EFFECTS OF ATMOSPHERIC DEPOSITION OF SULFUR, NITROGEN, AND MERCURY ON ADIRONDACK ECOSYSTEMS

FINAL REPORT 04-03 SEPTEMBER 2004

NEW YORK STATE ENERGY RESEARCH AND DEVELOPMENT AUTHORITY

NYSERDA



The New York State Energy Research and Development Authority (NYSERDA) is a public benefit corporation created in 1975 by the New York State Legislature. NYSERDA's responsibilities include:

- Conducting a multifaceted energy and environmental research and development program to meet New York State's diverse economic needs.
- Administering the **New York Energy \$mart**sm program, a Statewide public benefit R&D, energy efficiency, and environmental protection program.
- Making energy more affordable for residential and low-income households.
- Helping industries, schools, hospitals, municipalities, not-for-profits, and the residential sector, including low-income residents, implement energy-efficiency measures.
- Providing objective, credible, and useful energy analysis and planning to guide decisions made by major energy stakeholders in the private and public sectors.
- Managing the Western New York Nuclear Service Center at West Valley, including: (1) overseeing the State's interests and share of costs at the West Valley Demonstration Project, a federal/State radioactive waste clean-up effort, and (2) managing wastes and maintaining facilities at the shut-down State-Licensed Disposal Area.
- Coordinating the State's activities on energy emergencies and nuclear regulatory matters, and monitoring low-level radioactive waste generation and management in the State.
- Financing energy-related projects, reducing costs for ratepayers.

NYSERDA administers the **New York Energy \$mart**sm program, which is designed to support certain public benefit programs during the transition to a more competitive electricity market. Some 2,700 projects in 40 programs are funded by a charge on the electricity transmitted and distributed by the State's investor-owned utilities. The **New York Energy \$mart**sm program provides energy efficiency services, including those directed at the low-income sector, research and development, and environmental protection activities.

NYSERDA derives its basic research revenues from an assessment on the intrastate sales of New York State's investor-owned electric and gas utilities, and voluntary annual contributions by the New York Power Authority and the Long Island Power Authority. Additional research dollars come from limited corporate funds. Some 400 NYSERDA research projects help the State's businesses and municipalities with their energy and environmental problems. Since 1990, NYSERDA has successfully developed and brought into use more than 150 innovative, energy-efficient, and environmentally beneficial products, processes, and services. These contributions to the State's economic growth and environmental protection are made at a cost of about \$.70 per New York resident per year.

Federally funded, the Energy Efficiency Services program is working with more than 540 businesses, schools, and municipalities to identify existing technologies and equipment to reduce their energy costs.

For more information, contact the Communications unit, NYSERDA, 17 Columbia Circle, Albany, New York 12203-6399; toll-free 1-866-NYSERDA, locally (518) 862-1090, ext. 3250; or on the web at www.nyserda.org

STATE OF NEW YORK George E. Pataki Governor ENERGY RESEARCH AND DEVELOPMENT AUTHORITY Vincent A. DeIorio, Esq., Chairman Peter R. Smith, President

EFFECTS OF ATMOSPHERIC DEPOSITION OF SULFUR, NITROGEN, AND MERCURY ON ADIRONDACK ECOSYSTEMS

FINAL REPORT

Prepared for the

NEW YORK STATE ENERGY RESEARCH AND DEVELOPMENT AUTHORITY

Albany, NY www.nyserda.org

Mark R. Watson Project Manager

Prepared by

STATE UNIVERSITY OF NEW YORK COLLEGE OF ENVIRONMENTAL SCIENCE AND FORESTRY

Syracuse, New York

Dudley J. Raynal Myron J. Mitchell

SYRACUSE UNIVERSITY

Syracuse, New York

Charles T. Driscoll

and

NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION/ ADIRONDACK LAKES SURVEY CORPORATION

Ray Brook, New York

Karen M. Roy

NOTICE

This report was prepared by the State University of New York College of Environmental Science and Forestry, Syracuse University, and the New York State Department of Environmental Conservation/Adirondack Lakes Survey Corporation, in the course of performing work contracted for and sponsored by the New York State Energy Research and Development Authority (hereafter the "Sponsor"). The opinions expressed in this report do not necessarily reflect those of the Sponsor or the State of New York, and reference to any specific product, service, process, or method does not constitute an implied or expressed recommendation or endorsement of it. Further, the Sponsor and the State of New York make no warranties or representations, expressed or implied, as to the fitness for particular purpose or merchantability of any product, apparatus, or service, or the usefulness, completeness, or accuracy of any processes, methods, or other information contained, described, disclosed, or referred to in this report. The Sponsor, the State of New York, and the contractor make no representation that the use of any product, apparatus, process, method, or other information will not infringe privately owned rights and will assume no liability for any loss, injury, or damage resulting from, or occurring in connection with, the use of information contained, described, disclosed, or referred to in this report.

PREFACE

The New York State Energy Research and Development Authority (NYSERDA) is pleased to publish "Effects of Atmospheric Deposition of Sulfur, Nitrogen, and Mercury on Adirondack Ecosystems." The report was prepared by the State University of New York College of Environmental Science and Forestry, Syracuse University, and the New York State Department of Environmental Conservation/Adirondack Lakes Survey Corporation.

This project is somewhat different from other New York State Energy \$martSM Environmental Monitoring, Evaluation and Protection program (EMEP) projects in that it represents a collection of tasks addressing sometimes discrete hypotheses related to the effects of atmospheric deposition on Adirondack ecosystems. Several of the tasks were underway when the EMEP program was created, and had been funded by the utility industry prior to the restructuring of electric utilities in New York State. The EMEP program the provided the necessary support to continue this research in order to maximize the scientific value of the ongoing work. This report has also built upon other research projects supported by NYSERDA in an effort to increase the understanding of the causes and long-term impacts of acidic deposition in the Adirondacks.

Project findings have been summarized in this report. The detailed project results and methodologies are published in the peer-reviewed journal papers listed at the end of the report. If a paper has not yet been published on a project area, more detail is included in this report. It is our hope that this project will provide useful information needed for evaluating alternative policies for mitigating these impacts, and ultimately a better understanding of the response of affected ecosystems to anticipated environmental improvements.

ACKNOWLEDGMENTS

NYSERDA appreciates the input of project reviewers: Dr. Stuart Findlay, Scientist and Aquatic Ecologist, Institute of Ecosystem Studies; Mr. John Holsapple, Director, Environmental Energy Alliance of New York; and Dr. Scott Ollinger, Research Assistant Professor, Complex Systems Research Center, University of New Hampshire.

TABLE OF CONTENTS

Section	Page
Executive Summary	S-1
Project Findings	1-1
Analysis of Dissolved Organic Nitrogen (DON) in the ALSC Long Term Monitoring lakes	1-1
Estimation of the amounts of nitrogen fixation by speckled alder in Adirondack watersheds	1-3
Estimation of the distribution and abundance of speckled alder inputs to Adirondack wetlands	9
Analysis of time-series in the chemistry of precipitation and l	ake water1-8
Estimation of Mass Balances for ALSC ALTM Lakes	1-12
Application of the PnET-BGC model to ALTM sites	1-14
Evaluation of the historical rates of mercury deposition to the	e Adirondacks 1-18
Measurement of current rates of mercury deposition in the co	entral Adirondacks 1-20
Evaluation of the recovery of fisheries in the North Branch of	f the Moose River 1-22
References	2-1
Publications related to this research project	3.1

Executive Summary

Overview

The Adirondack region receives elevated levels of atmospheric deposition of sulfur (S), nitrogen (N), and mercury (Hg). Atmospheric deposition of strong acids has resulted in acidification of surface waters and increased uptake of Hg in fish. Despite reductions in sulfate emissions from power plants, surface waters in the Adirondacks have shown limited recovery from acidification. The United States Environmental Protection Agency (EPA) has indicated that additional reductions of S and N deposition may be required for the recovery of sensitive Adirondack lakes. The amount of reductions and resulting impact on recovery is still unknown.

The overall goal of this project was to increase the understanding of the causes and long-term impacts of acidic deposition in the Adirondacks and provide information needed for evaluating alternative policies for mitigating these impacts. This project has built upon previous research efforts. The analyses used data collected in three other projects supported through the NYSERDA Environmental Monitoring, Evaluation and Protection (EMEP) Program. Water samples and supporting data for analysis of the role of dissolved organic nitrogen (DON) in Adirondack watersheds were obtained from the Adirondack Lakes Survey Corporation (ALSC). Lake water chemistry data collected by the ALSC (Project 4915) were also used for time series analyses and estimation of lake/watershed mass balances performed in this project. Detailed information on the role of forest maturation in the regulation of drainage water chemistry and a calibration of the PnET-BGC model for analyzing element cycling was completed through another EMEP project "An Evaluation of the Recovery from Acidification of Surface Waters in the Adirondacks: Role of Watersheds and Forest Maturation (Project 4917)." This project also complemented work undertaken in the EMEP project "Mercury in Adirondack Wetlands, Lakes and Terrestrial Systems (project 4916)." This project also examined Hg deposition over time in the sediments of eight lakes to add to the understanding of mercury cycling.

