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# Water Quality and the Landscape: Long-term monitoring of rapidly developing suburban watersheds

New Hampshire Water Resources Research Center (NH WRRC)

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## **Water Quality and the Landscape: Long-term monitoring of rapidly developing suburban watersheds**

### **Statement of Critical Regional or State Water Problem**

New Hampshire's surface waters are a very valuable resource, contributing to the state's economic base through recreation (fishing, boating, and swimming), tourism and real estate values. Many rivers and lakes also serve as local water supplies. New Hampshire currently leads all New England states in the rate of development and redevelopment (2000 Census). The long-term impacts of population growth and the associated changes in land use to New Hampshire's surface waters are uncertain. Of particular concern are the impacts of non-point source pollution to the state's surface waters (e.g. septic, urban run off, road salt application, deforestation and wetland conversion). Long-term datasets that include year-to-year variability in precipitation, weather patterns and other factors will allow adequate documentation of the cumulative effects of land use change and quantification of the effectiveness of watershed management programs.

### **Statement of Results or Benefits**

The proposed project will provide detailed, high-quality, long-term datasets which will allow for a better understanding of the impacts of land use change and development on surface water quality. This could occur through the development, testing and refinement of predictive models, accurately assessing the impacts of watershed management practices, and potentially early warnings of dramatic changes to surface water quality in the region resulting from rapid development.

### **Objectives of the Project**

This project allows for the continued collection of long-term water quality data in New Hampshire. It will use UNH staff, students and volunteers from local communities to collect samples from the College Brook watershed (Durham, NH), the Lamprey River Watershed (coastal NH), and the Ossipee River Watershed (central NH).

Water samples will be collected from the following sub-projects.

The **College Brook** watershed, which is dominated by the University of New Hampshire, receives a variety of non-point pollution from several different land uses. pH, conductivity, and nutrient concentrations ( $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{PO}_4$ , DOC, TDN,  $\text{SiO}_2$ ) will be measured to assess water quality. Samples from 3 sites will be collected monthly throughout the year. Sampling of College Brook began in 1991. Sample collection will be done by UNH staff and/or students. The Water Quality Analysis Lab at UNH will analyze 2/3 of these samples as part of the non-federal match.

The **Lamprey River** has been sampled weekly and during rain events since October 1999. Samples are analyzed for total dissolved nitrogen (TDN), nitrate ( $\text{NO}_3\text{-N}$ ), ammonium ( $\text{NH}_4\text{-N}$ ), DON, DOC and orthophosphate ( $\text{PO}_4\text{-P}$ ). Additionally, samples

collected since October 2002 are also analyzed for dissolved inorganic carbon (DIC), pH, conductivity, dissolved oxygen (DO), temperature, total suspended sediment (TSS), particulate carbon (PC), particulate nitrogen (PN), silica and major anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ). In January of 2004, we began weekly sampling of additional stream sites throughout the Lamprey watershed for all above parameters except DIC, TSS, PC and PN. Stream data from 2004 showed that monthly sampling could be adequate to describe variation among sites throughout the watershed; therefore, the frequency of stream sampling was curtailed to monthly (instead of weekly) for 13 of our sampling sites. Three remaining stream sites (Lamprey River, North River and Wednesday Hill Brook - a small developed tributary) are still sampled weekly. These stream samples were analyzed by the Water Quality Analysis Lab at UNH.

In October of 2003, we initiated precipitation collection at numerous locations throughout the basin for analysis of nitrogen species,  $\text{PO}_4\text{-P}$ , DOM, major cations and anions and silica and also to monitor precipitation volume. Volunteers throughout the watershed were recruited to monitor precipitation volume at several stations in addition our stations used for both chemical analysis and volume recording. Precipitation data from 2004 indicated that chemistry does not vary significantly spatially, therefore we currently only sample from one collector in Durham, NH on an event basis. Homeowners have continued to monitor precipitation gages throughout the watershed as precipitation amount is spatially variable. These precipitation samples were analyzed by the Water Quality Analysis Lab at UNH.

