed for trends in pH and ANC in April months only for 143 sites and for color and ions for 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 except K, and color separately, predicting concentration vs. time.

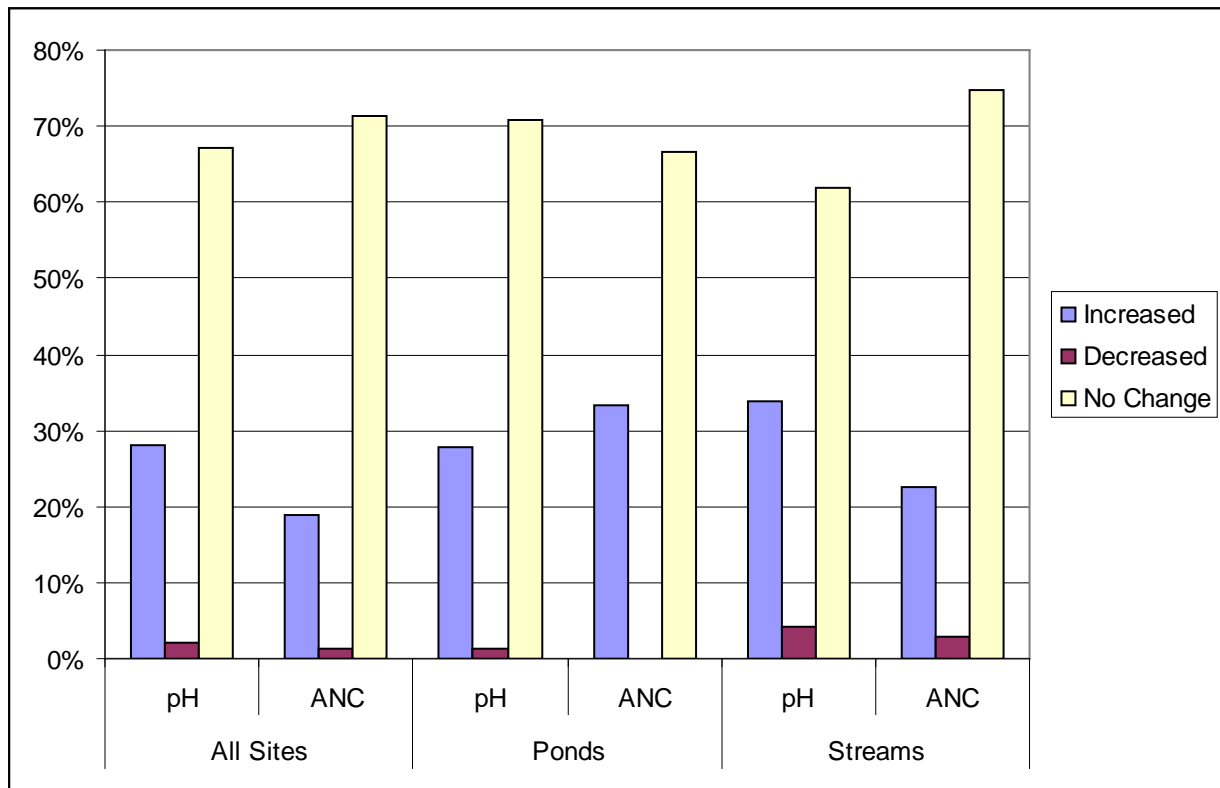
Trend analysis for pH and ANC

Table 1 displays the number of sites out of a maximum of 143 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 1: Trend analysis results for pH and ANC, April 1983 – April 2012

	All Sites		Ponds		Streams	
	pH	ANC	pH	ANC	pH	ANC
Increased	40	27	20	24	24	16
Decreased	3	2	1	0	3	2
No Change	96	102	51	48	44	53
Total	143	143	72	72	71	71

Those results are also graphed in Figure 1.


Figure 1. Percentage of site changes in pH and ANC, from trend analysis, April 1983-2012

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, more show an increase than a decrease in value: about a quarter of the sites saw an increase in pH and ANC, more so for pH than ANC over all. However, we see a difference between ponds and streams. More ponds saw an increase in ANC (33%) than in pH (28%), but for streams, more saw an increase in pH (34%) than in ANC (23%).

Compared with last year's results, these results are consistent for streams, but for ponds we notice a definite increase in number of sites with increased pH and ANC. This is not consistent with last year's results, but as we have only two years of new data for ponds, it will be interesting to see what the trend looks like in future years.