Atmospheric Deposition

Several aspects of this research have provided information that is relevant to policymakers and resource managers that are interested in the effects of air pollution on forest and aquatic ecosystems in the Adirondack region of New York. Ongoing measurements and those of colleagues suggest that wet deposition of SO_4^{2-} to the Adirondacks has decreased over the last 22 years. This decrease is consistent with decreases in

emissions of SO_2 for the source area for the Adirondacks and has resulted in a decrease in the wet deposition of H^+ to the region. In contrast, there has been no large change in concentrations and hence deposition of NO_3^- or NH_4^+ in precipitation over the monitoring period which is consistent with limited changes in emissions of NO_x and NH_3 for the source area of the region. Note that the decline in SO_4^{-2-} coupled with the lack of change in concentrations and deposition of NO_3^- suggest that the relative role of NO_x emissions in regulating the acidity of precipitation in the Adirondacks and elsewhere in the eastern U.S. has increased over the past 22 years.

Lake Chemistry

Long-term measurements of lake chemistry made by ALSC researchers have shown widespread and relatively uniform decreases in concentrations of SO₄²⁻ since measurements were initiated in the Adirondacks in the early 1980s. These long-term decreases are consistent with decreases in SO₂ emissions and wet SO₂²deposition. Taken collectively these observations are important because they indicate that the 1970 and 1990 Amendments of the Clean Air Act have helped reduce acidic deposition and inputs of SO_4^{2-} which are the major source of acidity to acid-sensitive lakes in the Adirondacks. The ALSC study shows, for the first time since measurements were initiated on lake chemistry in the Adirondacks, that acid neutralizing capacity (ANC) values are increasing in a large percentage of the lakes monitored (29 out of 48). These increases in ANC are due to widespread decreases in concentrations of SO_4^{2-} and decreases in NO_3^{-} in some Adirondack lakes. Both in-lake biological processing of N as well as N inputs and transformations associated with N fixation and the cycling, storage and export of N in wetlands add to the complexity of differential patterns of NO₃ concentration across the Adirondack region. The reason for the long-term decline in lake NO₃ is unclear. It is possible that this trend is due to changes in climate and/or hydrology. Although there have been clear improvements in the acid-base status of many Adirondack lakes the rate of ANC increase is relatively low. As a result, at the current rates of ANC increase it will be several decades before the most acid-impacted lakes will achieve adequate chemical recovery to allow for recovery of aquatic biota.

Fisheries Status in the North Branch of the Moose River

The above conclusion is consistent with the results of fish surveys conducted as part of this study for the North Branch of the Moose River. Utilizing historical surveys conducted in the 1930s, stocking records and a survey conducted in the early 1980s, it was concluded that acidic deposition decreased species richness in the area. Comparison of species richness of fish for sites in the North Branch of the Moose River in 2000 with results from these earlier studies shows that declines in species richness have stabilized and may be

slightly improving. These patterns in fisheries status are consistent with improvements in the acid-base status of surface waters in the Adirondacks.

Future Scenarios

As part of this study, calculations were conducted with the biogeochemical model PnET-BGC for four lake/watershed ecosystems. Results of this analysis clearly demonstrate that acidification of soil and water have resulted from inputs of acidic deposition over the last 150 years, and that chemical recovery has occurred over the last 30 years in response to the 1970 and 1990 Amendments to the Clean Air Act. Projections of potential future changes suggest that under current deposition patterns lakes will either continue to acidify or recover at a very slow rate. Model predictions suggest that additional reductions in SO₂ and NO_x emissions will help accelerate the rate of ANC increase but the period of chemical recovery will be decades.

Role of Vegetation

An understanding of site-specific biogeochemical linkages between vegetation and surface water is important in evaluating ecosystem responses to future reductions in atmospheric deposition. The composition of terrestrial and riparian wetland vegetation mediates changes in nitrogen concentration of soil and surface waters and contributes to a diversity of responses of ecosystems in the Adirondack region. Alder-dominated wetlands will be slower to recover than other wetland types because they serve as a source of N.

Mercury in Fish

Elevated concentrations of Hg in fish in Adirondack lakes are of concern. A survey of yellow perch in 26 Adirondack lakes in the early 1990s showed that 96 percent of sampled lakes and 66 percent of the fish sampled exceeded the U.S. Environmental Protection Agency criterion of 0.3 μg Hg/g fish flesh. Long-term measurements of atmospheric Hg deposition or concentrations of Hg in surface waters or fish tissue are not available. To help reconstruct patterns of Hg deposition to Adirondack lakes, sediment cores were collected from eight lakes and these cores were sectioned, dated using ²¹⁰Pb and analyzed for Hg concentrations. This analysis showed marked increases in sediment Hg deposition between 1820 and 1910. Sediment Hg deposition generally peaked from 1973 to 1995 with rates on average 5.8 times greater than pre-Industrial Revolution values. In recent years (~ 20 yrs) the region has experienced about a 33% decrease in Hg deposition. Moreover, sediment core analyses suggest that lake-watershed retention of Hg has decreased in the Adirondacks over the last 100 years. Understanding long-term and recent changes in Hg deposition is

important because controls of Hg emissions from electric utilities are anticipated. It will be critical to interpret the changes in Hg deposition that may result relative to long-term patterns that have occurred in the region.

Fisheries Status in Adirondack Lakes and Streams

Recovery of fish species in Adirondack lakes and streams was evaluated by comparing historic fish inventory surveys (1982-83) with contemporary sampling (2000). A net increase of two fish species was recorded in 2000; two species were not found in the recent survey and four species previously not found were recorded. Total species richness measured 18 species including native, exotic, and stocked species. Lakes devoid of fish in the early 1980s were still without fish in 2000. Waters without fish had a median pH of 4.8 compared to productive waters which had a median pH of 5.9. Lakes without fish were typically small in size (5 ha in area compared to 22 ha in lakes that supported fish). Comparative inventory data revealed that some fish species appeared to increase their acid tolerance over the sampling interval.

Project Findings

Solute Chemistry - The objectives of the first six tasks were designed to further the analysis of temporal and spatial patterns in the chemistry of major solutes in Adirondack waters. Objectives in this part of the project included building upon linkages to related research efforts and testing the following hypotheses:

Task 1. Analysis of Dissolved Organic Nitrogen (DON) in the ALSC Long Term Monitoring Lakes.

Hypothesis: Dissolved organic N (DON) is an important component of dissolved nitrogen in Adirondack waters and DON concentrations are strongly related to the concentrations of dissolved organic carbon (DOC).

Methods: The relationships between DON and other solutes, especially DOC, were investigated in 52 Adirondack lakes for the period 1998-2000 using solute chemistry concentration measurements and modeled mass balances. Solute chemistry was obtained from the ALSC Adirondack Long Term Monitoring (ALTM) lakes. Surface water samples were shipped from the ALSC to SUNY-ESF each month from the 52 low-order drainage or seepage lakes starting from January 1998. At SUNY-ESF, monthly samples for each lake were analyzed for NH₄, NO₃, DOC, and TDN (total dissolved N). Statistical analyses included univariate analyses for describing solute concentrations within specific lakes. Linear regression analyses were used to describe the relationship between DON and DOC. To examine the effects of land cover types, stepwise multiple regressions were performed to determine the relationships between percent forest or wetland vegetation cover type and mean monthly concentrations or monthly concentrations of N solutes and DOC. Percent lake-watershed as each vegetation cover type, including wetland/water class was calculated, using lake cover maps constructed based on the LANDSAT Thematic Mapper data, and a map of lake-watershed boundaries, obtained from the Adirondack Park Agency. Chemical analytical techniques included ion chromatography (NO₃), Wescan ammonia analyzer (NH₄), persulfate digestion (TDN) and Phoenix 8000 Total Carbon Analyzer (DOC). DON is calculated as $TDN - (NO_3 + NH_4)$.

Results: The mean annual concentrations and fluxes of DON were strongly related to the concentrations and fluxes of DOC at $R^2 = 0.64$ and 0.50, respectively (Ito et al. 2004). Both the DON and DOC concentrations and fluxes were higher at the lake-watersheds with larger percent wetland area. It has been reported (Campbell et al. 2000) that there are negative correlations between the concentrations or fluxes of NO_3^- or dissolved inorganic nitrogen (DIN) and C/N ratios in soils and stream waters. At the outlet of the ALTM lakes, there were no relationships between the concentrations or fluxes of NO_3^- and the DOC/DON ratios, suggesting that different processes are controlling the concentrations and fluxes of N species flowing out of the lake-watersheds. Although DON is closely related to DOC (Figure 1.1), the relationships of DON and DOC with elevation were different; the DON export was negatively related to elevation ($R^2 = 0.22$), in contrast to the DOC export, which did not show relationships with elevation.

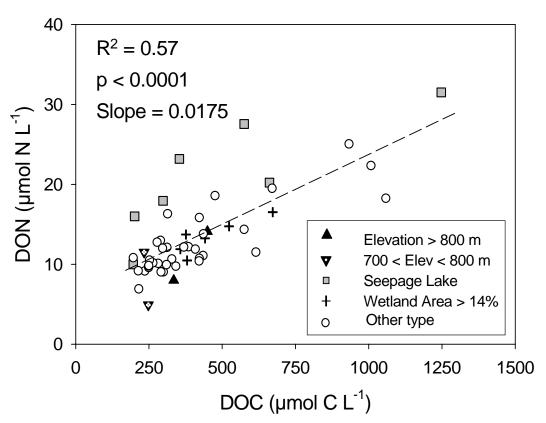


Figure 1.1 Relationships between DOC and DON for ALTM lake/watersheds (after Ito et al., 2004).