#### **Groundwater Chemistry and nutrient dynamics.**

Monthly ground water well samples have been collected from the James Farm and Wednesday Hill Brook (WHB) well fields in Lee, New Hampshire within the Lamprey River watershed. James Farm monthly samples were collected from October 1995 through December 2006. Wednesday Hill Brook monthly samples were collected from July 2004 through 2007. James Farm and WHB ground water data demonstrates higher  $\text{NO}_3^-$  concentrations with low dissolved organic carbon (DOC) concentrations as well as low  $\text{NO}_3^-$  concentrations with high DOC concentrations, which suggests possible denitrification influencing ground water  $\text{NO}_3^-$  concentrations. In order to better understand groundwater nutrient dynamics, a graduate student used a push-pull method to estimate in-situ ground water denitrification rates by adding just  $\text{NO}_3^-$  and both  $\text{NO}_3^-$  and DOC (dextrose). We hypothesized that the dextrose additions will decrease  $\text{NO}_3^-$  concentrations at a faster rate than the  $\text{NO}_3^-$  only additions. A Master of Science student worked on the project and contributed her unpaid time as non-federal match.

#### **SPARROW model estimates of Nitrogen in 5 coastal NH watersheds**

This research is focused on nitrogen in coastal New Hampshire. Nitrogen in coastal areas is a growing problem because excess nitrogen can have damaging effects on coastal ecosystems including eutrophication which can lead to harmful algal blooms. In the coastal areas of the United States nitrogen is the biggest threat to the health of estuaries. Currently coastal New Hampshire is not under eutrophic conditions but nitrogen inputs to the coast have increased in recent years so it is important measure and understand their sources.

In this research the SPARROW model was used to estimate the loading of nitrogen in five coastal New Hampshire watersheds. The SPARROW model, a spatially referenced regression model on watershed characteristics has been calibrated to New England and estimates nitrogen load based on features of the watershed. The SPARROW model estimates nitrogen using two main predictor variables; land surface characteristics, and channel characteristics. In the main SPARROW equation these two variables were re-worked using more detailed information to get a better estimate of nitrogen in coastal New Hampshire. Wetland area and stream channel density are the two areas where the most variability is expected to be found between SPARROW and actual watershed conditions.

The goal of this research is to get a better estimate of the nitrogen contribution in to coastal New Hampshire and to better understand the SPARROW model and its potential limitations in coastal areas. Also it may bring a new use for the SPARROW model where more detailed data can be input for more accurate results. The SPARROW model is often used to identify sensitive areas for nitrogen pollution and develop nutrient criteria so understanding its accuracy could be very important. Hopefully this research will lead to additional nitrogen research in coastal New Hampshire and the potential development of a model that can accurately estimate nitrogen loading in coastal areas. A Master of Science student will be working on the project and contributing her unpaid time as non-federal match.

### **Ossipee Watershed**

Volunteers of the Green Mountain Conservation Group will sample streams within the Ossipee watershed of New Hampshire. Samples will be collected every 2 weeks from May to November, and monthly during the winter months. There will be approximately 340 samples collected. Water chemistry ( $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{PO}_4$ , DOC, TDN) will be measured on selected samples by the WQAL. WRRC staff will assist in data interpretation.

### **Methods, Procedures and Facilities**

Samples will be collected at intervals described above. Samples for dissolved analyses will be filtered in the field using pre-combusted glass fiber filters (0.7  $\mu\text{M}$  pore size), and frozen or refrigerated (depending on method requirement) until analysis. All samples will be analyzed in the Water Quality Analysis Lab of the WRRC on the campus of UNH, Durham, NH.

The Water Quality Analysis Laboratory (WQAL) was established by the Department of Natural Resources in 1996 to meet the needs of various research and teaching projects both on and off the UNH campus. It is currently administered by the NH Water Resources Research Center and housed in James Hall. Dr. William McDowell is the Laboratory Director, and Jeffrey Merriam is the Laboratory Manager. Together, they have over 35 years of experience in water quality analysis, and have numerous publications in the fields of water quality, biogeochemistry, and aquatic ecology.

Methods for analyses include ion chromatography ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{-2}$  and  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ), discrete colorimetric analysis ( $\text{NH}_4$ ,  $\text{PO}_4$ ,  $\text{NO}_3/\text{NO}_2$ ,  $\text{SiO}_2$ ), and High

temperature Oxidation (DOC, TDN). All methods are widely accepted techniques for analysis of each analyte.

