



NYSERDA

Importance of Acidic and Mercury Deposition in Relation to Climate Change in the Adirondack Mountains: Biogeochemical Responses

Final Report Summary

NYSERDA's Promise to New Yorkers:

NYSERDA provides resources, expertise, and objective information so New Yorkers can make confident, informed energy decisions.

Mission Statement:

Advance innovative energy solutions in ways that improve New York's economy and environment.

Vision Statement:

Serve as a catalyst – advancing energy innovation, technology, and investment; transforming New York's economy; and empowering people to choose clean and efficient energy as part of their everyday lives.

Importance of Acidic and Mercury Deposition in Relation to Climate Change in the Adirondack Mountains: Biogeochemical Responses

Final Report Summary

Prepared for:

New York State Energy Research and Development Authority

Gregory Lampman
Senior Project Manager

Prepared by:

SUNY-ESF

Syracuse, NY

M.J. Mitchell
P. McHale

and

Syracuse University

Syracuse, NY

L. Lautz
C.T. Driscoll

and

University of Calgary

Calgary, Alberta (Canada)

B. Mayer

Notice

This report was prepared by SUNY-ESF, Syracuse University, and the University of Calgary in the course of performing work contracted for and sponsored by the New York State Energy Research and Development Authority (hereafter “NYSERDA”). The opinions expressed in this report do not necessarily reflect those of NYSERDA 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, NYSERDA, the State of New York, and the contractor 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. NYSERDA, 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.

NYSERDA makes every effort to provide accurate information about copyright owners and related matters in the reports we publish. Contractors are responsible for determining and satisfying copyright or other use restrictions regarding the content of reports that they write, in compliance with NYSERDA’s policies and federal law. If you are the copyright owner and believe a NYSERDA report has not properly attributed your work to you or has used it without permission, please email print@nyserda.ny.gov

Preferred Citation

New York State Energy Research and Development Authority (NYSERDA). 2015. “Importance of Acidic and Mercury Deposition in Relation to Climate Change in the Adirondack Mountains: Biogeochemical Responses” NYSERDA Report 15-04s. nyserda.ny.gov/publications

Abstract

Within the Huntington Forest in the central Adirondack Mountains of New York State there has been a significant decrease in the concentrations of the major anions in wet only deposition (e.g., sulfate [SO_4^{2-}] and nitrate [NO_3^-]) associated with acidification of soils and surface waters. These decreases are a direct function of the reduction of emissions from anthropogenic sources. Another major air pollutant, mercury (Hg), has shown no such decline. Concomitant with the decreases in “acid rain,” there has been an increase in the temperature and precipitation amounts as reflected in regional changes associated with climate change. The overall decrease in SO_4^{2-} in surface waters is being affected by the contribution of internal sulfur (S) sources (i.e., organic S, S-bearing minerals, SO_4^{2-} desorption) that appear to be most important in those lake/watershed systems with high levels of acid neutralizing capacity (ANC) and thus these internal S sources will likely not have a major influence on the recovery of soils and waters from acidification. The concentrations of NO_3^- in surface waters show marked annual variation with the amount of NO_3^- generation in the late summer/early fall appearing to be a major factor in determining the amount of NO_3^- loss during the period of snow melt, which is the period that dominates the amount of NO_3^- lost from forested watersheds. One of the most important forms of mercury (Hg) is the methylmercury form (MeHg), which is toxic and accumulates along terrestrial and aquatic food chains. The generation of MeHg is coupled with bacterial SO_4^{2-} reduction and hence those periods with high biotic activity generate the most MeHg and result in low SO_4^{2-} concentrations in ground and surface waters. A major challenge for scientists and policymakers is evaluating the entire range of factors including the decrease in “acid rain” and increasing influence of climate change on forest ecosystem structure and function.

Keywords

Acid rain, acidic atmospheric deposition, Adirondacks, climate, forests, methyl mercury, mercury, nitrogen, precipitation, sulfur, temperature, watersheds

Acknowledgments

We greatly appreciate that assistance of the Adirondack Ecological Center staff in the support of this research with special thanks to Charlotte Demers. We also thank Mario Martin-Alciati., Phil-Goo Kang, David Lyons, Kim McEathron, Mario Montesdeoca, Jonathan Masih-Das, Kelsey Nowak, Tyler Nowak, Dmitriy Shevets, Ben Tabor and Angela Vitale for their assistance in the laboratory and field. We also are grateful to Cheryl Liptak and Maureen Hale for their administrative support.

Table of Contents

Notice	ii
Preferred Citation	ii
Abstract	iii
Keywords	iii
Acknowledgments	iii
List of Figures	v
1 Introduction	6
1.1 Changes in Atmospheric Deposition in the Adirondacks	6
1.2 Mercury Deposition	7
1.3 Climate Change in the Adirondacks.....	9
1.3.1 Ice Record	9
1.3.2 Temperature and Precipitation.....	9
1.3.3 Discharge	11
2 Effects of Changing Climate on Biogeochemical Processes	13
2.1 Sulfur	13
2.2 Nitrogen.....	16
2.3 Mercury	19
3 Role of Future Changes in Climate and Atmospheric Deposition on the Biogeochemical Responses	23
4 References	25

List of Figures

Figure 1. Annual wet only deposition at Huntington Forest NADP/NTN site in the central Adirondack Mountains of New York State.....	7
Figure 2. Total annual mercury concentration and deposition at the Huntington Forest MDN site .	8
Figure 3. Annual precipitation change at the Tupper Lake NOAA (Station ID 308631) site in the central Adirondack Mountains of New York State	10
Figure 4. Annual temperature change at the Tupper Lake NOAA (Station ID 308631) site in the central Adirondack Mountains of New York State	11
Figure 5. Relationship between the annual discharge from the Arbutus Watershed and annual precipitation	12
Figure 6. Declines in SO_4^{2-} concentrations for 16 (14 drainage and 2 seepage lakes) of the 17 original Adirondack Long-Term Monitoring Lakes (ALTM) from 1984 through 2010....	14
Figure 7. Effect of discharge amount on sulfur budget discrepancy with sulfate concentration normalized to the amount of discharge showing	14
Figure 8. Hydrograph of early fall storm at Archer Creek (within the Arbutus Watershed)	15
Figure 9. Relationships between soil moisture content and the mobilization of SO_4^{2-}	16
Figure 10. Hydrograph from Archer Creek in winter 2003 showing the relationship between snowpack depth, discharge, temperature and NO_3^- concentrations	17
Figure 11. Relationship between annual winter/spring NO_3^- concentrations and fall NO_3^- concentrations at Archer Creek	18
Figure 12. Relationship between SO_4^{2-} concentrations and MeHg concentrations as a function of season (growing versus dormant) at Archer Creek.....	21
Figure 13. Relationships between DOC concentrations and total Hg and MeHg concentrations in Arbutus Lake and Sunday Pond in the Adirondack Mountains	22
Figure 14. Interactions between acidic deposition and climate change in affecting forested watersheds including other extrinsic factors important for forest ecosystem processes such as ecological services	24