The DON concentrations were also negatively related to elevation at $R^2 = 0.33$. The DON export was weakly and negatively related to the N input ($R^2 = 0.09$, p = 0.035). The DON concentrations were inversely related to the NO_3^- concentrations at the ALTM lake outlet more strongly than the relationship between the DOC and NO_3^- concentrations suggesting that different factors were controlling contributions of DON and DOC in these lake-watersheds. In general, the DOC/DON export ratios from the lake-containing watersheds were lower than those from forest floor leachates or streams in New England and were intermediate between the values of autochthonous and allochthonous dissolved organic matter (DOM) reported for various lakes. The DOC/DON ratios for seepage lakes were lower than those for drainage lakes. In-lake processes regulating N exports may include denitrification, planktonic depletion, degradation of DOM, and autochthonous production of DOM and the influences of in-lake processes were also reflected in the relationships with hydraulic retention time (Ito et al. 2004).

This study indicates that there are many factors regulating concentrations and losses of N species in lake water across the Adirondack landscape. It is unlikely that there will be a strong cause and effect relationship between decreases in emissions and deposition of N species, and concentrations in Adirondack surface waters. However, it seems that lakes in the southwestern Adirondacks, where atmospheric N deposition is greatest and lakes are most acid-sensitive, will show the greatest response to changes in N deposition.

Task 2. Estimation of the amounts of nitrogen fixation by speckled alder in Adirondack watersheds.

Hypothesis: Nitrogen fixation by speckled alder is an important source of nitrogen to the Adirondack landscape.

Concerns about N pollution in the Adirondacks have prompted many studies linking N deposition to acidification of surface waters, N saturation and other environmental effects. Experimental studies and modeling efforts have accounted for many of the sources and sinks of N in surface waters, but few investigations have documented the importance of internally generated N. Wetlands are thought to serve as sinks for inorganic N but shrub wetlands containing N-fixing plans may function as net N sources. Comparative studies of nitrogen content of foliage between speckled alder and non-fixing species were undertaken.

Methods: We estimated N inputs to shrub-dominated wetlands through N fixation using ¹⁵N abundance and acetylene reduction methods (Hurd et al. 2001). Comparisons between different sites were also made. Analysis of variance (ANOVA) followed by means tests were used to detect species and siterelated differences. Ion exchange resin bags were employed to estimate the accumulation of NH₄ and NO₃ in surface waters in high-, low- and non-alder wetlands. Data were analyzed using ANOVA.

Results: Alder derives 85-100% of its foliar N from N_2 -fixation (Figure 2.1). At an intensive study site, alder foliage contained 37-43 kg N per hectare, derived primarily from the atmosphere. This input level compares with atmospheric deposition of N of 8-10 kg N per hectare in the region (Aber et al. 2003). Speckled alder in Adirondack wetlands relies on atmospheric fixation to meet its N nutritional needs. When leaves abscise and decompose, N in foliage is mineralized and subsequently NO_3 is released to surface water.

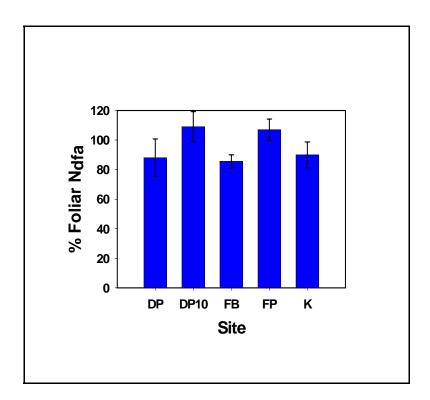


Figure 2.1 Percent of foliar N in speckled alder derived from atmospheric N_2 at five Adirondack wetland sites (Hurd et al. 2001).

NH₄ and DON accumulated in wetlands during the growing season, indicating that riparian wetlands are a transient pool of N. Nitrate in the channel water in riparian wetlands dominated by alder exceeded that in non-alder wetlands by 6 times at periods of maximum streamflow (April) and by 2 times in the summer (Figure 2.2). Nitrification is stimulated in alder wetlands, and the produced NO₃ contributes to elevated N during periods of peak flow. Where wetlands occupy a substantial proportion of the watershed area, N additions by alder are important for watershed budgets. At both the local watershed and landscape scales, the effects of reducing atmospheric deposition by emission reductions will depend on the biogeochemical attributes of the watershed and landscape, including the presence of alder-dominated shrub wetlands. Alder-dominated wetlands will be slower to recover than other wetland types because they continue to serve as a source rather than a sink of N.

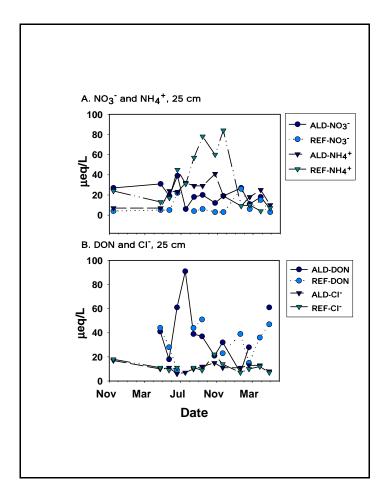


Figure 2.2 Nitrate, ammonium, dissolved organic nitrogen and chloride in alder and non-alder riparian reaches of an Adirondack shrub wetland at substrate depth of 25 cm (after Hurd and Raynal 2004).

Task 3. Estimation of the distribution and abundance of speckled alder and its contribution to nitrogen inputs to Adirondack wetlands.

Hypothesis: Speckled alder is a major constituent of shrub wetlands in the Oswegatchie-Black and Upper Hudson watersheds and contributes nitrogen to surface waters.

Wetlands are abundant in the Adirondack Mountains of New York. For example, within the Oswegatchie-Black drainage system, 15% of the total area is classified as "wetland." Shrub-dominated wetlands constitute about 28% of the wetland complex (Kiernan et al. 2003). Many shrub-dominated wetlands support vigorous populations of the nitrogen-fixing shrub, speckled alder. In association with a microbial symbiont, this colonial successional shrub fixes large quantities of foliar nitrogen. Concentrations of nitrogen in alder leaf tissue ranges from 2.6-3.0%. Alder/willow wetlands are the second most common wetland type in the Adirondack region; only forested wetlands are more abundant.

Methods: Twenty randomly selected palustrine wetlands were located and sampled to estimate the size and abundance of alder. Using alder abundance data, the range of nitrogen fixation and inputs to alder wetlands was estimated to project nitrogen inputs by alder at the regional watershed scale. The abundance of speckled alder in representative Adirondack shrub wetlands was compared using analysis of variance statistical methods (Kiernan et al. 2003). Allometric equations, based on linear regression of log-transformed stem diameter and biomass, were used to estimate alder biomass at each site. Using these data, a representative subset of readily accessible sites was selected for ground truthing the wetland category type and sampling actual density of alder. Mineralization and nitrification rates were assessed in wetlands using buried ion exchange resin bags followed by inorganic N extraction and analysis. Groundwater concentrations of nitrogen and pH were also measured.

Results: Alder was generally abundant but was not found in every wetland classified as "alder/willow wetland" in the GIS data. Alder averaged 35% of the total vegetative stems with densities similar to that of central New York wetlands (Table 3.1).

Table 3.1. Mean total shrub layer density (stems ha⁻¹), mean alder density, and percent alder in studied wetlands.

		Total	Alder	%
OB	SS1/EM1	12880	4568	35
	SS1	22620	6777	30
	Total	16776	5451	32
UH	SS1/EM1	20597	5802	28
	SS1	22373	10979	49
	Total	21307	7873	37
	Overall	19041	6662	35 ^a

a-Range from 0-99%

Where alder was present, it constituted about 50% of the total shrub stems and accounted for at least 98% of the total stem density in 10% of the wetlands sampled. Foliar biomass ranged from 0-1261 kg per hectare with an average of 377 kg per hectare (Table 3.2).

Alder foliage contributed 112 metric tons of fixed nitrogen to the Oswegatchie Black drainage and 80 metric tons to the Upper Hudson system. It is estimated that the total nitrogen contribution from fixation in alder-dominated wetlands ranged from 0-30 kg N per hectare per year. At nine sites, fixed foliar nitrogen equaled or exceeded atmospheric nitrogen deposition (~10 kg per hectare per year) and exceeded by more than 150% of deposition in 20% of the wetlands. Overall, fixed nitrogen measured 191 metric tons, about 2.5% of total areal atmospheric deposition. Locally, in specific alder-dominated wetlands, nitrogen addition from alder exceeds atmospheric deposition by as much as 300%.

Table 3.2. Estimated foliar biomass and foliar N contribution to studied wetlands.