## **Principal Findings and Significance**

### College Brook

Previous work on College Brook in the early 1990's (McDowell unpublished) shows that the UNH campus had a severe impact on water quality and was negatively affecting stream biota and the integrity of downstream ecosystems. By any yardstick, campus operations could not be considered sustainable. There was clear evidence that the UNH incinerator was causing excessive organic matter loading, resulting in high biochemical oxygen demand (BOD) and low dissolved oxygen (DO) in stream water. Since the incinerator has been closed, BOD and DO are no longer at levels detrimental to in-stream biota. Our monthly sampling regime was scaled back beginning October 2006 to the 3 stations that have historically shown the greatest changes, and we eliminated the BOD and TSS measurements (both which change little over the reach since the incinerator was closed). The most downstream sampling location is now closer to where the stream empties into the Oyster River in an effort to better quantify inputs to the Great Bay estuary. We also added a 4<sup>th</sup> site that was previously sampled at Pettee Brook in May 2008. Analyses of samples collected through 2007 have been completed and we are in the process of updating our website

[http://www.wrrc.unh.edu/current\\_research/collegebrook/collegebrookhome.htm](http://www.wrrc.unh.edu/current_research/collegebrook/collegebrookhome.htm).

Dissolved Oxygen (DO) in the brook is lower at the upstream stations. This difference is presumably due to hydrologic properties of the upstream sampling location which resembles a wetland (i.e. slow flow, higher organic matter and organic carbon). DO increases downstream as flow becomes faster and re-aeration higher.

Data from 2000-2007 indicates that the stream is strongly impacted by road salt at its origin, which is essentially a road-side ditch leading to a wetland area. Average Sodium and Chloride concentrations, as well as specific conductance, appear to have remained reasonably constant since 2001, but are much higher than in 1991. Concentrations are highest at the upstream stations and tend to decline downstream as the stream flows through the athletic fields and then increase as the stream passes through the heart of campus and downtown Durham.

Another export to Great Bay that is a cause of concern is nitrogen and especially nitrate. As College Brook becomes more aerated as it moves downstream ammonium decreases and nitrate increases indicating that nitrification is occurring in the stream channel, however the mass of each and an increase in total nitrogen indicates that there is additional sources of nitrate to the stream. This is possibly from fertilization of the athletic fields and/or storm water runoff. There also appears to be a slight, but insignificant, increase in nitrate over time. This will need to be closely monitored as algal blooms and loss of Eelgrass have become a concern in Great Bay.

### The Lamprey River Hydrologic Observatory

The Lamprey River watershed is a rural watershed located in southeastern NH and is under large development pressure as the greater area experiences rapid population growth. The Lamprey River Hydrologic Observatory (LRHO) is a name given to the entire Lamprey River basin as it serves as a platform to study the hydrology and biogeochemistry of a suburban basin and is therefore used by the UNH community as a focal point for student and faculty research, teaching and outreach. Our goal for the long-term Lamprey water quality monitoring program is to document changes in water quality as the Lamprey watershed becomes increasingly more developed and to understand the controls on N transformations and losses. We have continued to sample the Lamprey River at the USGS gauging station in Durham, NH (referred to as "LR 73.3"), the North River at the former USGS gauging station in Epping, NH (NR 26.9) and a small tributary to the Lamprey River in Lee, NH (WHB 1.03) on a weekly basis and 13 other stations throughout the watershed on a monthly basis.. The USGS discontinued the operation of the North River gauging station in October 2006 and since then we have been recording weekly stage height and calculating flow based on the USGS rating curve. We are able to record stream flow at WHB 1.03 using an electronic distance meter in combination with a rating curve that we have developed for this site. We have also developed a stream flow model for WHB 1.03 where daily discharge can be estimated from meteorological measurements (such as precipitation and temperature) and this model is useful for estimating historic flows. We continue to collect precipitation at Thompson Farm (UNH property located in Durham, NH) to document nitrogen inputs to the basin and work with NOAA/AIRMAP in an attempt to link to precipitation chemistry to air mass chemistry.

Results of stream chemistry to date show a significant increase in nitrate concentrations over time in the Lamprey River (Figure 1). Preliminary analysis of long-term sample collection (weekly since 2004, various intervals since 2000) shows that nitrate is also increasing over time in the North River, but not in Wednesday Hill Brook. We have shown previously that stream water nitrate is related to watershed population density (Daley 2002) and since suburbanization continues to occur throughout the greater Lamprey River and North River watersheds, population growth is likely responsible for the increase in stream water nitrate. Wednesday Hill Brook watershed is near its development capacity, unless the Town of Lee, NH changes its zoning regulations, and the lack of increase in WHB nitrate may be due to the limited population growth in this watershed.