1 Introduction

1.1 Changes in Atmospheric Deposition in the Adirondacks

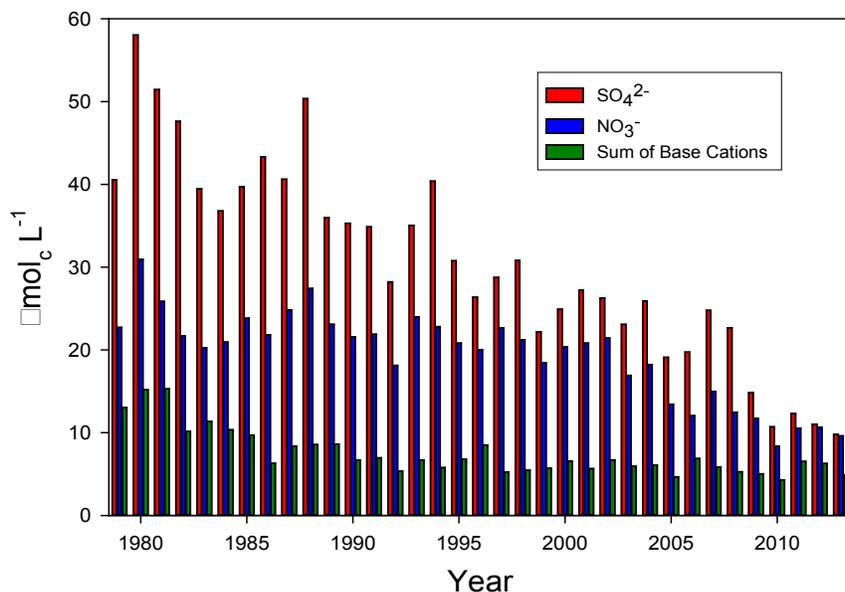
The Adirondack Mountains in New York State (USA) have been a focal region for research on the deleterious impacts of acidic deposition (“acid rain”) since observations in the 1970s and 1980s showed a substantial decline in the fisheries (Kretser et al. 1989a and 1989b; Driscoll et al. 1991a and 1991b). The Adirondacks have historically received high sulfur (S) and nitrogen (N) deposition compared to many regions in the United States. In addition, acidic soils and shallow surficial deposits make the region highly sensitive to acidification (Driscoll et al. 2009).

Major components of acidic inputs include wet and dry deposition of oxides of sulfur and nitrogen (Mitchell and Driscoll 2004). The emission of sulfur oxides from powerplants and other sources in the atmospheric source area of the Midwest and Northeast and the subsequent transport to the Adirondacks and other regions of the northeast U.S. have been clearly documented (Driscoll et al. 2001, Mitchell et al. 2013). Sulfur emissions and resultant deposition in the U.S. peaked in the mid-1970s as a result of air quality management programs and have been subsequently declining. Oxides of nitrogen are derived from a broader range of sources including electric power generation plants and high temperature combustion in vehicles. Nitrogen oxide emissions in the U.S. peaked in 2003 and have declined in recent years. These temporal emission patterns are reflected in observations from the National Atmospheric Deposition Program’s National Trends Network (NADP/NTN) station that measures wet only deposition in Huntington Forest (HF) in the Central Adirondacks (Station ID NY20; Figure 1). From 1979 to 2013, there have been declines in the precipitation concentrations of sulfate (SO_4^{2-}) ($-1.0 \mu\text{mol}_c \text{L}^{-1} \text{yr}^{-1}$; $p < .0001$; $r^2 = 0.76$) and nitrate (NO_3^-) ($-0.44 \mu\text{mol}_c \text{L}^{-1} \text{yr}^{-1}$; $p < .0001$; $r^2 = 0.72$), coincident with decreases in emissions.

Another important component of atmospheric nitrogen inputs is ammonium (NH_4^+). The emissions of ammonium are poorly estimated but thought to be relatively constant since the early 1990s (USA EPA, 1999). The proportion of NH_4^+ in dissolved inorganic nitrogen (DIN) has been increasing during the measurement period from approximately 30% in the early 1980s to approximately 50% currently ($+0.5\% \text{yr}^{-1}$; $p < .0001$; $r^2 = 0.52$). The declines in the strongly acidifying compounds SO_4^{2-} and NO_3^-

have resulted in a concomitant increase of pH of wet deposition from approximately 4.3 (early 1980s) to approximately 5.0 (early 2010s). This increase in pH would have been greater if there had not been a concomitant decrease in the sum of base cations, $\Sigma[\text{Ca}^{+2}+\text{Mg}^{+2}+\text{Na}^{+}+\text{K}^{+}]$, in wet only precipitation for this same period ($-0.21 \mu\text{mol}_c \text{L}^{-1} \text{yr}^{-1}$; $p < .0001$; $r^2 = 0.62$) (Figure 1).

Figure 1. Annual wet only deposition at Huntington Forest NADP/NTN site in the central Adirondack Mountains of New York State



In addition to wet deposition, atmospheric inputs of dry deposition include gases, aerosols, and particulates. For HF, dry S deposition was estimated to contribute approximately 24% of the total S atmospheric deposition from 1984 to 2002 (Mitchell et al. 2013). Dry deposition of N was a larger component (34 and 40%) of total N deposition during the periods from 1986 to 1988 and from 1992 to 1993, respectively (Mitchell et al. 2001). These percent dry deposition values are substantially higher than those reported from the more recent period from 2005 to 2013 during which dry deposition of S and N constituted 9% and 8%, respectively, based on values from the NADP/NTN (<http://nadp.sws.uiuc.edu/NTN/>) and CASTNET (<http://epa.gov/castnet/javaweb/index.html>) programs.