OB	Foliar	Foliar N	UH	Foliar	Foliar N
	biomass	(kg ha ⁻¹)		biomass	(kg ha ⁻¹)
SS1/EM1					
Bisby Rd.	0	0 Cheney Pond 75		75	2
Cascade Lk	57	1	Deer Pond 1	339	8
Brandy Brook	577	13	Gull Pond	35	1
Limekiln Lk	0	0	Mineville Rd	996	23
Mitchell Pond 2	0	0	Northwoods Rd	640	15
Moss Lake	601	14	Rock Lake 2	263	6
Means	206	5	Means	391	9
SS1					
Mitchell Pond 1	0	0	Cedar River Fl	342	8
Big Moose Lk	139	3	Deer Pond 2	319	7
Nick's Lake	1261	30	Gull Outlet	0	0
Red River	608	14	Rock Lake 1	968	23
Means	502	12	Means	407	10

Task 4. Analysis of time-series in the chemistry of precipitation and lake water.

Hypothesis: Despite marked decreases in precipitation and lake water SO_4^{2-} in response to decreases in SO_2 emissions, little long-term change in lake pH or acid neutralizing capacity has resulted.

Methods: Long-term changes in the chemistry of wet deposition and lake water were investigated in the Adirondack region of New York. Temporal trends analyses of both precipitation chemistry and lake water chemistry were conducted using the non-parametric seasonal Kendall Tau (SKT) time series procedure (Hirsch and Slack 1984). The SKT test is a robust test for monotonic

trends in time-series data which are non-normal and characterized by seasonality. Use of SKT methodology corrects for data with moderate levels of serial correlation and is widely used in time-series analyses of precipitation and surface water data.

Results: Marked decreases in concentrations of SO_4^{2-} and H^+ have occurred in wet deposition at two National Atmospheric Deposition Program (NADP) sites since the late 1970s (Figure 4.1). These decreases are consistent with long-term declines in emissions of SO₂ in the eastern U.S. Changes in wet NO₃ deposition and NO_x emissions have been minor over the same interval. Through measurements made through the ALSC ALTM program many lakes have exhibited marked decreases in concentrations of SO₄², which coincide with decreases in atmospheric S deposition (Figure 4.2). Concentrations of NO₃ have also decreased in several Adirondack lakes. As atmospheric N deposition has not changed over this period, the mechanism contributing to this apparent increase in lake/watershed N retention is not evident. Widespread and marked decreases in lakewater concentrations of SO₄²⁻ + NO₃⁻ have resulted in increases in acid neutralizing capacity (ANC) and pH, and a shift in the speciation of monomeric Al from toxic inorganic species toward less toxic organic forms in some lakes. Extrapolation of current rates of ANC increase suggests that the time frame of chemical recovery of Adirondack lakes at current rates of decreases in acidic deposition will be several decades. Several Adirondack lakes have shown long-term increases in concentrations of dissolved organic carbon (DOC). Increases in DOC may reflect an increase in inputs or a decrease in the retention of naturally occurring organic acids which partially offset decreases in $SO_4^{2-} + NO_3^{-}$. This analysis is discussed in detail in Driscoll et al. (2003).

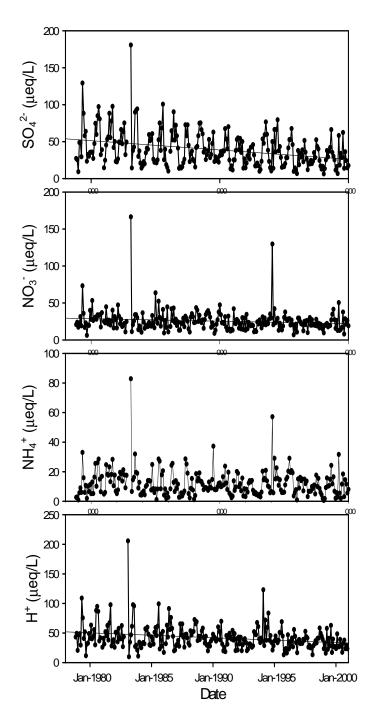


Figure 4.1 Time series of long-term trends in concentrations of solutes in wet deposition at the Huntington Forest in the Adirondacks. A statistically significant trend is indicated by a solid line.

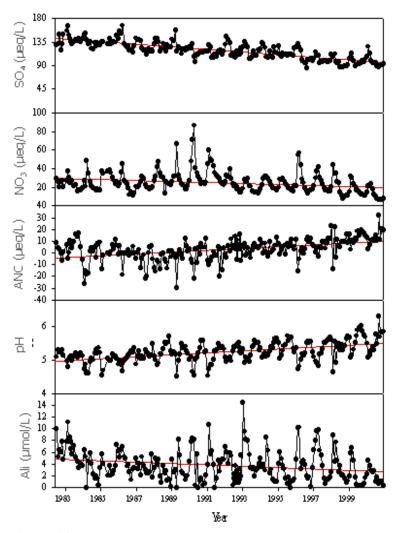


Figure 4.2 Time series of long-term trends in the concentrations of solutes in Big Moose Lake. A statistically significant trend is indicated by a solid line.

Task 5. Estimation of Mass Balances for ALSC ALTM Lakes.

Hypothesis: Mass balances will show that the lake watersheds in the Adirondacks are a net source of S, Ca and ANC and a net sink for atmospheric inputs of N; variations in solute retention/release will vary with landscape features (e.g., presence of wetlands, seepage versus drainage lakes, surficial geology).

Methods: Relevant data included NADP precipitation data, climatic data, hydrologic data from Huntington Forest, and ALSC ALTM data. As part of this study lake/watershed mass balances of major solutes (i.e., SO₄²⁻, NO₃⁻, NH₄⁺, Ca²⁺, ANC, Mg²⁺, Na⁺, K⁺, Al, Cl⁻, DOC, DON, H₄SiO₄, H⁺) were calculated for the ALTM lakes using procedures developed by Driscoll et al. (1998). These mass balances were conducted with regional estimates of precipitation quantity (Driscoll et al. 1998), precipitation chemistry and dry deposition (Ollinger et al. 1993). To determine lake/watershed outputs, lake outflow (calculated using PnET (Aber and Federer 1992) was multiplied by the monthly concentrations of lake chemistry determined at ALTM sites. It was assumed that this approach could be used to determine accurate solute mass balances.

Results: Elemental mass balance analyses have been developed using the atmospheric deposition model developed by Ito et al. (2002) combined with model estimates of drainage water losses and measured solute chemistry for the ALTM lake/watersheds. Calculations of mass balances for nitrogen for the ALTM Lakes/Watersheds have been completed (Ito et al. 2004) with the analyses of the mass balances of the other major solutes being in progress.

Nitrogen input increased from the northeast to the southwest in the region (Figure 5.1) (Ito et al. 2002). Nitrogen output had a wider range than the N input and the N output did not exhibit a distinctive spatial pattern. However, N input was weakly, but significantly correlated with N output and NO₃ output, suggesting some influence of atmospheric N input on the N output in the ALTM lake-watersheds.

Wet N deposition was also related to the fraction of N removed or retained within the watersheds (i.e., the fraction of net N hydrologic flux relative to wet N deposition, calculated as [(wet N deposition minus lake N drainage loss) / wet N deposition)] (Figure 5.2).

Wet N deposition (mol N ha-1 yr-1)

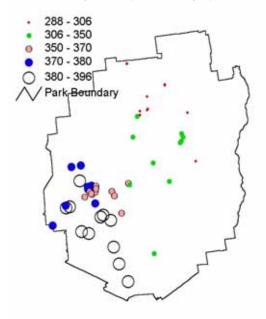


Figure 5.1. Nitrogen deposition at ALTM lake/watersheds in the Adirondack Mountains of New York (Ito et al. 2004).

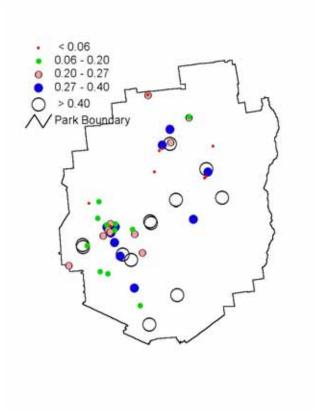


Figure 5.2 N retention coefficients of ALTM lake/watersheds (Ito et al., 2004)

In addition to wet N deposition, watershed attributes also had effects on the exports of NO₃⁻, ammonium (NH₄⁺), dissolved organic nitrogen (DON), and DOC, the DOC/DON export ratio, and the N flux removed or retained within the watersheds (i.e., net N hydrologic flux, calculated as [wet N deposition less lake N drainage loss]). Elevation was strongly related with the lake drainage losses of NO₃⁻, NH₄⁺, and DON, net NO₃⁻ hydrologic flux (i.e., NO₃⁻ deposition less NO₃⁻ drainage loss), and the fraction of net NO₃⁻ hydrologic flux, but not with the DOC drainage loss. Both DON and DOC drainage losses from the lakes increased with the proportion of watershed area occupied by wetlands, with a stronger relationship for DOC. The effects of wetlands and forest type on NO₃⁻ flux were evident for the estimated NO₃⁻ fluxes flowing from the watershed drainage area into the lakes, but were masked in the drainage losses flowing out of the lakes. The N fluxes removed or stored within the lakes substantially varied among the lakes. Our analysis demonstrates that for these northern temperate lake-containing watershed ecosystems, many factors, including atmospheric N deposition, landscape features, hydrologic flowpaths, and retention in ponded waters, regulated the spatial patterns of net N hydrologic flux within the lake-containing watersheds and the loss of N solutes through drainage waters.