Despite the rapid suburbanization that is occurring throughout southeast NH and the associated increase in road application, sodium and chloride concentrations have decreased recently in the Lamprey. However, we believe this is due to dilution from two 100 year floods occurring in May 2006 and April 2007. Annual exports (kg/ha/yr) of sodium and chloride have actually increased consistently since 2003. Variation of sodium and chloride concentrations among Lamprey and College Brook sub-basins are directly related to impervious surfaces and the associated road salt application (Figure 2).

Results of precipitation monitoring show that wet deposition is the largest input of N to the Lamprey watershed and precipitation chemistry can be linked to air mass chemistry.

DOC and TDN in precipitation are related to biogenic air mass sources,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$  and  $\text{SO}_4\text{-S}$  are related to urban/industrial air masses and Na and Cl are weakly related to ocean aerosols.

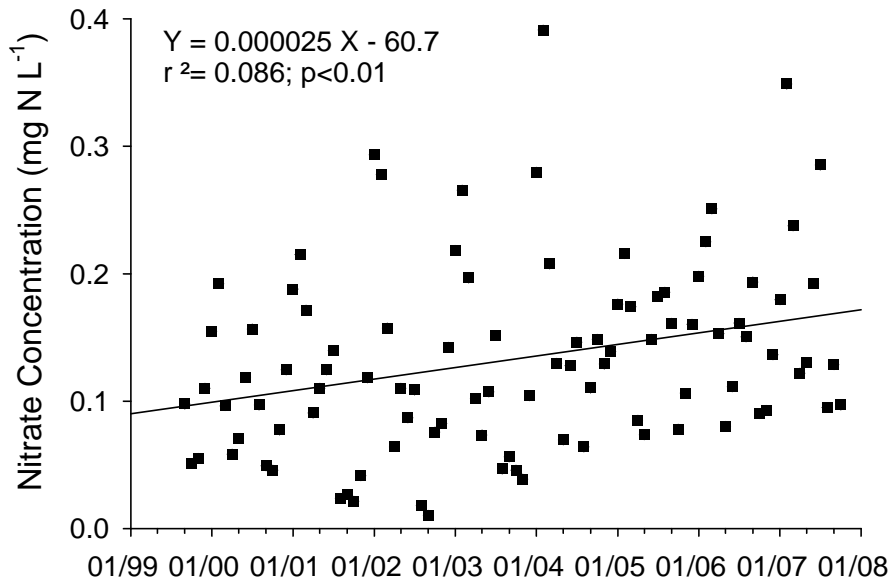


Figure 1. Average monthly nitrate concentrations over time in the Lamprey River at the USGS gauging station in Durham, NH.

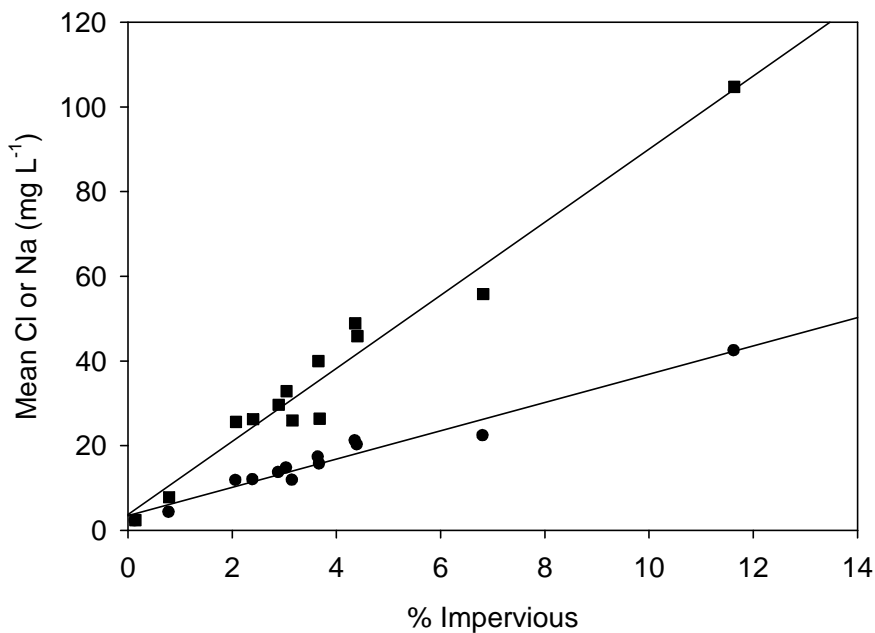


Figure 2. Average sodium and chloride concentrations versus impervious surfaces in Lamprey and College Brook sub-basins.