1.2 Mercury Deposition

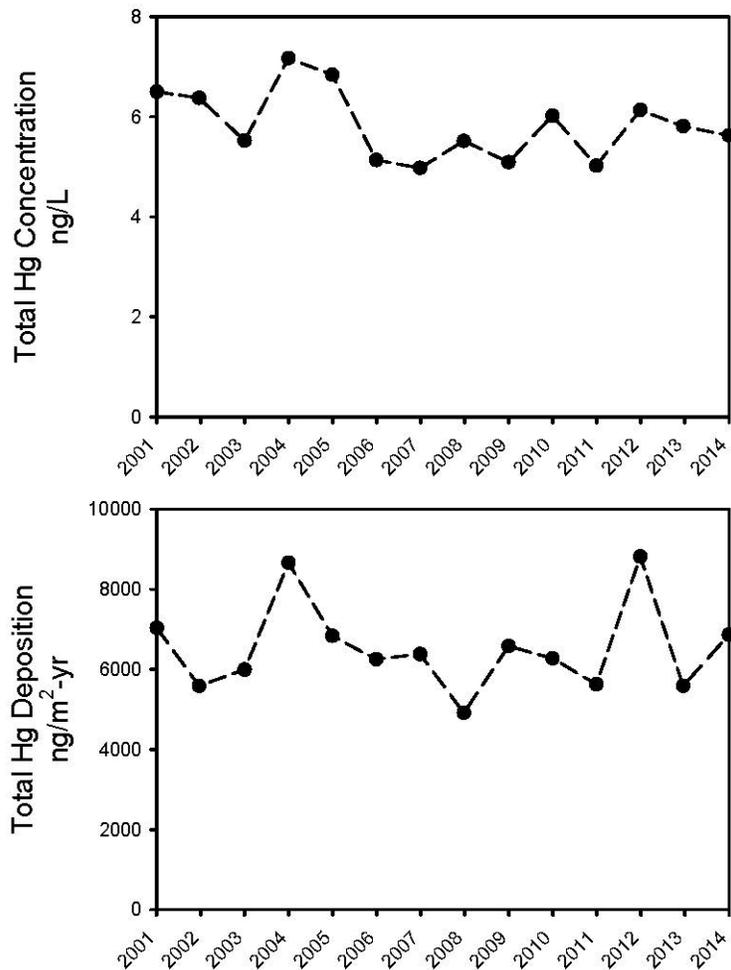
Northern forest ecosystems, including the Adirondacks, are sensitive to atmospheric mercury (Hg) deposition (Evers et al. 2007). Atmospheric deposition is the predominant input of Hg to remote watersheds like the Adirondacks (Fitzgerald et al. 1998; Driscoll et al. 2013). The inputs and fate of

Hg to the Huntington Forest Ecosystems were examined through long-term measurements of wet Hg deposition and by conducting Hg mass budgets in forested watersheds over the annual cycle.

Measurements of wet Hg deposition have been made at the HF since 2000 as part of the National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN).

Average annual volume weighted Hg concentration in precipitation at HF for the study period (2011-2014) was 5.84 ng/L (Figure 2). To date, there has been no significant long-term trend in annual volume weighted concentrations of Hg in precipitation at the HF. The time series of weekly Hg concentrations in precipitation exhibit seasonal patterns, with low concentrations occurring in the beginning of January, increasing through March, and then decreasing through July. Over the course of the study, 90% of the measured total Hg concentrations in weekly precipitation samples were less than 13.6 ng/L.

Figure 2. Total annual mercury concentration and deposition at the Huntington Forest MDN site



Wet Hg deposition (ng/m^2) exhibits a similar seasonal pattern over time with wet Hg generally being lower in the beginning of January, increasing through March, decreasing through July, increasing through the fall and finally decreasing again at the beginning of January. Average annual wet Hg deposition for the study period was $6,530 \text{ ng}/\text{m}^2\text{-yr}$ (Figure 2) at the HF. To date, there is no significant long-term trend in annual wet Hg deposition at the HF; indeed year-to-year variation in annual wet Hg deposition is strongly controlled by the quantity of precipitation that occurs for that year. Although there have been recent decreases in emissions of Hg in the eastern U.S., these decreases are not reflected in concentrations or deposition of Hg in precipitation at the HF.

Mercury exchange processes evaluated at the HF include wet deposition, dry deposition, foliar accumulation, throughfall, litterfall, soil evasion, and vertical and horizontal soil drainage loss. The Hg transport processes were quantified by integrating data collected from different sources over recent years (2004-2011). Dry Hg deposition ($16.3 \mu\text{g m}^{-2} \text{ yr}^{-1}$) is more important than wet Hg deposition ($6.3 \mu\text{g m}^{-2} \text{ yr}^{-1}$) at the HF; most of the atmospheric Hg deposition ($> 60\%$) was retained in the forest soils where litterfall ($17.2 \mu\text{g m}^{-2} \text{ yr}^{-1}$) was the major input pathway. (The fate of Hg inputs is described in a following section).

1.3 Climate Change in the Adirondacks

1.3.1 Ice Record

Recently Beier et al. (2012) used ice phenology records (1975-2007) for five lakes in the HF in the Adirondacks to evaluate climate change. Their study found rapidly decreasing trends of up to 21 days less ice cover over the record that was attributed mostly due to later freeze-up and partially due to earlier break up. An evaluation of local meteorological factors suggested that November and December temperatures and snow depth consistently predicted ice-in for these lakes. Furthermore recent trends of aboveground warming and decreasing snow during these months were consistent with later ice formation.

1.3.2 Temperature and Precipitation

These results from the lake ice records are consistent with other studies in the northeast U.S. that have shown significant warming in recent decades (Campbell et al. 2011, Frumhoff et al. 2007, Hayhoe et al. 2007). NOAA meteorological data were analyzed for Newcomb, NY. The weather station at Newcomb had a change in location (Station ID 305711, Latitude 43.9667, Longitude -74.2167, Elevation 494 m to Station ID 305714, Latitude 43.9708, Longitude -74.2219, Elevation 502 m, on Dec. 1967 through present). Meteorological data was also analyzed from the Tupper Lake NOAA (Station ID 308631,

Latitude 44.2308 Lon. -74.4383, Elevation 512 m) station (37.1 km NW from Newcomb) for which data were available for a longer period and at a single location with different station IDs. Tupper Lake precipitation and temperature results are available from 1899 to present. For these analyses, the period from 1900 through 2013 was used because the record for 1899 was incomplete. Both annual and monthly changes were examined using regression analyses and included those years in which the monthly data were incomplete. But when some of the monthly data were absent, those years without monthly values were not used in the analyses of annual trends.