Task 6. Application of the PnET-BGC model to ALTM sites.

Methods: PnET-BGC is an integrated biogeochemical model formulated to simulate the response of soil and drainage water in northern forest ecosystems to changes in atmospheric deposition and land disturbances. In this study, the model was applied to several representative sites in the Adirondack region of New York. These Adirondack sites include an acid sensitive watershed (Constable Pond; ANC \sim -8 μ eq/l), a relatively insensitive watershed (Arbutus Pond; ANC \sim 67 μ eq/l), a dystrophic lake/watershed (West Pond; DOC \sim 630 μ molC/l, ANC \sim 2 μ eq/l) and a watershed with mature forest (Willy's Pond, ANC \sim -10 μ eq/l).

Results: The results of model simulations showed that the output from PnET-BGC was consistent with observed surface water chemistry for all the sites (Figure 6.1). The model captured much of the annual and interannual variations in major surface water solutes. The model simulated internal fluxes of major elements compared well with measured values from other studies. In addition, an ANC budget was developed based on the element and solute fluxes simulated by PnET-BGC for each site. ANC budget analysis allowed the examination of the relative importance of biogeochemical processes in production and consumption of ANC.

Mineral weathering was the major source of ANC for all the sites. Roles of cation exchange and

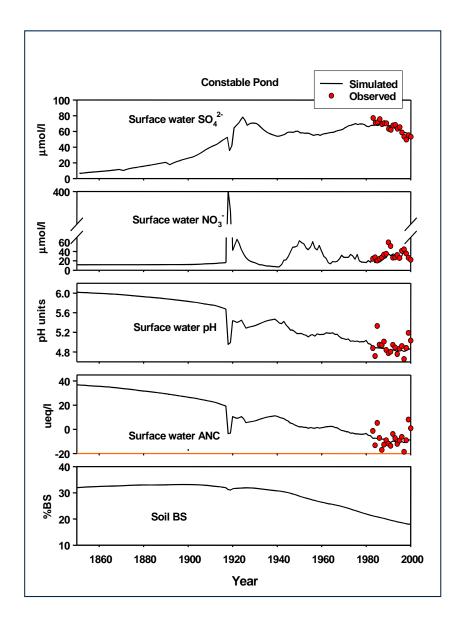


Figure 6.1 Model simulation of the time series of solutes and soil from Constable Pond. Measured annual volume-weighted observations are presented for comparison.

biotic processes (the cumulative effect of mineralization, immobilization, nitrification, foliar and root

uptake) were site specific, but mostly acted as a source of ANC. Sulfate desorption was a small source of acidity, while atmospheric deposition was the dominant source of acidity (i.e. >90%) for all the sites. A detailed description of this aspect of this project is provided in Chen et al. (2004).

The model was also used to evaluate the response of the four forest ecosystems to changes in atmospheric deposition and land disturbances (Figure 6.2). Model simulations showed that over the last 150 years, acidic deposition contributed to depletion of exchangeable nutrient base cations, enhanced mobilization of Al and accumulation of S within the soil. Model simulations also showed that acidic deposition resulted in elevated concentrations of inorganic monomeric Al and SO_4^{2-} and low values of pH and ANC in surface waters. Model results also indicated that over the short-term, forest harvests resulted in enhanced leaching of NO_3^{-} and base cations. Over the long-term, however, forest harvests had little influence on drainage output of NO_3^{-} and surface water base cation concentrations, pH, and ANC.

The model was also used to predict the responses of these forest ecosystems to three formulated emission control scenarios. Model simulations indicated that under the 1990 CAAA (Clean Air Act Amendments), these ecosystems showed little recovery after 2010. Additional reductions in strong acid inputs will result in significant benefits in terms of recovery from acidification. Under a formulated aggressive control scenario, surface water ANC of these ecosystems was predicted to recover at rates ranging from 0.35 μ eq L⁻¹yr⁻¹ to 0.65 μ eq L⁻¹yr⁻¹. Chen and Driscoll (2004) provides additional information on this aspect of the study.

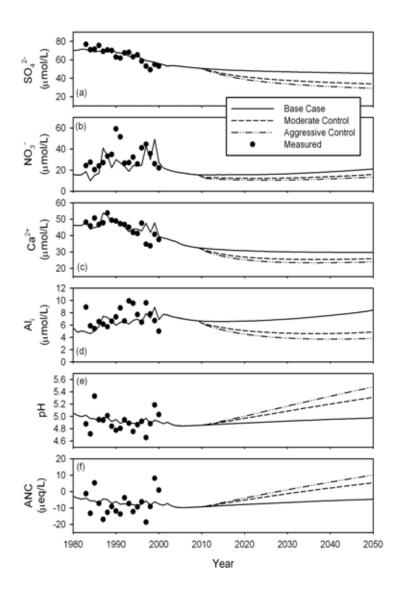


Figure 6.2 Model projections of the response of solutes in Constable Pond to projected future changes in acidic deposition. These scenarios were considered: deposition anticipated in the 1990 Amendments of the Clean Air Act (1990 CAAA) and modest and aggressive scenarios for additional emission controls for electric utilities beyond the 1990 CAAA.

Mercury Deposition - The objectives of the next group of tasks are designed to further understanding of mercury in atmospheric deposition and Adirondack lake sediments. Objectives in this part of the project include expanding the collection station at Huntington Forest to include a Hg deposition collector, building upon linkages to related research efforts, and testing the following hypotheses:

Task 7. Evaluation of the historical rates of mercury deposition to the Adirondacks.

Hypothesis: Deposition of mercury in the Adirondacks has decreased over the last 15 years in response to decreases in atmospheric deposition of mercury.

Methods: Sediment cores were collected from eight remote lakes in the Adirondack region of New York in the summer of 1998. These cores were sectioned, dated by ²¹⁰Pb and analyzed for Hg. Relevant data included concentrations of total and methyl Hg, and activity of ²¹⁰Pb with depth in sediment cores; Hg data (Lorey and Driscoll 1999). Aliquots of sediment were analyzed for total Hg and methyl Hg. Total Hg concentrations were determined by HNO₃ digestion and cold vapor atomic fluorescence spectrometry (CVAFS; Benoit et al. 1994). Methyl Hg was determined by distillation/aqueous phase methylation and CVAFS detection (Liang et al. 1994). An evaluation of changes in the fraction of total Hg occurring as methyl Hg with time allowed inference about the changes in the rate of supply of methyl Hg to downstream lakes possibly resulting from increases in wetlands in the watershed. The Hg_T fluxes were calculated to provide sediment Hg deposition on a historical timescale. Deposition of Hg in the sediments of the recent cores was compared to the results from the 1982 PIRLA study (which were determined using similar methods) to investigate recent (~15 yr) changes in lake Hg deposition. Rates of sediment Hg deposition were compared to the ratio of the watershed area to the lake surface area by linear regression to determine the contribution of mercury derived from direct atmospheric deposition and from watershed inputs.

Results: All Adirondack lakes showed an increase in Hg_T flux beginning from 1820 to 1910, with a maximum sediment Hg flux occurring from 1973 to 1995 (Figure 7.1).

The ratio of maximum sediment Hg flux to values evident before Hg increases (circa 1850) was 5.8. Seven of the eight lakes have shown decreasing fluxes from maximum values with an average

decrease of 33%. The sediment Hg fluxes are positively correlated to the watershed areas and to lake surface area ratios. Analysis of sediment cores suggests that lake-watershed retention of mercury has decreased over the last 100 years (Figure 7.2). The contribution of Hg derived from watershed runoff to the total sediment deposition has increased since pre-industrial times. These profiles showed relatively good agreement to sediment profiles from cores for the same eight lakes collected around 1982. The additional 15 years of data (Lorey and Driscoll 1999) given by the new cores provides additional evidence of recent declines in lake sediment Hg deposition.

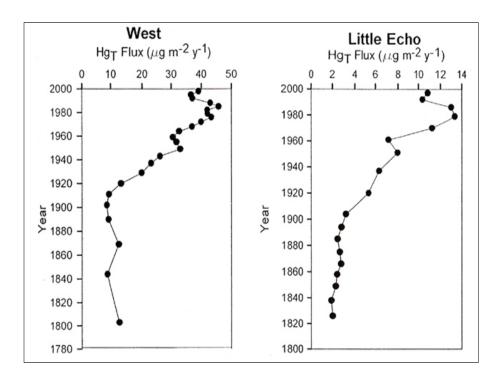


Figure 7.1 Sediment Hg deposition to West Pond and Little Echo Pond in the Adirondacks over time. Increases in sediment Hg deposition in the early 1900s have been followed by decreases in the latter portion of the century. Note Little Echo Pond is a perched seepage lake and is probably representative of direct changes in wet Hg deposition.