### Groundwater Chemistry and nutrient dynamics.

Hydrogeologic characteristics and groundwater physical properties and chemical constituents were evaluated in the James Farm well field located in Lee, NH, USA from 1995 to 1996, and from James Farm and Wednesday Hill Brook (WHB) from 2004 to 2006. There were no clear seasonal  $\text{NO}_3^-$  patterns in the James Farm or WHB well field. In general, wells located in the north and southwest areas of the James Farm well field had higher mean  $\text{NO}_3^-$  and wells located in the center of the well field had lower mean  $\text{NO}_3^-$  concentrations. In the WHB well field, upslope groundwater had  $\text{NO}_3^-$  concentrations of 3.0 – 4.0 mg  $\text{NO}_3\text{-N/L}$  and downslope groundwater next to the stream had nitrate levels of less than 0.1 mg  $\text{NO}_3\text{-N/L}$ . In most James Farm wells, there was no significant change in groundwater nitrate between the 1995-1996 and 2004-2006 sampling periods. However, in well A4 nitrate increased from 0.4 to 1.0 mg  $\text{NO}_3\text{-N/L}$  and in well A7 nitrate increased from 1.0 to 2.0 mg  $\text{NO}_3\text{-N/L}$  between 1995-1996 and 2004-2006. There are no clear trends showing changes in nitrate concentrations over time in the WHB well field from 2004-2006. Based on this data, we currently recommend quarterly sampling of these well fields for 2008

The “push-pull” method estimated denitrification potential at James Farm by adding different quantities of nitrate and dissolved organic carbon to riparian groundwater. The constituents measured were nitrate, ammonium, total dissolved nitrogen, dissolved organic carbon, sulfate, bromide, chloride, sodium, magnesium, potassium, calcium, and silica. Patterns of nitrogen concentration in ambient riparian groundwater suggested that denitrification might be occurring as groundwater flowed through the center of the well field. Field experiments with the push-pull method, however, showed that substantial N loss did not occur even with large amounts of added nitrate and dissolved organic carbon. Short groundwater residence times may have been responsible for the lack of denitrification.

### SPARROW model estimates of Nitrogen in 5 coastal NH watersheds

The New England SPARROW model was recalibrated to 31 sub-basins in Lamprey River watershed and 8 sub-basins in the Oyster River watershed for a total of 39 calibration sites in coastal NH. Most of the Nitrogen export data used for calibration purposes were collected and analyzed with WRRC funding and WRRC staff and student interpretation. Stream samples were all analyzed in the WQAL at UNH. Land use data input into the model was updated with NWI wetlands to better characterize these abundant features in the coastal landscape which are often misinterpreted by landsat imagery (used to develop land use GIS layers) as either forests or open water instead of forested wetlands and open wetlands. The final coastal NH model had parameter coefficients that were similar to the NE SPARROW, but the standard errors around these coefficients were reduced. The coastal NH model had a  $R^2$  of 0.89 and a MSE of -0.14. Wetlands were not a significant source or loss term in the NE SPARROW, but were included as a source variable in the coastal NH model. This is likely due to the contribution of DON from wetlands. The newly calibrated coastal NH model was then applied to the Lamprey, Oyster, Exeter, Chochoeco and Salmon Falls Rivers which comprise the major tributaries to Great Bay. The coastal NH model predicted lower N exports for Great Bay tributaries (average of



2.0 kg/ha/yr) compared to the NE SPARROW (average of 5.0 kg/ha/yr). Six samples were collected (in the spring and fall) from each of the major Great Bay tributaries and used to estimate annual flux from these watersheds. The coastal NH model was better at predicting N flux from the Great Bay tributaries than the NE SPARROW model (Figure 3). These results have large implications for establishing TMDL limits in coastal NH. The NE SPARROW over-estimates N flux in coastal NH and does not accurately identify all N source variables for this coastal region.