Ions and Color

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

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

Table 3: Trend analysis results for ions and color

	April 1983 - April 2012		
	No Change	Increased	Decreased
Mg	23	0	2
Si	18	0	7
Mn	24	0	1
Fe	24	0	5
Al	25	0	0
Ca	22	0	3
Na	22	3	0
K	n/a	n/a	n/a
Cl	12	13	0
NO3	17	7	1
SO4	2	21	2
Color	5	20	0

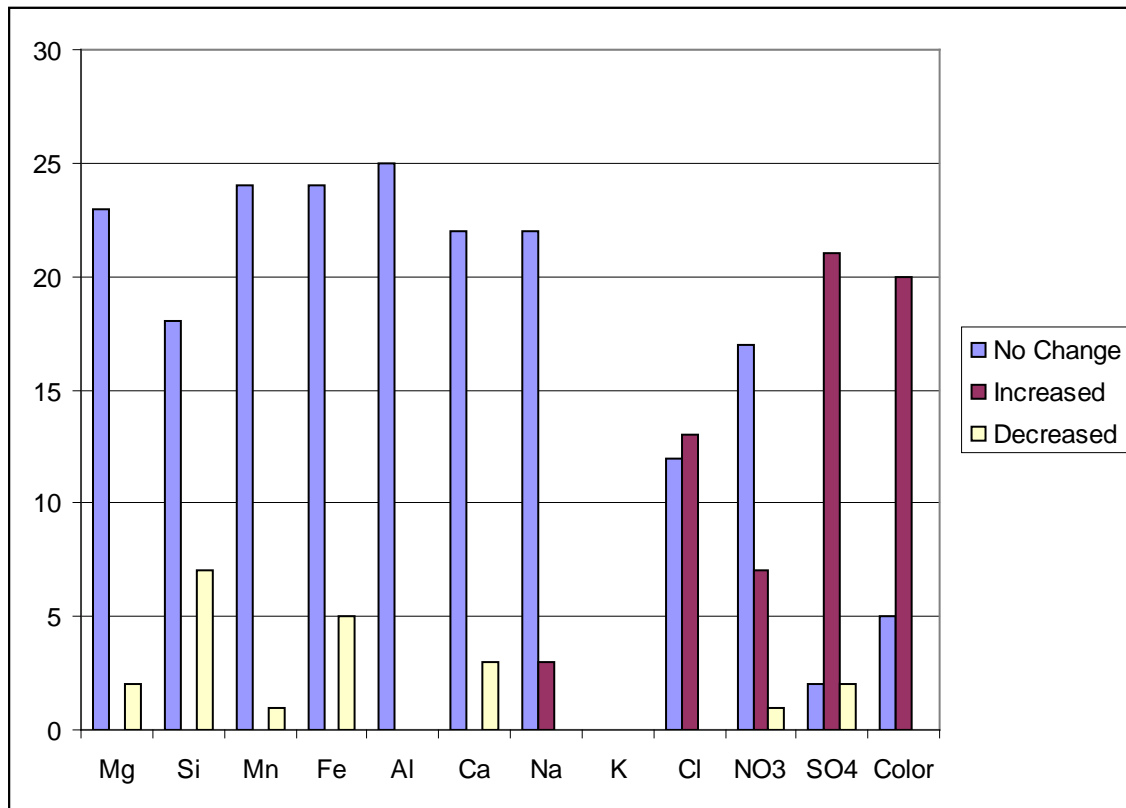


Figure 3: Results of trend analysis for ions and color for 25 long-term sites, April 1983-2012

This year the results look different than in previous years. The only consistent result is that color has decreased at almost all sites. Most cations show no significant change over time for the 25 sites we are following. The exception, as in the past, is for sodium, but this year it increased in only three sites.

All anions show significant changes. Chloride still never decreases with time, and increases for more than half of the sites. Nitrate's change is less definite, but it clearly increases for about a third of the sites and decreases for only one site. Sulfate shows the most unexpected change, a significant increase for 22 sites, vs. a strong decrease for 85% of the sites last year.

Discussion

While last year saw a heavy and late-melting snow cover, this year we had no snow cover to speak of in the winter, and by monitoring day on April 15, most of Massachusetts was under drought conditions. Some water bodies were extremely low, and we saw "dirty" samples because there was so little water to sample from that some of the stream or pond bottom had to be scraped with the sample bottle. While this might be the reason for the unexpected changes we are seeing in this year's data, we will examine the raw data more thoroughly in the coming months to ensure that the proper sites were sampled and lab reports are accurate.



Student Support

- 1 BS student in Mathematics at UMass Amherst
- 1 PhD student in Chemistry at UMass Amherst.

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, 2011 – June 30, 2012

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

Overview

The Upper Blackstone Wastewater Treatment Facility upgrades based on the 2001 permit are now fully operational, and water quality monitoring was conducted between May 2011 and December 2011 to help assess response of the river to reduced nutrient concentrations in the effluent. In the future, these data will be utilized to help evaluate the ability of the model to capture this response. Sampling for nutrient analysis was conducted monthly, including co-sampling with the Narragansett Bay Commission (NBC) of three Rhode Island sites along the mainstem of the Blackstone River. In addition to nutrient sampling, WRRC staff conducted a second sampling run each month to collect water quality samples for chlorophyll-a analysis only, and to collect qualitative data about algae blooms and macrophyte coverage.