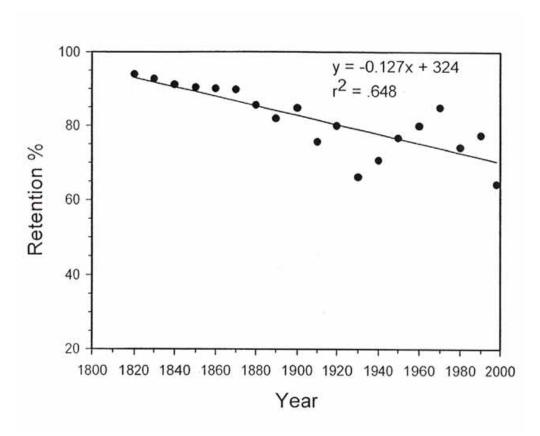


Figure 7.2 Changes in Adirondack lake watershed retention of Hg estimated from lake sediment cores. This analysis suggests that the relative retention of mercury in Adirondack watersheds has decreased over the last 100 years.

Task 8. Measurement of current rates of mercury deposition in the central Adirondacks.

Hypothesis: Contemporary atmospheric deposition of mercury compares favorably with mercury deposition estimated from lake sediments. Atmospheric mercury deposition represents the predominant source of mercury to Adirondack lake/watersheds.

Methods: Wet deposition of mercury was calculated using data collected from the NADP/Mercury Deposition Network (MDN) program and precipitation quantity. Summary statistics were calculated such as seasonal concentrations of mercury in precipitation, seasonal patterns in mercury deposition, annual volume-weighted concentrations of mercury and annual wet deposition of mercury. Annual wet deposition of mercury was compared to values of mercury deposition obtained in surficial lake sediments described in Task 7. Relevant data included weekly concentrations of total mercury in precipitation and precipitation quantity. Protocols developed for the NADP/MDN were

followed. For the analysis conducted it was assumed that wet deposition of mercury measured at the site is representative of the region.

Results: An MDN site was established at Huntington Forest in 2000 to assess wet deposition of total and methyl mercury for the Adirondack region. Samples were collected weekly for total mercury and quarterly for methyl mercury. The mean concentration (± standard deviation) of total mercury for the study period was 7.3±5.0 ng/L, with a range of values of 1.3 to 29.2 ng/L (Figure 8.1).

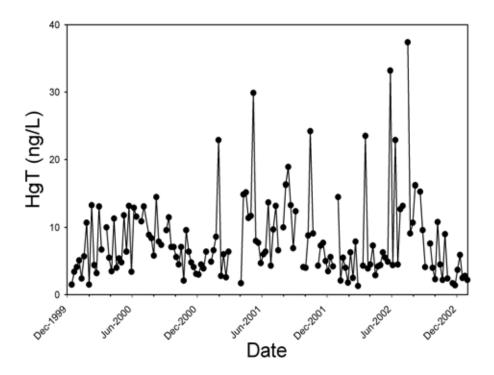


Figure 8.1 Time series of total Hg concentrations collected in precipitation at the Huntington Forest.

The mean concentration of methyl mercury was 0.042 ± 0.001 ng/L. Annual wet deposition of total mercury for the study period has been $9.4~\mu\text{g/m}^2$ -yr and the annual wet deposition of methyl

mercury for the study period was $0.02~\mu g^{-}/m^{2}$ -yr. These values are similar to other values reported for wet deposition of total and methyl mercury in northeastern North America. Wet deposition of total mercury was very close to values reported for the deposition of mercury in surface sediments of a perched seepage lake in the Adirondacks (see previous task). The second hypothesis cannot be addressed solely from the MDN data. However, together with intensive studies from the EMEP project "Mercury in Adirondack Wetlands, Lakes and Terrestrial Systems" a detailed understanding emerges of mercury inputs to Adirondack watershed ecosystems. Atmospheric deposition is indeed the major pathway of mercury inputs to forested watersheds in the Adirondacks. However, wet mercury deposition is not the dominant input. Rather dry deposition which includes mercury deposition to leaf surfaces that washes off during precipitation events (throughfall) plus mercury which is absorbed by the leaf and is deposited to the forest floor as litter is the major pathway of mercury input to Sunday Lake watershed (70% of total inputs).

Fishery Recovery - The objectives of the final research task were to further the understanding of the degree of recovery of fisheries, to build upon linkages to related research programs, to sample fish populations in the watershed of the North Branch of the Moose River, and to test the following hypothesis. This section contains more detail than previous sections because journal articles have not been published to date.

Task 9. Evaluation of the recovery of fisheries in the North Branch of the Moose River (NBMR).

Hypothesis: The richness of fish species in the North Branch of the Moose River has increased over the past 15 years in response to decreases in acidic deposition.

Methods Overview: Comprehensive fisheries surveys were conducted during the summer of 2000 on 16 lakes and 11 streams within the Big Moose watershed. Sampling locations, level of effort, and methodology employed duplicated that of the 1982-83 survey (Schofield and Driscoll 1987). Graded mesh experimental gillnets, trap nets, and baited minnow traps were employed for a minimum of 24 hours in the lake systems. Electro-fishing techniques (backpack electro-shockers and D.C. generators) were used to assess fish populations in streams. All sampling protocols were those used by the ALSC and the NYS Department of Environmental Conservation (NYSDEC). Fish populations were evaluated by examining species presence/absence, relative abundance, frequency of

occurrence, and spatial distribution within the system as well as biological attributes of fish present (length frequency, age and condition).

Between May and October 2000, selected lakes and streams constituting the NBMR were surveyed to investigate changes in fish species composition occurring since a 1982/1983 survey (Schofield and Driscoll 1987). NYSDEC sampling activities coincided with this group at two lakes. Since all sampling efforts employed the protocol described below, species lists for these waters represent the pooled collection of both groups.

Lake surveys

Emulating the initial survey, the 2000 survey used several gear types and techniques to comprehensively fish for species with different sizes, habitat selections, and movement patterns. Lake sampling gear comprised graded mesh gill nets (38-89 mm stretch, 46 m long, 1.5 m deep), monofilament minnow nets (19 mm mesh, 9 m long, 1.5 m deep), seines (6 mm mesh, 5 m long, 1.2 m deep), Alaska style trap nets (6 mm mesh, 3 m diameter bag), and baited minnow traps (6 mm mesh). Generally, researchers gear fished each lake for 24 hours except when obvious loading with fish or desire to prevent sport fish mortality necessitated shorter employment durations. Lake surface area determined the quantity of gear necessary to effectively survey a given water according to standard NYSDEC protocol. Waters were sampled using gill nets, minnow nets, and minnow traps and augmented with seines in Lake Rondaxe, Moss Lake, Darts Lake, and Big Moose Lake and trap nets in Big Moose Lake.

Stream surveys

Backpack D.C. electrofishing units were used to sample individual stream reaches for 30 meters in an upstream direction. Three to nine reaches were fished per stream, selecting following reaches various distances upstream from previous ones. Although no reaches were enclosed with blocking seines to prohibit fish emigration during sampling, the distance traveled between successive reaches likely ensured the sampling independence of any given reach. Additionally, the varied character and logistic limitations of most streams required a technique capable of efficiently sampling reaches to allow for the visiting of other areas potentially harboring species.

Surface water samples collected at each lake and the first and last reach of every stream provided a chemical reference for the observed species differences between sites. The ALSC laboratory analyzed surface water samples to quantify chemical parameters including pH, ANC, speciated aluminum, base cations, and acidic anions according to standardized techniques (Baker et al. 1990).

Independent sample *t* tests determined significant differences between the mean number of species occurring in high and low pH waters. An additional objective was to determine which physical parameters of the aquatic environment contributed to differential species richness among survey waters. Multiple stepwise linear regression isolated those variables significantly contributing to species number variability. Data transformations coupled with normality and homogeneity of variance testing ensured the integrity of linear model assumptions. Results were accepted as significant at the P=0.05 level.

Results:

Fish species distribution in the NBMR

The 2000 survey included five lakes that were not sampled in 1982/83 but omitted one lake that was previously sampled. The species caught in these six lakes were excluded from comparisons between surveys. Additionally, the study only compared species caught in the fourteen streams commonly sampled by both surveys. Previously sampled NBMR lakes and streams yielded eighteen species during 2000, an increase of two species from those collected in 1982/1983. Collected formerly, the finescale dace (Phoxinus neogaeus) and the splake (Salvelinus fontinalis x Salvelinus namaycush) did not appear in 2000, while four species appeared after not being collected in 1982/1983. The NBMR watershed was historically stocked with Atlantic salmon (Salmo salar) and largemouth bass (Micropterus salmoides). Although their absence from the former survey is unexplained, their collection in 2000 may have resulted from recent introductions by private groups (personal communication- Al Schiavone, NYSDEC). The longnose dace (Rhinichthys cataractae) and the lake trout (Salvelinus namaycush), native species formerly absent and presumed to be extinct from the NBMR, represent the remaining additional species collected in 2000. Stocking during the late nineties explains the appearance of lake trout in collection waters. The fourteen lakes and streams yielding no fish during the 2000 survey were primarily NBMR headwaters with a median pH of 4.8 while the median pH of waters yielding fish was 5.9. The median surface area of lakes yielding or not yielding fish was 21.6 and 5.0 hectares respectively.