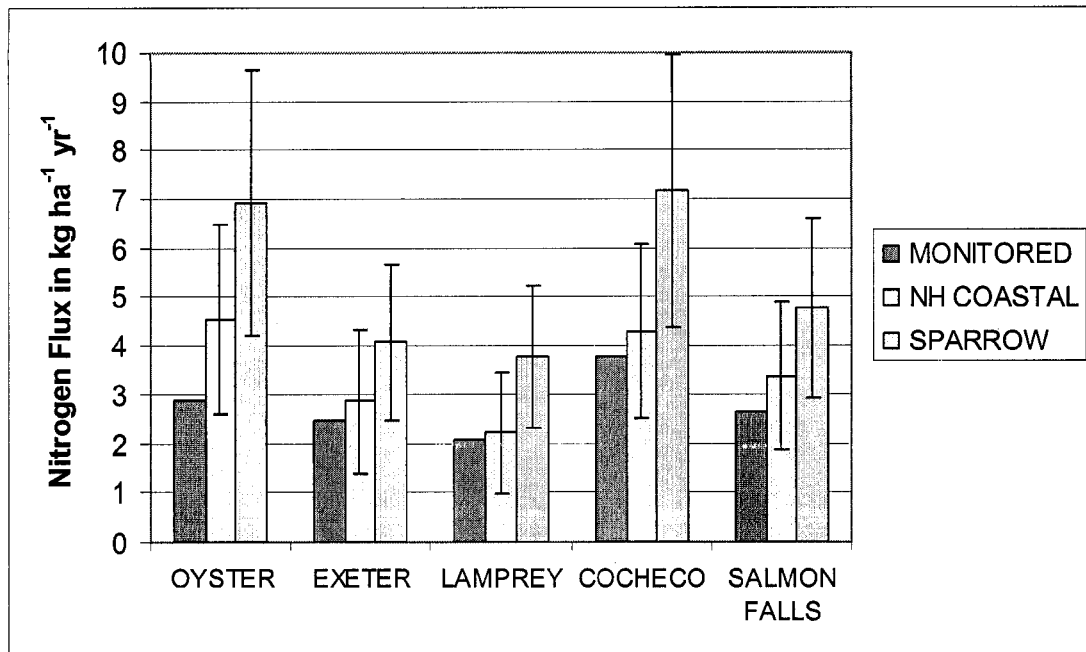


Figure 3. Flux estimates for each watershed based on WRRC monitored loads, coastal NH SPARROW predicted loads and NE SPARROW predicted loads.

#### Ossipee Watershed

Collaboration with the Green Mountain Conservation Group and their sampling of the Ossipee River watershed has continued to be beneficial. Volunteers sampled streams within the watershed every 2 weeks from April through October, and monthly winter sampling at 7 sites, with approximately 340 samples collected from 30 sampling locations. Many presentations were made to planning boards, conservation commissions and other local government groups (see Information Transfer section below). Data have been used to heighten awareness of the impacts of excessive road salting and snow dumping in local streams. Communication with local road agents has led to the remediation in one development where road salting was an issue. Samples collected and data generated from this funding have shown an improvement in water chemistry following reduced salting and snow dumping. Data has also been useful in promoting low impact development techniques and best management practices where new development has been proposed in proximity to rivers and streams within the watershed.

#### **Material in Preparation:**

McDowell, W.H., M.L. Daley, B. Sive, R. Talbot. Factors controlling atmospheric deposition at a coastal suburban site. *Journal of Geophysical Research (Atmospheres)*.

#### **Conference Proceedings & Abstracts**

McDowell, W.H. 2007. Biogeochemistry of a suburban basin. Marine Biological Laboratory, January 2007.

Daley, M.L., L.A. Buyofsky, W.H. McDowell. 2007. Linking Groundwater Quality to Landscape Characteristics in the Lamprey River Basin. The New Hampshire Water Conference, Concord, NH. April 2007.

McDowell, W.H. 2007. Biogeochemistry of a suburban basin. University of New Hampshire. November 2007.

McDowell, W.H. 2007. Water Quality in the Suburbanizing Lamprey River Basin. The New Hampshire Watershed Conference, Concord, NH. November 2007.