This report summarizes the results of the nutrient sampling, including presentation of co-sampling and duplicate results. Qualitative data about algae blooms and macrophyte coverage, as well as Chlorophyll *a* results, will be presented under separate cover. The report is organized as follows: Section 2.0 presents the sampling locations and dates, Section 3.0 presents the analysis and sampling methods utilized, and Section 4.0 presents a summary of the results. A brief discussion of the results relative to past data collected for the river is under development, as the full set of nutrient results just became available.

Sampling Locations, Parameters and Dates

Starting in May 2011, sampling for nutrient analysis was conducted monthly, including co-sampling with the Narragansett Bay Commission (NBC) of three Rhode Island sites along the mainstem of the Blackstone River, Figure 1 and Table 1. This sampling effort built upon an effort begun in late summer 2010. Maps showing the spatial location of individual sampling sites are included in Appendix A. Sampling locations were selected to correspond with locations monitored by the Massachusetts Department of Environmental Protection (MassDEP) in 2008. The samples were analyzed for dissolved ammonium (dNH_4^+), dissolved nitrite-nitrate (dNO_2^- - dNO_3^-), dissolved Orthophosphate (dPO_4^-), dissolved Nitrite (dNO_2^-), dissolved total nitrogen (DTN), total suspended solids (TSS), and Chlorophyll *a*, Table 2. Nutrient samples were analyzed at the UMass Environmental and Water Resources Engineering (EWRE) Research Laboratory, the TSS samples were analyzed at the UBWPAD lab,

and the Chlorophyll *a* samples are in the process of being analyzed at the UMass Environmental Analysis Laboratory (EAL). Samples collected at the three Rhode Island locations were analyzed at both EWRE and the NBC laboratories. NBC has been sampling these locations on a monthly basis for the past several years; the duplicate results thus provide context to differences in lab methods and potentially allow some inferences about past water quality along the mainstem Massachusetts portions of the river. Additional quality control and quality assurance samples were collected, as described in the methods section, including split samples, laboratory duplicates, and performance standard analyses. In addition to nutrient sampling, WRRC staff conducted a second sampling run each month to collect water quality samples for Chlorophyll *a* analysis only, and to collect qualitative data about algae blooms and macrophyte coverage. The locations of the Chlorophyll *a* sampling were more focused on impoundments, while the nutrient sampling was more focused on run-of-river locations. However, several sites were sampled during both collection runs. Sampling dates are summarized in Table 3.

Blackstone River Watershed Nutrient Assessment Locations



"UMass WRRC Blackstone River Nutrient Monitoring 2011",
Elizabeth Finn [map]. MassGIS Data, 2011.
Using: ArcView [GIS software]. Version 9.3. Redlands, CA:
Environmental Systems Research Institute, Inc., 1992-2010.

Figure 1: 2011 Nutrient Sampling Locations


Table 1: Nutrient Sampling Sites

Site ID#	Site Name	Latitude	Longitude	HSPF Reach
¹ Rte 116	Rte 116 Bikepath Bridge, Pawtucket, RI	41.938009	-71.433899	228
¹ Slater Mill	Slater Mill Dam, Pawtucket, RI	41.876959	-71.381924	200
¹ State Line	State Line, RI	42.009932	-71.52944	290
W0505	McCracken Rd., Millbury, MA	42.20277	-71.778046	400
W0680	New Millbury St bridge, Worcester, MA	42.22778189	-71.78735524	414
W0767	At USGS gage 01110500 near Sutton St. bridge, Northbridge, MA	42.153873	-71.65203977	348
W1017	Singing Dam (downstream), Sutton, MA	42.18086002	-71.73011265	378
² W1023	Bridge St/Canal St, Blackstone, MA	42.016783	-71.538522	276
W1242	Route 122A, Grafton, MA	42.17728889	-71.68788468	360
W1243	Depot St., Grafton, MA	42.17384662	-71.68057473	358
W1763	Riverlin St. Millbury, MA	42.192725	-71.751822	384
W1764	Riverdale St. Northbridge, MA, upstream of dam exiting Riverdale Pond	42.139165	-71.639719	342
W1765	Rte. 122, Uxbridge, MA	42.055088	-71.6163	308
W1779	Below Rice City Pond Sluice Gates, Hartford St., Uxbridge, MA	42.097283	-71.62248	326

¹ Locations of co-sampling with NBC

² This site was only sampled 5/18/2011 and was subsequently dropped from the standard nutrient monitoring run

Table 2: Water quality parameters monitored

Dissolved Ammonium (dNH ₄)
Dissolved Nitrite-Nitrate (dNO ₂ -NO ₃)
Dissolved Orthophosphate (dPO ₄)
Dissolved Nitrite (dNO ₂)
Total dissolved nitrogen (TDN)
Total suspended solids (TSS)
Chlorophyll <i>a</i>