The distances between the HF to Newcomb and Tupper Lake are approximately 3 and 30 km, respectively. Significant relationships were not found over time in either the annual or monthly temperature and precipitation records for Newcomb, NY. This lack of significant change may be attributed to the relatively short record (e.g., starting in 1940 and the change in the location of the weather station). However for Tupper Lake, significant ($p < 0.001$) increases were found in annual precipitation of 2.8 mm yr^{-1} (28 cm per century) (Figure 3) and a trend ($p = 0.10$) of increasing mean annual temperature ($0.06 \text{ }^\circ\text{C yr}^{-1}$ or $0.6 \text{ }^\circ\text{C per century}$) (Figure 4). Note that the months with significant increases in precipitation ($p < 0.05$) occurred during the fall and winter periods (i.e., October, November, January, and February).

Figure 3. Annual precipitation change at the Tupper Lake NOAA (Station ID 308631) site in the central Adirondack Mountains of New York State

Slope = 2.8 mm yr^{-1} ; $p < 0.001$

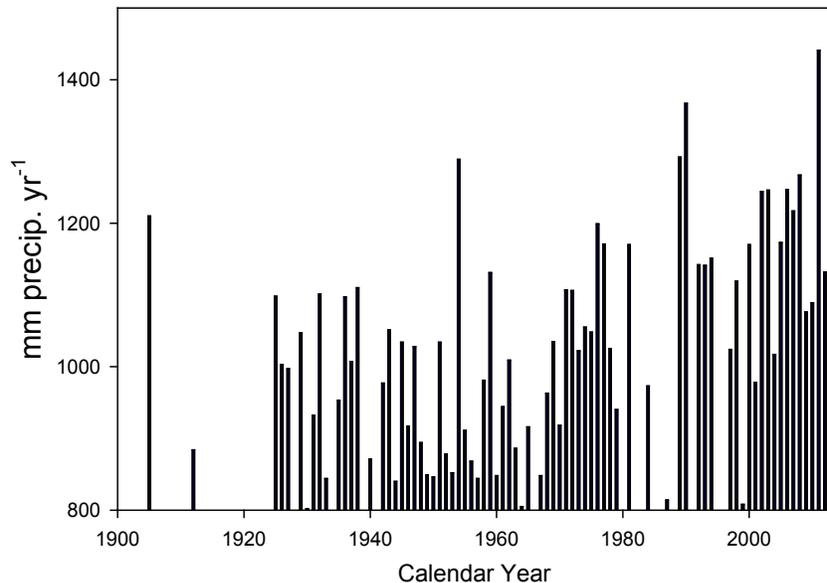
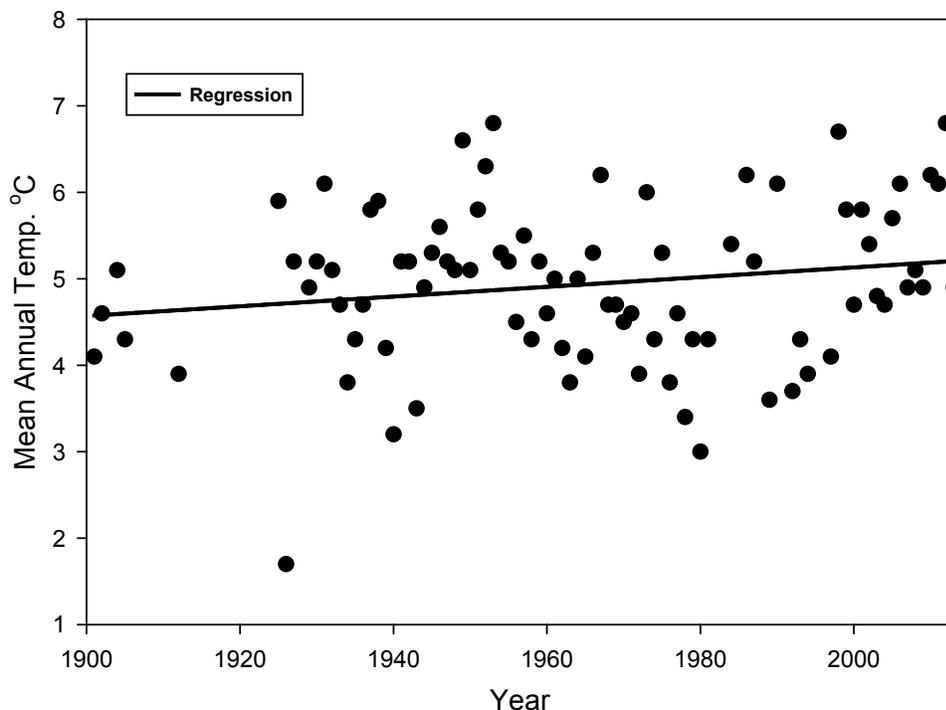


Figure 4. Annual temperature change at the Tupper Lake NOAA (Station ID 308631) site in the central Adirondack Mountains of New York State

Slope = $0.06\text{ }^{\circ}\text{C yr}^{-1}$; $p=0.1$



Climate change is occurring over the entire northeast United States, including the Adirondacks (Huntington et al. 2009). A recent report has provided supporting information derived from broad range of sources that indicate trends of increases in temperature and precipitation in the Adirondack region (Horton et al. 2011). The results from Tupper Lake also agree well with the more detailed measurements at Indian Lake in the Adirondacks that have shown a change through the 1900s of $0.7\text{ }^{\circ}\text{C}$ per century (Rosenzweig et al. 2011). Horton et al. (2014) reported for Indian Lake that there was a significant greater temperature increase from 1901 to 2010 of $0.12\text{ }^{\circ}\text{C}/\text{decade}$. Such differences among locations may be due to local edaphic conditions that can affect meteorological variables.