Following Mather (1890), Greeley and Bishop (1932), and Schofield and Driscoll (1987), ten species collected in 2000 are considered native, six are exotics, and two were historically stocked. While Lake Rondaxe retained a species assemblage similar to that found in 1982/1983, both Darts Lake and Big Moose Lake yielded four more species in 2000 (Table 9.1, see attached). Across the drainage area, nine of twenty-one lakes surveyed in both periods yielded more species in 2000 primarily through additions of cyprinids and centrarchids. Five of the nine lakes yielding additional species lie in the Cascade-Moss-Rondaxe sub-basin of the drainage characterized by high pH waters (median pH 7.0). Ten lakes yielded the same number of species in both surveys while only two yielded fewer species in 2000.

Waters surveyed in 2000 with pH greater than 6 yielded significantly more species than those with pH less than 6 (streams- t = 3.479, 39 df, p-value = 0.001; lakes- t = 4.465, 24 df, p-value = 0.000). Mirroring the findings of the 1982/1983 survey, both surface area and pH significantly contributed to varying species numbers in NBMR lakes during 2000 ($R^2 = 0.761$). While pH also contributed to varying NBMR stream species numbers (p-value = .001), the low R^2 value from this test (0.216) suggests that much species number variability in streams remains unexplained.

Given the documented changes in NBMR species composition over time, the authors of this study wished to optimize the description of the species complex during 2000. The study implemented minor deviations from the 1982/83 survey design to increase the probability of catching all species present. Sampling effort was comparable in both surveys, but the stream sampling technique and use of monofilament minnow nets in lakes limit the direct comparison of relative catch between surveys. Nine lakes yielded additional species in 2000 but some additional species were caught with minnow nets. After excluding fish caught with minnow nets from species totals, all nine lakes continued to yield from one to four additional species confirming that most additions did not result from different sampling methods. Despite the variability that sampling differences may introduce in a replicated survey, it is reasonable to believe that the presence of fish defines the suitability of a water for fish presence. Further, it is the absence of a species from survey collection that stimulates uncertainty regarding sampling differences and begs the question of whether absence is realized or represents failure to catch. It is possible that some species in given waters were not caught during the 1982/83 survey due to small population sizes or sampling limitations. Therefore, appearance of these species during 2000 could result from populations growing to catchable levels in response to subtle water

quality improvements or simply the serendipitous catch of species formerly missed. For this reason, interpreting a species as absent from any water is speculative and we focus instead on species presences. Exceptions where true species absence can be reasonably assumed include waters that have historically yielded no fish, possess chemical environments which exceed the tolerance of potential colonizers, or are spatially isolated from potential colonization.

Waters isolated by barriers, falls, or high stream gradients occur in the NBMR drainage but most waters yielding fish are physically connected through passable waterways. Vannote et al. (1980) proposed that the connected waters of a drainage system represent a continuum characterized by continual species assemblage adjustments. These adjustments maintain a dynamic equilibrium which maximizes energy utilization of fish while minimizing their energy loss. Baker et al. (1996) demonstrated the ability of brook trout (*Salvelinus fontinalis*) to behaviorally regulate their exposure to episodically acidic conditions through movements to more chemically tolerable areas. Despite the physical connectedness of the NBMR and opportunities for fish species to distribute accordingly, the chemical unsuitability of adjoining waters can represent a behavioral obstruction rivaling any physical barrier. Thus, opportunity for immigration/emigration alone is insufficient to explain differential distribution patterns identified in replicate surveys. Soranno et al. (1999) reported that the substantial geologic heterogeneity of the NBMR has an overriding influence on the interlake variability of chemical environments. For this reason, fish immigration/emigration opportunity must be considered in harmony with the geochemical disposition of individual waters to adequately assess effects of anthropogenic acidification on fish distribution.

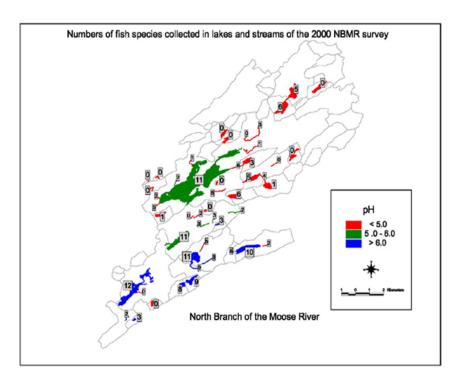


Figure 9.1 Species richness of fish and chemical conditions in the North Branch of the Moose River in 2000.

The composition of the NBMR fish community exhibited a long period of relative stability from 1882-1931 after which, marked changes became manifest. By the 1950s, declines in sportfish condition and evidence of recruitment failure appeared in the drainage basin. The 1982/83 survey demonstrated that species distribution patterns in the early eighties reflected existing acidity gradients in the watershed. The 2000 survey indicates that this relationship continues to exist. Schofield and Driscoll (1987) observed a longitudinal gradient of increasing species numbers downstream through the NBMR, while Baldigo and Lawrence (2001) found the same pattern in other New York State waters. Both studies relate this phenomenon to the acidic conditions (low pH, high concentrations of inorganic monomeric aluminum) often found in headwater portions of a drainage. The number of species caught in NBMR waters during 2000 is shown in Figure 9.1 and illustrates an ongoing pattern of greater species richness downstream through the drainage. The Cascade-Moss-Rondaxe sub-basin of the NBMR continued to yield the most species in the drainage with many native cyprinids found in the higher pH waters typical of this branch. As seen in 1982/83, young-of-the-year brook trout appeared in streams of the Cascade-Moss-Rondaxe sub-basin suggesting that adults continue to use these areas for spawning. Young-of-the-year brook trout also appeared in Pancake Hall Creek and the outlets of Squash Pond and West Pond, areas historically used for spawning but apparently

unused during the early eighties. Occurrence at these sites during 2000 may reflect the spawning activity of a particular brook trout strain (Little Tupper) stocked in Big Moose Lake during the late nineties or simply represent the failure to catch young of the year fish during the earlier survey.

Lakes that yielded no fish in 1982/83 continued to yield no fish in 2000 suggesting that increases in ANC have not been adequate to allow for colonization despite the presence of immigration opportunity. While creek chub (*Semotilus atromaculatus*) and brook trout were the most widely distributed NBMR species in 2000, exotics continued to be well represented in acidic waters with yellow perch (*Perca flavescens*) representing the most abundant NBMR species. Small lakes with low pH yielded few species in 2000 presumably due to the low diversity of potential habitats and water chemistry which exceeded the apparent tolerance of sensitive potential colonizers. This situation was expected and detected in both surveys.

Despite many similar findings between surveys, the apparent tolerance of some NBMR species to acidification has changed (Table 9.2). Using criteria described by Schofield and Driscoll (1987) to tentatively define sensitive (pH>6), indeterminate (appearing across pH ranges), and tolerant (pH<5) species, it appears that certain species inhabited lower pH waters during 2000. The creek chub, brook trout, and pumpkinseed sunfish (Lepomis gibbosus) shifted to a tolerant classification while the common shiner (Notropis cornutus) is now considered indeterminate. The banded killifish (Fundulus diaphanus) alone shifted from a less to more sensitive category in 2000 while all native cyprinids other than the creek chub and common shiner remained sensitive. The 1982/83 study identified the possible genetic adaptation to acid stress by yellow perch inhabiting Big Moose Lake. Similar adaptation by other NBMR species may explain why they appeared in waters formerly considered too acidic for their occupation. However, the failure to catch these species in lower pH waters during the previous survey cannot be discounted as a potential explanation for apparent increased tolerance in 2000. Only two waters yielded fewer species in 2000 contrasting the 1982/83 findings which identified many progressive upstream losses since 1931. Windfall Pond yielded four fewer species in 2000 despite having a pH (7.3) significantly above the observed minimum tolerance of any NBMR species. The individual fish record for Windfall Pond showed creek chub dominating this water and its associated tributaries. Schlosser (1988) described the creek chub as a common predator capable of impacting other cyprinid species including those primarily disappearing from Windfall Pond. Thus, the species assemblage here may equilibrate through natural competition mechanisms.

Table 9.2. Sensitivity classes of fish in the North Branch of the Moose River (after Schofield and Driscoll 1987).

Sensitive	Indeterminate	Tolerant
blacknose dace	white sucker	brown bullhead
longnose dace	common shiner	pumpkinseed sunfish
northern redbelly dace	largemouth bass	yellow perch
rock bass	banded killifish	golden shiner
smallmouth bass	lake trout	brook trout
Atlantic salmon		creek chub
		central mudminnow

The record of historical management activities (stocking, reclaiming, and liming) and additional NBMR fisheries surveys provided insight to the changing complexion of NBMR species composition. The presence of certain sportfish species in various waters is explained by stocking while the appearance of other species could be explained by recolonization following lake reclamation. Distinguishing the effects of management activities on species assemblage from those induced by anthropogenic acidification is uncomplicated when complete management documentation is available. NBMR surveys conducted after 1982/83 but prior to 2000 (ALSC 1984-1987, ALSC 1992-1999) provided an additional source of information for evaluating species changes through time. However, the continued appearance/disappearance of species in observational studies is troublesome when no clear or convenient explanation for observed changes exists. Regardless, the 2000 survey confirmed the ongoing patterns of species distribution limited by acidity gradients and greater species richness in larger, high pH waters. Future surveys of the NBMR could elucidate whether the apparent species increases found in 2000 also represent a pattern of biological recovery following decreases in acidic deposition and improvements in water chemistry.