Table 3: 2011 sampling dates and parameters monitored

Site ID#	Sampling Date and Assessment Type (N = Nutrients, C = Chlorophyll a)														
	*18-May	*19- May	8 – Jun	15 – Jun	29 – Jun	13 – Jul	27 – Jul	10 – Aug	24 – Aug	7 – Sep	21 – Sep	5 – Oct	19 – Oct	2 – Nov	16 - Nov
Rte 116*	N, C			N, C		N, C		N, C		N, C		N, C		N, C	
Slater Mill*	N, C			N, C		N, C		N, C		N, C		N, C		N, C	
State Line*	N, C			N, C		N, C		N, C		N, C		N, C		N, C	
W0505		N, C		N, C		N, C		N, C		N, C		N, C		N, C	
W0669			C		C		C		C		C		C		C
W0670			C		C		C		C		C		C		C
W0680		N, C		N, C		N, C		N, C		N, C		N, C		N, C	
W0767		N, C		N, C		N, C		N, C		N, C		N, C		N, C	
W1017		N, C		N, C		N, C		N, C		N, C		N, C		N, C	
W1023	N, C														
W1242		N, C	C	N, C	C	N, C	C	N, C	C	N, C	C	N, C	C	N, C	C
W1243		N, C	C	N, C	C	N, C	C	N, C	C	N, C	C	N, C	C	N, C	C
W1258			C		C		C		C		C		C		C
W1763		N, C		N, C		N, C		N, C		N, C		N, C		N, C	
W1764		N, C	C	N, C	C	N, C	C	N, C	C	N, C	C	N, C	C	N, C	C
W1764B			C		C		C		C		C		C		C
W1765	N, C			N, C		N, C		N, C		N, C		N, C		N, C	
W1779	N, C		C	N, C	C	N, C	C	N, C	C	N, C	C	N, C	C	N, C	C
Fisherville			C		C		C		C		C		C		C
UBWPAD			C		C		C		C		C		C		C

* Sites sampled over two days as procedures/routine for sampling was established

Methods

Nutrients Sampling Methods

At each sampling site, a clean 2 or 4-liter collection vessel was rinsed 3 times with the sample water before final collection of the sample. The sample in the collection



vessel was then transferred into 2 clean 1-liter bottles, which were also rinsed 3 times with the sample water previous to final sample collection. One bottle was labeled for TSS analysis and the other for nutrient analysis. Both were put into coolers packed with ice until they could be transferred to the lab. The bottle labeled for nutrient analysis was held for no more than 2 hours (more often less than that) before being filtered through a 47 mm glass fiber filter.

Before filtering each sample, all equipment and containers were rinsed three times with deionized (DI) water. The filtering process was set up with vacuum flask, filter holder, glass fiber filter, and filling funnel. The filter was placed rough side up on the filter holder. Using a graduated cylinder, the sample volume was measured out and recorded. The measured sample was then poured into the filling funnel and the hand-operated vacuum pump operated until the vacuum reached 15 psi. When the entire measured sample had been filtered, the filling funnel was removed, the filter carefully removed from the filter holder with forceps, folded in half (green side in), and placed in the air-drying box. The filtered sample was then transferred to another clean, sterile 500ml container and put in the cooler for transport back to the lab, where it was frozen until it could be analyzed. When all samples had been filtered the drying box was plugged in and the sample filters were completely air-dried. The filters were then removed with forceps, placed in aluminum foil, and labeled with site name, date, time of sampling, and volume of water filtered. The protocol utilized followed the Massachusetts Water Watch Partnership field sampling protocols for Chlorophyll *a* (MWWP 2001; Appendix B). On the days when only chlorophyll sampling was required, the filtered sample water was discarded, leaving only the filter, processed as described above. Field sampling methods and sampling frequency are summarized in Table 4 below.

Table 4. Field Sampling Methods

<i>Parameter</i>	<i>Field Method</i>	<i>Frequency</i>
Chlorophyll <i>a</i>	SOP - MWWP http://www.umass.edu/tei/mwwp/pha.html	2x per month
TSS	"Grab-Sample"	monthly
Nutrients	"Grab-Sample"	monthly