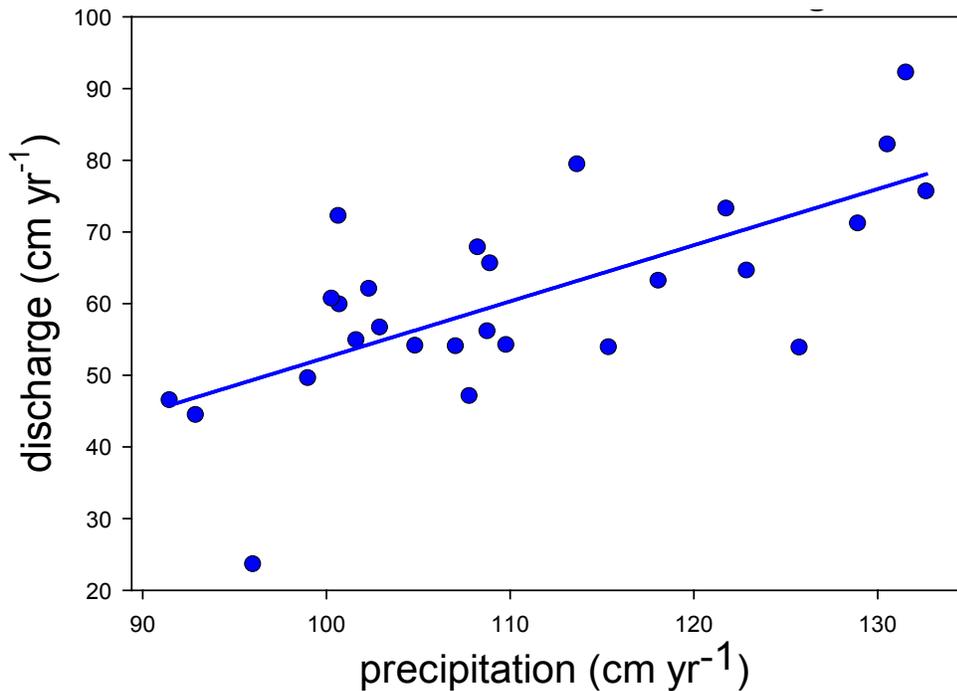
1.3.3 Discharge

The changes in temperature coupled with changes in precipitation affect hydrological processes including snow depth, snow duration, rain on snow events and discharge (Campbell et al. 2011, Hayhoe et al. 2007, Huntington 2003). For example, results at Hubbard Brook Experimental Forest (HBEF) in New Hampshire indicated that an earlier snowmelt and the diminishing length of snowpack are advancing the timing of peak discharge and reducing the level of peak discharge occurring with snowmelt

(Campbell et al. 2011). Despite substantial variation among years in precipitation inputs and discharge, there was a significant linkage between the amount of precipitation and discharge as shown for Arbutus Lake at HF (years 1984-2010) (Figure 5) ($\text{cm yr}^{-1} \text{ discharge} = -25.9 + 0.48 \text{ cm precipitation yr}^{-1}$; $r^2=0.48$; $p<0.0001$). Increases in precipitation would likely lead to greater amounts of stream discharge in the future. The means (standard deviations) of precipitation, discharge and calculated evapotranspiration for the period of measurement were 111 (12), 61 (14) and 50 (12) cm yr^{-1} (45% evapotranspiration), respectively. The calculated evapotranspiration values of the Arbutus Lake Watershed are very similar to those for the HBEF (45 to 60 cm yr^{-1}) (Bailey et al. 2003).

Figure 5. Relationship between the annual discharge from the Arbutus Watershed and annual precipitation

$\text{cm yr}^{-1} \text{ discharge} = -25.9 + 0.48 \text{ cm precipitation yr}^{-1}$; $r^2=0.48$; $p<0.0001$



2 Effects of Changing Climate on Biogeochemical Processes

2.1 Sulfur

The decrease in the atmospheric emissions of S, and the resultant decrease in both wet and dry deposition, is clearly reflected in decreases in SO_4^{2-} concentrations in surface waters. This decrease is shown in the Adirondack Long-Term Monitoring (ALTM) program that originally started with 17 lakes in 1982 to monitor concentrations of major solutes including SO_4^{2-} (Driscoll and van Dreason 1993). Results were used from 16 (14 drainage and 2 seepage lakes) of the 17 original Adirondack Long-Term Monitoring Lakes (ALTM) from 1984 through 2010 and found significant ($p < 0.001$) declines (average for all lakes; $-2.14 \mu\text{mol}_e \text{L}^{-1} \text{yr}^{-1}$) in SO_4^{2-} concentrations (Figure 6). Although there has been a decline in SO_4^{2-} concentrations, the formulation of lake-watershed S budgets (atmospheric inputs - drainage water losses) showed that there were significant internal watershed sources (i.e., net S release from soil mineral weathering, mineralization of organic S and/or SO_4^{2-} desorption). The relative amount of internal SO_4^{2-} released (i.e., sulfur budget discrepancy) for each of the lake/watersheds was related to normalized discharge (Figure 7).

Other studies examining hydrological events have found that following a period of wetness that was preceded by dry conditions that some of the previously immobilized reduced sulfide was re-oxidized to SO_4^{2-} and mobilized in soil leachates and surface waters (Eimers et al. 2004a and 2004b, Mitchell et al. 2006, Kerr et al. 2012). This mobilization of a watershed-internal SO_4^{2-} source can be shown by examining both chemical and isotopic changes over a hydrograph for a storm event (Figure 8). The stream SO_4^{2-} concentrations increased with increased discharge at Archer Creek at the HF while the S and O isotope ratios of SO_4^{2-} are lower in the middle of the storm suggesting that this SO_4^{2-} was derived from reduced sulfide minerals (Mitchell et al. 2006). These studies indicate that the biogeochemical regulation of SO_4^{2-} in watersheds is shifting from the dominant influence of atmospheric deposition to internal watershed supply which is particularly influenced by meteorological factors, especially moisture conditions (Mitchell et al. 2011, Mitchell and Likens 2011). These general relationships between hydrological/soil moisture conditions and SO_4^{2-} mobilization to soil, ground, and surface waters are depicted in Figure 9.