Table 9.1. Species of fish observed in the three largest lakes of the North Branch of the Moose River during three surveys.

•	Lake Rondaxe					Dart Lake					 Big Moose Lake					
Species	1931		1982		2000		1931		1982		2000	1931		1982		2000
lake trout																
brook trout																
lake whitefish																
round whitefish																
smallmouth bass																
largemouth bass																
rock bass																
yellow perch																
pumpkinseed sunfish																
white sucker																
longnose sucker																
brown bullhead																
banded killifish																
stickleback																
slimy sculpin																
lake chub																
creek chub																
common shiner																
golden shiner																
blacknose dace																
northern redbelly dace																
finescale dace																
longnose dace																
Atlantic salmon																
splake																
Total Number	11		12		12		10		7		11	14		7		11

References

- Aber, J.D., and C.A. Federer. 1992. A generalized, lumped-parameter model of photosynthesis, evapotranspiration and net primary production in temperate and boreal forest ecosystems. Oecologia 92:463-474.
- Aber, J.D., C.L. Goodale, S.V. Ollinger, M.-L. Smith, A.H. Magill, M.E. Martin, R.A. Hallett, J.L. Stoddard and NERC Participants. 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? BioScience 53:375-390.
- Baker, J.P., S.A. Gherini, S.W. Christensen, C.T. Driscoll, J. Gallagher, R.K. Munson and R.M. Newton. 1990. Adirondack Lake Survey: An Interpretive Analysis of Fish Communities and Water Chemistry, 1984-87. Adirondack Lakes Survey Corporation, Ray Brook, NY.
- Baker, J.P., J. Van Sickle, C.J. Gagen, D.R. DeWalle, W.E. Sharpe, R.F. Carline, B.P. Baldigo, P.S. Murdoch, D.W. Bath, W.A. Kretser, H.A.. Simonin and P.J. Wigington, Jr. 1996. Episodic acidification of small streams in the northeastern United States: Effects on fish populations. Ecological Applications 6:422-437.
- Baldigo, B.P. and G.B. Lawrence. 2001. Effects of stream acidification and habitat on fish populations of a North American river. Aquatic Sciences 63:196-222.
- Benoit, J.M., W.F. Fitzgerald, and A.W.H. Damman. 1994. In Mercury Pollution: Integration and Synthesis. Watras, C.J., and J.W. Huckabee Eds. Lewis Publishers, Boca Raton, pp. 187-202.
- Campbell, J.L., J.W. Hornbeck, W.H. McDowell, D.C. Buso, J.B. Shanley and G.E. Likens. 2000. Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochemistry 49:123-142.
- Driscoll, C.T., K.M. Postek, D. Mattei, K. Sequoia, J.D. Aber, W.J. Ktretser, M.J. Mitchell and D.J. Raynal. 1998. The response of lake water in the Adirondack region of New York to changes in acidic deposition. Environmental Science and Policy 1: 185-198.
- Greeley, J.R. and S.C. Bishop. 1932. Fishes of the area with annotated list. In: A Biological Survey of the Oswegatchie and Black River Systems. Suppl. 21st Ann. Rep. NY Cons. Dept. 1932, pp. 54-92.
- Hirsch, R.M., and J. R. Slack. 1984. A nonparametric trend test for seasonal data with serial dependence. Water Resources Research 20:727-732.
- Ito, M., M.J. Mitchell and C.T. Driscoll. 2002. Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York. Atmospheric Environment 36:1051-1062.
- Liang, L., M. Horvat, and N.S. Bloom. 1994. An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection. Talanta 41:371-379.
- Lorey, P. and C.T. Driscoll. 1999. Historical trends of mercury deposition in Adirondack Lakes. Environmental Science and Technology 33: 718-722.

Mather, F. 1890. Adirondack Fishes. In: The 19th Ann Rep. (1888-1889), New York State Fisheries Commission, pp. 124-182.

Ollinger, S.V., J.D. Aber, G.M. Lovett, S.E. Millham, R.G. Lathrop, and J.M. Ellis. 1993. A spatial model of atmospheric deposition for the northeastern U.S. Ecological Applications 3:459-472.

Schlosser, I.J. 1988. Predation rates and the behavioral response of adult brassy minnows (Hybognathus hankinsoni) to creek chub and smallmouth bass predators. Copeia 3:691-697.

Schofield, C.L. and C.T. Driscoll. 1987. Fish species distribution in relation to water quality gradients in the North Branch of the Moose River. Biogeochemistry 3:63-86.

Soranno, P.A., K.E. Webster, J.L. Riera, T.K. Kratz, J.S. Baron, P.A. Bukaveckas, G.W. Kling, D.S. White, N. Caine, R.C. Lathrop and P.R. Leavitt. 1999. Spatial variation among lakes within landscapes: ecological organization along lake chains. Ecosystems 2:395-410.

Vannote, R.L., G.W. Minshall, K.W. Cummins, J.R. Sedell and C.E. Cushing. 1980. The river continuum concept. Canadian Journal of Fisheries and Aquatic Sciences 37:130-137.

Publications:

Detailed research results related to this project were published in the following journal articles:

Task 1:

Ito, M., M.J. Mitchell, C.T. Driscoll and K.M. Roy. 2004. Nitrogen input-output budgets for lake-watersheds in the Adirondack region of New York. Biogeochemistry (in press).

Mitchell, M.J. 2001. Linkages of nitrate losses in watersheds to hydrological processes. Hydrological Processes 15: 3305-3307.

Mitchell, M.J., C.T. Driscoll, S. Inamdar, G.G. McGee, M.O. Mbila and D.J. Raynal. 2003. Nitrogen biogeochemistry in the Adirondack Mountains of New York: hardwood ecosystems and associated surface waters. Environmental Pollution 123: 355-364.

Task 2:

Hurd, T.M., D.J. Raynal and C.R. Schwintzer. 2001. Symbiotic N-fixation of *Alnus incana ssp. rugosa* in shrub wetlands of the Adirondack Mountains. Oecologia 126: 94-103.

Hurd, T.M. and D.J. Raynal. 2004. Comparison of nitrogen solute concentrations within alder (*Alnus incana spp. rugosa*) and non-alder dominated wetlands. Hydrological Processes (in press).

Task 3:

Kiernan, B.D., T.M. Hurd and D.J. Raynal. 2003. The influence of *Alnus incana spp. rugosa* on inorganic nitrogen movement in shrub wetlands of the Adirondack Mountains, New York. Environmental Pollution 123: 347-354.

Task 4:

Driscoll, C.T, K.M. Driscoll, K. Roy and M. Mitchell. 2003. Chemical response of Adirondack lakes to declines in acidic deposition. Environmental Science and Technology 37: 2036-2042.

Task 5:

Ito, M., M.J. Mitchell and C.T. Driscoll. 2002. Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York. Atmospheric Environment 36: 1051-1062.

Ito, M., M.J. Mitchell, C.T. Driscoll and K.M. Roy. 2004. Nitrogen input-output budgets for lake-watersheds in the Adirondack region of New York. Biogeochemistry (in press).

Mitchell, M.J., P.J. McHale, S. Inamdar and D. J. Raynal. 2001. Role of within-lake processes and hydrobiogeochemical changes over 16 years in a watershed in the Adirondack Mountains of New York State, USA. Hydrological Processes 15: 1951-1965.

Mitchell, M.J., C.T. Driscoll, J.S. Owen, D. Schaefer, R. Michener and D.J. Raynal. 2001. Nitrogen biogeochemistry of three hardwood ecosystems in the Adirondack region of New York. Biogeochemistry 56: 93-133.

Task 6:

Chen, L., C.T. Driscoll, S. Gbondo-Tugbawa, M.J. Mitchell and P.S. Murdoch. 2004. The application of an integrated biogeochemistry model (PnET-BGC) to watershed ecosystems in the Adirondack and Catskill regions of New York. Hydrological Processes (in press).

Chen, L. and C. T. Driscoll. 2004. Modeling the response of soil and surface waters in the Adirondack and Catskill regions of New York to changes in atmospheric deposition and land disturbances. Atmospheric Environment (in press).

Task 7:

Lorey, P. and C.T. Driscoll. 1999. Historical trends of mercury deposition in Adirondack Lakes. Environmental Science and Technology 33: 718-722.

Lorey, P., C.T. Driscoll and D. Engstrom. 2004. Changes in the historical mercury deposition in Adirondack Lake sediments and the role of lake watersheds (in preparation).

For information on other NYSERDA reports, contact:

New York State Energy Research and Development Authority 17 Columbia Circle Albany, New York 12203-6399

> toll free: 1 (866) NYSERDA local: (518) 862-1090 fax: (518) 862-1091

> > info@nyserda.org www.nyserda.org

EFFECTS OF ATMOSPHERIC DEPOSITION OF SULFUR, NITROGEN, AND MERCURY ON ADIRONDACK ECOSYSTEMS

FINAL REPORT 04-03

STATE OF NEW YORK GEORGE E. PATAKI, GOVERNOR

NEW YORK STATE ENERGY RESEARCH AND DEVELOPMENT AUTHORITY VINCENT A. DEIORIO, ESQ., CHAIRMAN PETER R. SMITH, PRESIDENT