Nutrients and Chlorophyll Analysis Methods

The nutrient samples were analyzed at the UMass EWRE Research Laboratory, the TSS samples were analyzed at the UBWPAD lab, and the Chlorophyll *a* samples are in the process of being analyzed at the UMass EAL. For the three co-sampling sites, nutrients were also analyzed at the Narragansett Bay Commission Laboratory for data comparison. For an additional quality control check, nutrient samples taken on 8/10/2011 and 11/30/2011 from all sites were also analyzed at the UBWPAD laboratory. In addition, three quality control (QC) samples were randomly collected on each nutrient sampling day, and two on each Chlorophyll *a* only sampling day. These samples were taken as "split samples" (a second aliquot from the same sample bottle), labeled as "QC", and treated in the same way as the regular samples. Nutrient QCs were analyzed at the UMass EWRE Research Lab with the regular samples, and chlorophyll *a* QCs will be analyzed at the UMass EAL. The methods for analysis at the three labs are outlined in Table 5. As a further quality assurance quality control measure, midway through the sampling season, the UMass EWRE Research Laboratory conducted an equipment and procedures performance



review. To do this, they purchased commercially available performance standards to compare against their standards and results. All results for their in-house standards and the commercial performance standards matched well; there were no significant difference between the two standards and analysis results for the standards were within acceptable error bounds.

Table 5. Laboratory analysis methods

<i>Laboratory</i>	<i>Parameter</i>	<i>Method</i>	<i>Detection Limit</i>
Narragansett Bay Commission	Dissolved NH ₃	EPA 349	7 ppb
	Dissolved NO ₂ -NO ₃	EPA 353.4	6 ppb
	Dissolved PO ₄	EPA 365.5	5 ppb
	Dissolved Silicate	EPA 366	20 ppb
	Dissolved Nitrite	EPA 353.2	5 ppb
	Tot. Dissolved Nitrogen	Lachat QuikChem Method 31-107-04-3-A	100 ppb
	TSS	Standard Method 2540D	2 ppm
	Chlorophyll-a	Chlorophyll extraction and analysis with a Turner Fluorometer (URI/GSO's method)	1 ppm
UBWPAD	Dissolved NH ₃	EPA 350.1	70 ppb
	Dissolved NO ₂ -NO ₃	EPA 353.2	20 ppb
	Dissolved PO ₄	Hach 8048	17 ppb
	Dissolved Nitrite	STD Method 18th ed., 4500NO ₃ -F	50 ppb
	Tot. Dissolved Nitrogen	EPA 351.2	240 ppb
	TSS	Standard Method 2540D	2 ppm
UMass EWRE	Dissolved NH ₄ ⁺	IC	20 ppb
	Dissolved NO ₂ -NO ₃	STD Method 20th ed., 4110B	5 ppb
	Dissolved POR	STD Method 20th ed., 4110B	20 ppb
	Dissolved Nitrite	STD Method 20th ed., 4110B	5 ppb
	Tot. Dissolved Nitrogen	STD Method 20th ed., 5310B	200 ppb
UMass EAL	Chlorophyll <i>a</i>	STD Method 20th ed., 10200 H	1 ppm

Results

Nutrient analysis results are provided in Appendix C as follows:

- NBC nutrient analysis results for the three co-sampling locations, reported by date and location, and including QC split sample results;



- EWRE nutrient analysis results for the 13 mainstem sampling locations, including the three NBC co-sampling locations;
 - UBWPAD analysis results for TSS;
 - Comparison of the QC split sample results for EWRE, NBC, and UBWPAD, including the percent difference between the two aliquots;
 - Comparison between EWRE and NBC lab results for the three co-sampling locations, including the percent difference between the results;
 - Comparison between NBC and UBWPAD lab results for the three co-sampling locations, including the percent difference between the results;
 - Comparison between EWRE and UBWPAD lab results for the three co-sampling locations, including the percent difference between the results;
 - Comparison between EWRE and UBWPAD lab results for all of the sampling locations, including the percent difference between the results.
- Comparisons between the 2011 and 2008 data are currently underway.

In general, conditions in the watershed during the 2011 sampling season were wet. The monthly average mean daily discharge in 2011 is compared with the 1929 to 2009 average in Table 6 for the Blackstone River USGS monitoring station located at Woonsocket. In particular, flows during the late summer and fall months were high compared to historical flows. Data for all of 2011 is not yet available, but precipitation conditions in the watershed appear to also have been high in 2011 (Table 6).

Table 6. Summary of 2011 flow and precipitation conditions

	Monthly Mean Discharge (cfs) USGS Station 01112500		Monthly Precipitation (in) Worcester Regional Airport	
	2011	1929 – 2009 average	2011 *	1996 -2010 average
Jan	708	976	2.52	3.63
Feb	1,064	1,020	5.25	3.15
Mar	2,834	1,500	3.99	4.45
Apr	1,671	1,450	5.54	4.13
May	1,109	898	3.85	3.81
Jun	964	644	6.91	4.41
Jul	437	348	2.20	4.38
Aug	1,309	307		3.25
Sep	1,815	323		4.05
Oct	1,434	454		4.71
Nov	1,530	668		3.74
Dec	1,814	894		4.04

* Data after July 2011 is not yet available through the National Climatic Data Center

Data between the three laboratories agrees well for TDN, typically with less than a 5% difference. Percent differences between the laboratory results are greater for PdO4 and the nitrogen subspecies. In general, NBC analysis results tend to be higher, and EWRE analysis results tend to be lower. There is no indication of analysis, sample mishandling, or equipment errors at any of the labs; it is believed that differences in the data results are related to the analysis methods utilized.