Figure 6. Declines in SO_4^{2-} concentrations for 16 (14 drainage and 2 seepage lakes) of the 17 original Adirondack Long-Term Monitoring Lakes (ALTM) from 1984 through 2010

Mean change: $-2.14 \mu\text{mol}_c \text{L}^{-1} \text{yr}^{-1}$; $p < 0.00001$ for each lake

From Mitchell et al. 2013

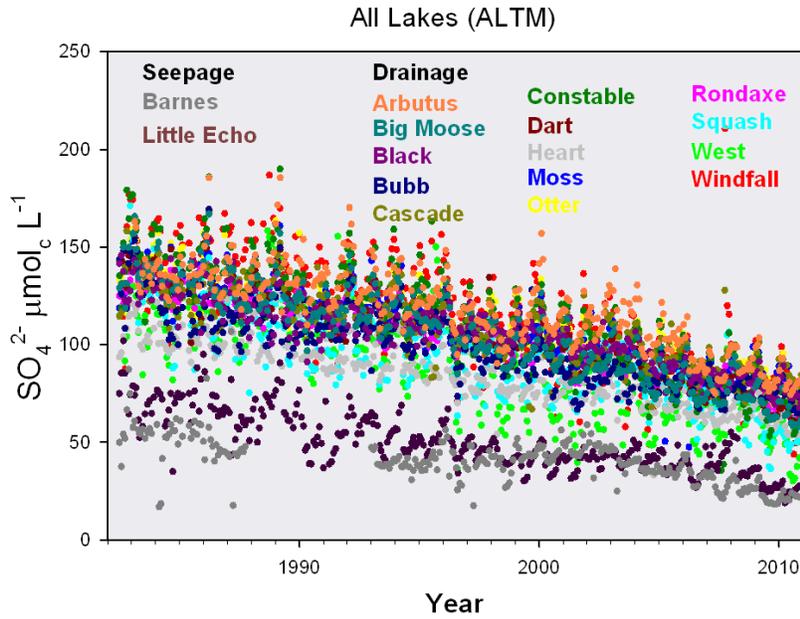


Figure 7. Effect of discharge amount on sulfur budget discrepancy with sulfate concentration normalized to the amount of discharge showing

From Mitchell et al. 2013

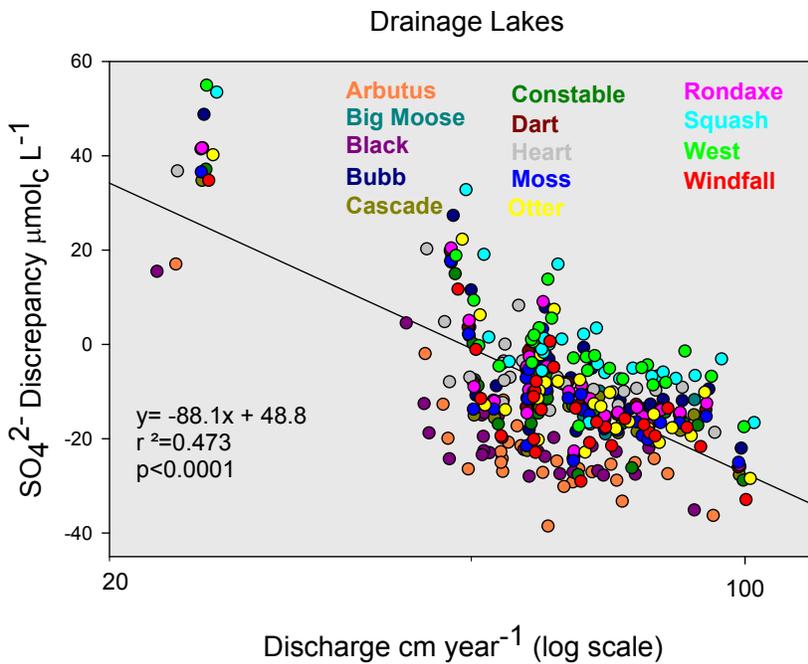


Figure 8. Hydrograph of early fall storm at Archer Creek (within the Arbutus Watershed)

The increase in SO_4^{2-} concentration is shown peaking at the greatest discharge being derived from the oxidation of previously reduced sulfide with characteristic lower $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of SO_4^{2-} .

From Mitchell et al. 2006 used with kind permission of Springer Science+Business Media