McDowell, W.H. 2007. Biogeochemistry of a suburban basin. New Hampshire Estuaries Project Meeting. December 2007.

McDowell, W.H., M.L. Daley, B. Sive, R. Talbot. 2007. Linking Atmospheric Deposition to Airmass Chemistry at a Coastal Rural Site. American Geophysical Union fall meeting, San Francisco, December 2007.

McDowell, W.H. 2008. Biogeochemistry of a suburban basin. Harvard Forest, Harvard University. March 2008.

McDowell, W.H. 2008. Biogeochemistry of a suburban basin. University of Connecticut, Storrs, CT. March 2008.

#### **Dissertations and Theses:**

Legere, K.A. September 2007. Nitrogen loading in coastal watersheds of New Hampshire: an application of the SPARROW model. *Masters Thesis*, University of New Hampshire, Durham, NH.

Traer, K. December 2007. Controls on denitrification in a northeastern coastal suburban riparian zone. *Masters Thesis*, University of New Hampshire, Durham, NH.

#### **Information Transfer:**

McDowell, W.H. and Daley, M.L. 2008. Current Research in the Lamprey River Watershed. Lamprey River Advisory Committee meeting. January 2008.

#### **Symposia Organized and Funded:**

First Annual NH Water Conference, April 2007, Concord NH (Organizing

committee, provided partial funding, over 300 attendees)

Annual NH Watershed Conference, November 2007, Concord NH (Organizing committee, provided partial support, over 200 attendees)

First Annual Lamprey River Hydrologic Observatory Symposium, Durham, NH (totally funded and organized, over 50 attendees)

Presentations made by the Green Mountain Conservation Group staff.

- 3/10/2007 OWC Workshop w/ Board & Town Rep's (GIS, land use planning, watershed planning)
- 3/24/2007 Natural Resource Based Planning Workshop (regional meeting, Tamworth)
- 4/8/2007 Water Quality Monitoring Program & Training
- 4/14/2007 Water Monitoring Programs Training
- 4/28/2007 Drinking Water Protection Conference
- 5/3/2007 Watershed Ordinances, How to Write/Pass Ordinances, Groundwater Protection Workshop
- 5/29/2007 Camp Calumet Program (OLT & lake water testing with students)
- 6/1/2007 Camp Calumet Program (OLT & lake water testing with students)
- 6/7/2007 Water Quality Reporting/Summer Camp Director Meeting (OLT & VLAP)
- 6/13/2007 WQM program Sandwich school
- 6/14/2007 OWC Workshop Chocorua (land use planning, watershed planning)
- 7/3/2007 Camp Calumet Program (OLT)
- 7/3/2007 Camp Marist Program (macro/OLT)
- 7/13/2007 NH Green Yards/BMP Open House w/ DES in Berlin
- 7/21/2007 Watershed Weekend (water quality, lake management/protection)
- 7/17/2007 Camp Calumet Program (OLT)
- 7/31/2007 Camp Calumet Program (OLT)
- 8/14/2007 Calumet Program (OLT)
- 8/15/2007 Drinking Water Protection workshop Concord
- 8/22/2007 Macro Training (expansion of WQM program)
- 9/5/2007 Tamworth Learning Circles School Program (RIVERS, macro)
- 9/10/2007 Sandwich Elementary School Program (RIVERS, macro)
- 9/15/2007 GIS/Drinking Water Protection Workshop w/ UNHCE Chocorua
- 10/1/2007 Effingham Planning Board/Conservation Commission Presentation (NR Guide)
- 10/7/2007 Madison Planning Board/Conservation Commission Presentation (NR Guide)
- 10/9/2007 Water Monitoring/Macro Sampling in Watershed/Mongolia Presentation Effingham
- 10/27/2007 Ossipee & Freedom Planning Board/Conservation Commission Presentation (NR Guide)
- 10/28/2007 Tamworth Planning Board/Conservation Commission Presentation (NR Guide)
- 12/6/2007 Sandwich Planning Board/Conservation Commission Presentation (NR Guide)
- 1/31/2008 OWC Workshop Chocorua (watershed planning, Guide follow up)

2/5/2008 Ossipee Planning Board Meeting (BMPs, Frenchman's Brook wqm data)  
2/22/2008 BMPs, Drinking Water Protection NH DES Training for Town Officials

**Number of students supported:**

Two Master's students and one undergraduate hourly employee