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Student Support

- 1 Undergraduate, Mathematics
- 1 MS Geosciences

Information Transfer and Outreach

The Center relies heavily upon the Internet for information transfer. Several of the Center's projects have significant Internet information transfer elements that are still in existence and utilized today. One of these is the Acid Rain Monitoring Project (ARM) described above, and another is the Massachusetts Stormwater Evaluation Program described below.

1. Innovative Stormwater Technology Transfer and Evaluation Project

Principal Investigator: Jerry Schoen, MA Water Resources Research Center, UMass Amherst

Start Date: 07/01/2010

End Date: 06/30/2012

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

Funding Source: MassDEP

Descriptors: Stormwater; Water Quality; Nonpoint Pollution

The Massachusetts Dept of Environmental Protection (MassDEP) awarded WRRC a two and a half year grant to continue a project originally begun in FY'05 and initially continued in FY '07. The goal of this project is to provide technology transfer information about innovative stormwater Best Management Practices (BMP) to MassDEP, conservation commissions, local officials, and other BMP Users. The project maintains and updates the database already in place (www.mastep.net), by adding information on new studies performed on BMPs previously listed on the MASTEP web site as well performance data on BMPs to the site. These pertain both proprietary



BMPs and Low Impact Development BMPs. The MASTEP web site now has approximately 84 technologies profiled. WRRC staff participated in meetings of the Massachusetts Stormwater BMP working group, gathered to generate recommendations for a volume to flow conversion method for purposes of sizing flow-based stormwater treatment BMPs. MassDEP has taken the group's recommendations under advisement. WRRC staff made a presentation on MASTEP, BMP performance, and stormwater regulations to an audience of 20 at the January 24, 2012 Congress of Lakes and Ponds annual meeting, and to an audience of 25 at an April 12, 2012 Massachusetts Watershed Coalition Stormwater Seminar. The project will be continued into FY 2013 with another grant from MassDEP, funded through the Clean Water Act Section 319 grant program administered by US EPA.

2. Connecticut River Targeted Watershed Initiative

Principal Investigator: Jerry Schoen, MA Water Resources Research Center, UMass Amherst

Start Date: December 1, 2007

End Date: December 31, 2013

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

Funding Source: USEPA 604B grant program USEPA Targeted Watershed Initiative Grant Program

Descriptors: Connecticut River; Water Quality; Volunteer Monitoring; Information Technology

Problem and Research Objectives

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

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



WRRC organized and conducted a Water Quality Monitoring program to document *E. coli* bacteria levels at 26 sites along the river in the project's first 2 years, as described in the Center's 2009-2010 annual report.

WRRC staff also conducted nutrient sampling to evaluate effectiveness of agricultural best management practices (BMPs) in reducing phosphorus runoff into a tributary of the Mill River in Hadley, MA. Staff sampled above and below the UMass Hadley Farm. To date, pre-installation sampling has been successfully completed; post installation sampling is ongoing. Samples are analyzed at the UMass Environmental Analysis Laboratory.

Outreach and Education / Technology Transfer

WRRC continues to maintain data from this project to the Connecticut River website established for the Tri-State Connecticut River Targeted Watershed Initiative (<http://www.umass.edu/tei/mwwp/ctrivermonitoring.html>). This site is currently hosted and maintained by the Water Resources Research Center at UMass Amherst.

3. Stream Continuity Project

Principal Investigator: Scott Jackson, Environmental Conservation, UMass Amherst

Start Date: Spring 2000

End Date: Ongoing

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

Funding Source: UMass Extension

Descriptors: Stream Crossings; Water Quality; Fish Passage

Under a memorandum of understanding with UMass extension, WRRC 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, WRRC staff reviewed entered data for inconsistencies and to account for a change in field measurements and served as the database coordinator.



4. Water Quality Analyses Support for Massachusetts Volunteer Monitors

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

Start Date: 1/1/2012

End Date: 6/30/2013

Reporting Period: 1/1/2012 / 6/30/2012

Funding Source: Massachusetts Department of Environmental Protection

Descriptors: Water Quality, Laboratory Analyses, Volunteer Monitoring

Background

Citizen volunteers have monitored their local surface waters in Massachusetts for a couple of decades, to fill in the knowledge gaps in water quality information as state agencies can not monitor all water bodies every year.

In 1990, the Massachusetts Water Resources Research Center created a program called the Massachusetts Water Watch Partnership to assist volunteers in running credible surface water monitoring projects. A few years later, the State of Massachusetts began funding lab assistance to volunteer groups, by subsidizing the cost of quality assurance samples and some analyses (Total Phosphorus and chlorophyll *a*) through the Water Resources Research Center's Environmental Analysis Laboratory (EAL).