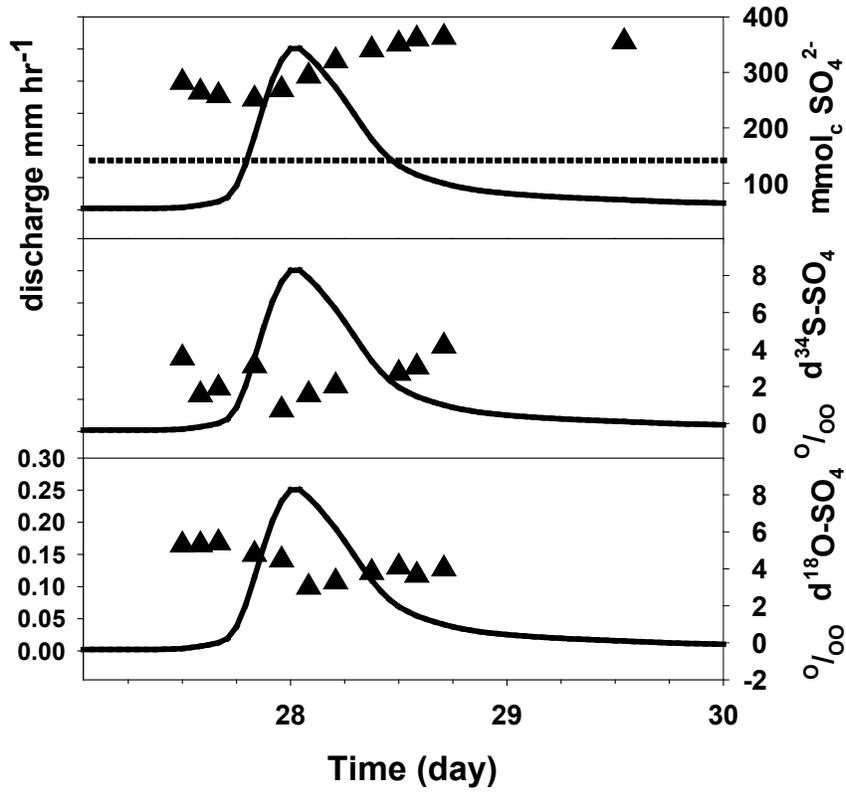
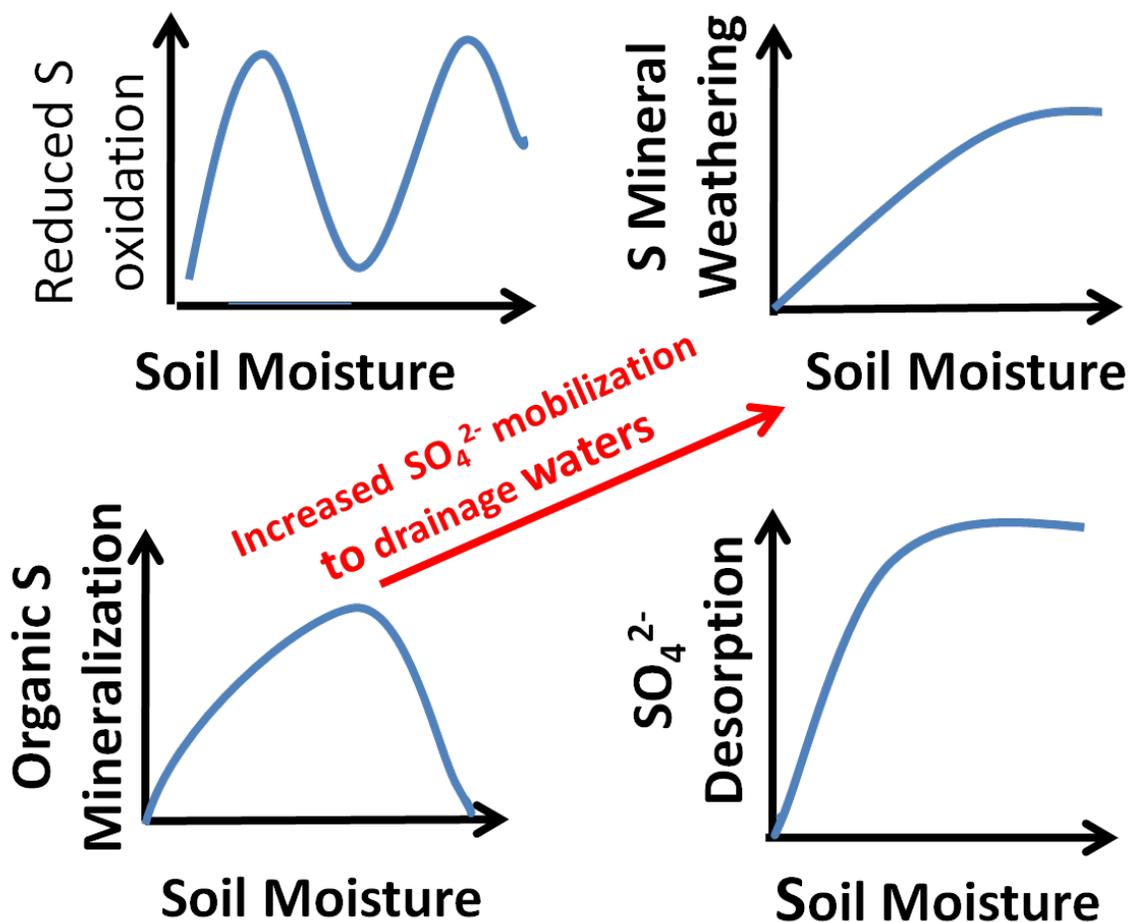


Figure 9. Relationships between soil moisture content and the mobilization of SO_4^{2-}

Conceptual diagram showing the relationships between water availability and SO_4^{2-} generation from various internal S sources in a watershed. All four internal S sources are predicted to show increases in SO_4^{2-} mobilization with greater water availability as predicted with climate change in the Northeast US. Most cases show a monotonic increase in SO_4^{2-} release with greater moisture and resultant increase in discharge.



2.2 Nitrogen

There has been increasing concern (Aber et al. 2003, Binkley et al. 2004, Fenn et al. 1998, Vitousek et al. 1997) about the deleterious impacts of excess N to ecosystems. Forested watersheds may be particularly sensitive to elevated N inputs (Mitchell 2011). This concern has been amplified as SO_4^{2-} concentrations have become lower and NO_3^- concentrations have become a more dominant contributor to acidification in soils and surface waters especially in association with snowmelt a period in which biotic demand for N is low (Mitchell et al. manuscript in prep). The relationship between snowmelt and NO_3^- losses has been shown for numerous watersheds (Figure 10; e.g. Archer Creek, Adirondacks). Examining

well-studied watersheds in the Northeastern U.S. and Southeastern Canada showed that 12 out of 15 watersheds experienced a pattern for which the NO_3^- concentrations in October to December were excellent predictors of January to May NO_3^- concentrations in surface waters including the snowmelt period (e.g., Figure 11; e.g., Archer Creek).

Figure 10. Hydrograph from Archer Creek in winter 2003 showing the relationship between snowpack depth, discharge, temperature and NO_3^- concentrations