EAL developed an analytical method for Total Phosphorus (TP) that allowed detection at very low levels (5 µg/L), which is of great importance to lake groups, as it allows them to determine whether their lakes are eutrophied or not. Some groups applied and received grants of their own to run monitoring programs on their water bodies, and used EAL for the analyses needed in their program. EAL also refined a method for sampling and analyzing chlorophyll *a* samples.

Due to aging equipment, EAL stopped providing TP and chlorophyll analyses two years ago. Volunteer groups were left with no viable alternative to have their lake and stream samples analyzed. Through a grant from the Massachusetts Department of Environmental Protection (MADEP) 319 program, EAL was able to purchase a new spectrophotometer in order to resume those analyses.

Objectives

This project aims to reinstate EAL analytical services to volunteer groups and others in the State and provide a number of free analyses to citizen groups.

Another goal is to assist any volunteer group complete a Quality Assurance Project Plan who needs one in order to qualify for free analyses.

Finally we plan to apply for and obtain certification from the State for the analysis of Total Phosphorus.

Results

A Shimadzu spectrophotometer and an electric sterilizer were purchased as well as a computer to process the analytical data. WRRRC staff was trained on the new equipment and started running test samples for the analysis of chlorophyll *a*. Free



samples were analyzed for 2 groups, and many samples were also analyzed for the Blackstone project described above in this report.

Our TP SOP was sent to MADEP for review and changes to the method were initiated. WRRC staff was trained to perform TP analyses on the spectrophotometer and ran some test samples before starting the analysis of samples sent in by volunteer groups.

5. 2011 Water Resources Conference

Principal Investigators: Dr. Paula Rees, Marie-Françoise Hatte, MA Water Resources Research Center

Start Date: 3/1/2011

End Date: 2/29/2012

Reporting Period: March 1, 2011 – February 29, 2012

Funding Source: USGS 104B

Descriptors: Water Quality, Water Quantity, Climatological Processes

Focus Categories: Education; Management & Planning; Climatological Processes

The Water Resources Research Center organized the eighth annual Water Resources Conference on the UMass Amherst campus on April 7, 2011. While the conference took place in April 2011, most of the work for this conference was accomplished in the reporting period. The Cooperative State Research, Education, and Extension Service New England Regional Program again cooperated in planning the conference. Four additional co-sponsors helped underwrite the cost of the conference.

Thirty-two posters were presented and there were 30 platform presentations in three concurrent sessions. The presentations were grouped into the following 9 sessions:

- Climate Change and Stream Crossings in the Northeast
- Monitoring and Detecting Harmful Algal Blooms
- Nutrients Management in Water
- Climate Change Adaptation Implementation Strategies
- Fish Passage and Stream Continuity
- Findings of the Connecticut River Targeted Watershed Initiative
- Climate Change Adaptation and Decision Making
- Tools for Water Management in the Connecticut River Basin
- Stormwater and Low Impact Development

There were three Plenary Addresses at the beginning of the conference:

- "The University Perspective" by Rick Palmer, Professor and Department Head, Dept. of Civil and Environmental Engineering, UMass Amherst
- "The State of Massachusetts Perspective" by Vandana Rao, Assistant Director for Water Policy, Mass. Executive Office of Energy and Environmental Affairs
- "The New England Regional Perspective" by Jessica Cajigas, Environmental Analyst, New England Interstate Water Pollution Control Commission.

The Keynote Address was given by Dr. Richard Vogel, Professor of Civil and Environmental Engineering and Director of the Graduate Program in Water: Systems,



Science and Society, Tufts University, on "Water Resources Planning in a Changing World."

181 people registered for the event, representing 14 colleges and universities, 23 companies, 15 governmental agencies, 4 non-profit organizations, and 13 municipalities.

Twenty-four students (from 6 different institutions) participated in the Best Student Poster Competition, evaluated by 14 judges. Liam Bevan of UMass Amherst Geosciences (and a WRIP research project awardee this fiscal year) and Barbara DeFlorio of UMass Amherst Veterinary & Animal Sciences tied for first place. Bevan's poster was entitled "Water Flux at Till/ Bedrock Interfaces in Central Massachusetts." DeFlorio's poster's title was: "Optimizing Vegetative Filter Strips Treating Runoff from Turf."

Student support

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

6. Information Technology

WRRC is involved in three projects using information technology for environmental research, teaching and outreach.

- 1) The Center's work on the EPA-funded Tri-State Watershed Initiative in the Connecticut River watershed is described above.
- 2) The Center collaborated with the UMass Center for Educational Software Development, the Biology Departments of the Boston and Amherst campuses, and the Landscape Architecture and Regional Planning Program on a successful proposal to the National Science Foundation's Course, Curriculum and Laboratory Improvement Program (CCLI, now renamed to Transforming Undergraduate Education in Science, Technology, Engineering and Mathematics; TUES). This project, begun in July 2010 and named SeeTrees, is based on developing content and testing software and hardware options to enhance learning and scientific discovery in field courses. This is being done to support courses with a significant field component in which the students do field projects on plants. The essence of the project is to improve the way students learn to see and communicate their observations among their peers and to the broader community. New instructional methods are being introduced into the classes which involve mobile technologies including digital cameras, PDAs and cell phones in conjunction with open source Internet tools. These are used in the field and laboratory to (1) familiarize students with plants, plant characters and habitats, (2) identify species and habitats, (3) record observations that are automatically geo-tagged and time stamped, and (4) review and synthesize field observations. Jerry Schoen of the Center is the project manager. A no-cost extension was received from NSF, allowing the project to continue until December 2012 and continue this work for a 3rd semester for two of the courses involved. A proposal has been submitted to NSF to continue and expand the work in FY 2014.
- 3) The Center is collaborating with the Center for Educational Software Development, Department of Environmental Conservation, Trout Unlimited and other partners to develop and raise funds for The River's Calendar, a citizen-science climate change monitoring project focused on impacts to



phenology of riparian areas in coldwater fisheries, and consequent recreational and economic impacts. Pilot efforts in Massachusetts and Oregon are currently underway, testing sampling and organizational methods. Fundraising for this is an ongoing process. Jerry Schoen of the Center organized a session on climate change and phenology of aquatic systems at the Society for Freshwater Science annual meeting in Louisville, KY in May 2012. Schoen also presented a talk on a literature review of climate change impacts to aquatic invertebrate phenology.

- 4) Jerry Schoen of the Center assisted the Information Technology Minor Program planning and organization of the 2012 Information Communication Technology (ICT) Summit, held on March 2, 2012. Schoen serves on the Information Technology Curriculum Committee.

7. Environmental Analysis Laboratory

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

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

In this past year, EAL continued to provide laboratory support for the Acid Rain Monitoring Project, including a quality-control program for pH and alkalinity and analytical determinations for a suite of 15 parameters. The quality-control program for volunteer-monitoring groups continued for pH, alkalinity and dissolved oxygen.

Analytical services were provided for four university researchers, primarily for anions and cations. Collaboration with Dr. Julian Tyson of the Chemistry Department continues on a consulting basis, and has provided anion and cation analysis for this fiscal year.

EAL also resumed analyses of chlorophyll *a* (see report above) and prepared for resuming the analysis of Total Phosphorus.

Student Support

1 PhD Student, Chemistry Department.



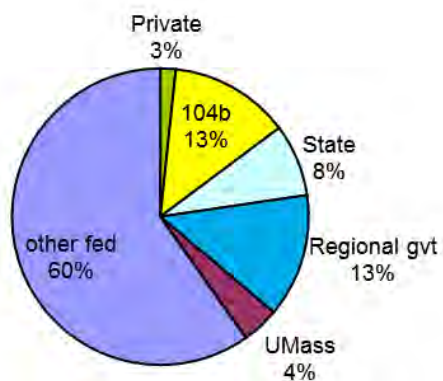
Financial Overview

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 WRRC.

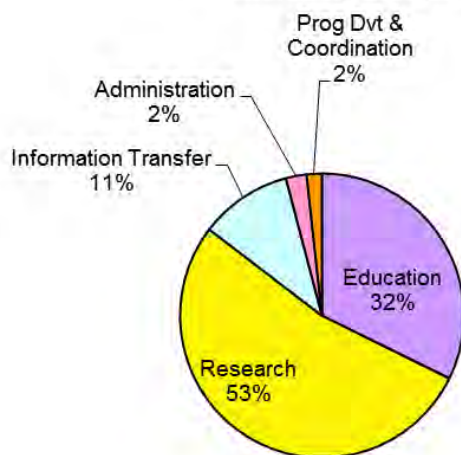
Total revenues amounted to \$704,585:

USGS:	\$389,094
USGS 104B:	\$ 92,335 broken down as follows:
	\$29,953 Ramsburg research project
	\$21,681 Conference
	\$16,622 Administration
	\$5,000 Hellweger research Project
	\$5,999 Woodruff research project
	\$4,984 Park research project
	\$9,096 Tyson research project
UMass (Director)	\$ 24,487
Extension	\$ 13,470
ARM Project	\$ 25,000
CT River TWI	\$ 4,110
MASTEP	\$ 21,057
ICT Summit	\$ 4,300
SeeTrees	\$ 18,600
Blackstone River	\$ 90,798
Conference Revenues	\$ 5,830
EAL	\$ 5,971
Lab Analyses Support	\$ 9,533

Awards by Sponsor Type



Awards by Category



Awards by Funding Source