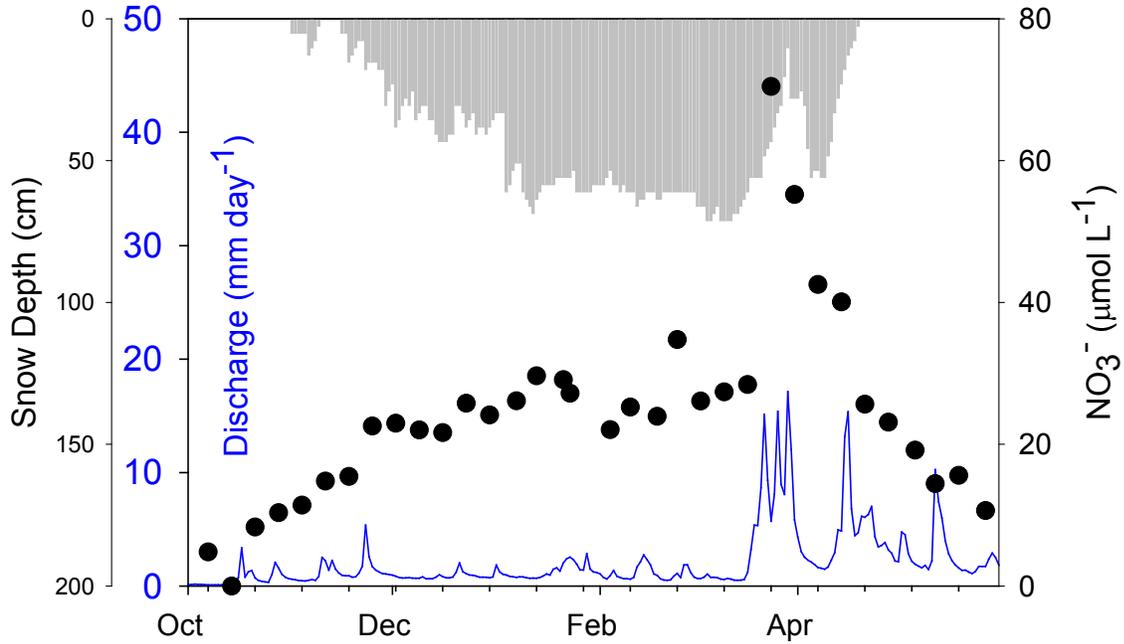
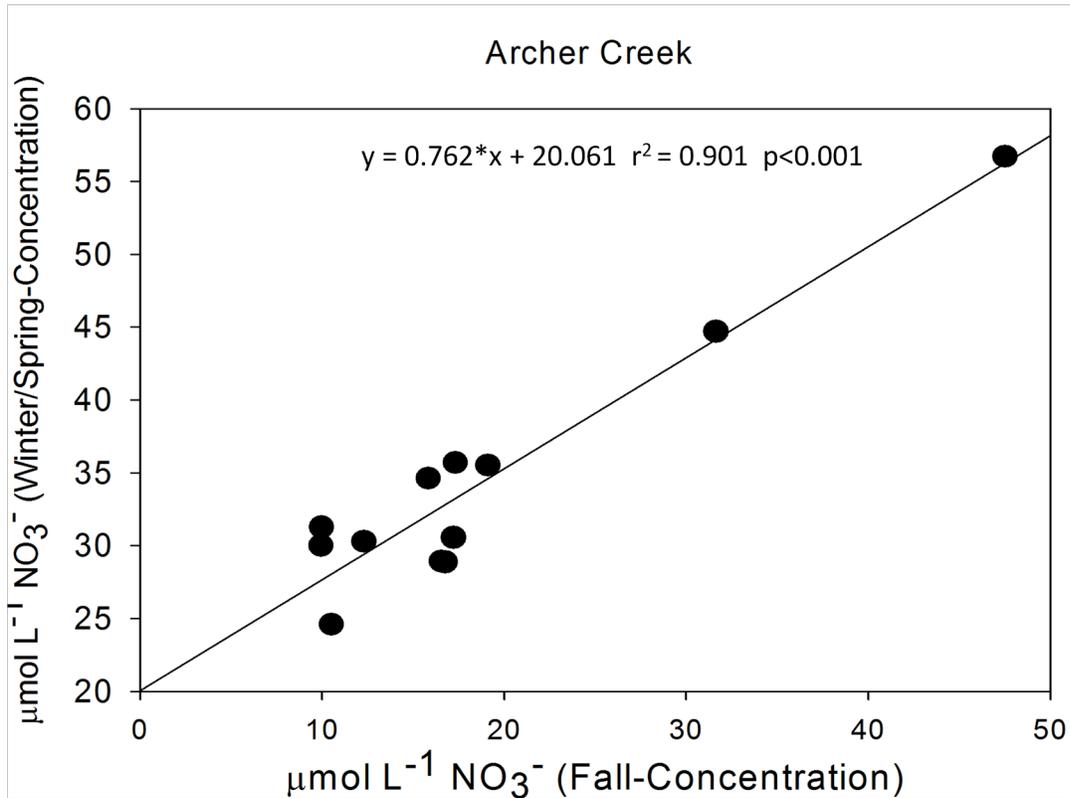


Figure 11. Relationship between annual winter/spring NO_3^- concentrations and fall NO_3^- concentrations at Archer Creek



One of the most intriguing questions of watershed N dynamics is what is regulating the long-term temporal patterns in NO_3^- concentrations and fluxes in surface waters draining forested watersheds (Mitchell et al. in prep.). There has been considerable conjecture on the causes for temporal changes. The “N saturation” hypothesis suggests that over time, as N biotic demand is reached, that the concentration of NO_3^- in surface waters will increase (Aber et al. 2003, Stoddard 1994), but long-term monitoring of surface waters in the northeast United States have not found a consistent pattern of increasing trends. In many cases, there are long-term decreases in NO_3^- concentrations (e.g., Goodale et al. 2003, Driscoll et al. 2007, Yanai et al. 2013). The causes for these temporal patterns have not been ascertained (Aber et al. 1991, Groffman et al. 2009, Mitchell et al. 1996). However, the coincidence of annual N export temporal patterns among surface waters within a region suggest some type of temporal synchronization such as that associated with climate (Goodale et al. 2003).

Climatic factors that have been shown to have a marked impact on NO_3^- loss from forests include soil frost (Fitzhugh et al. 2003, Groffman et al. 2001) and rain on snow events (Eimers et al. 2007, Casson et al. 2010, Kurian et al. 2013). The recent climatic trends of more precipitation amounts in the winter, shorter periods of snow cover and more rain on snow events will be further amplified based on climate change predictions for the northeast U.S. including the Adirondacks and may result in greater NO_3^- export. In addition, climate change will have long-term impacts on watershed N biogeochemistry through the alteration of soil processes and the composition of the forest vegetation which have been shown to have marked impacts on the cycling of N (Mitchell et al. 1992, Christopher et al. 2006, Lovett et al. 2009).

2.3 Mercury

Concentrations of total Hg (THg) and methylmercury (MeHg) were monitored in Archer Creek at the HF (Selvendiran et al. 2008 and 2009). Similar temporal patterns were observed for upland and wetland waters for THg and dissolved organic carbon (DOC), though the concentrations were distinctively different. The highest stream concentrations of DOC and THg occur under the lowest flow conditions during June and July. Low flow in combination with more highly reducing conditions and higher temperatures in the wetlands of Archer Creek during the summer increased the production of DOC. The average concentration of DOC in wetland streams increased almost twofold during the growing season (10.4 mg/L) relative to the non-growing season (5.8 mg/L). In the upland stream, DOC concentrations increased only slightly, from 3.2 mg/L to 4.3 mg/L during the growing season. Elevated discharge that followed dry periods during late fall and early summer also resulted in elevated concentrations of DOC and THg in stream water. Although no apparent seasonal patterns were evident, THg closely followed the pattern in DOC concentrations ($r^2 = 0.80$; $\alpha = 0.05$), highlighting the role of DOC in THg transport at Archer Creek. The strong influence of DOC in the transport of THg has been reported from other studies (Driscoll et al. 1995, Dennis et al. 2005).

Marked differences in temporal patterns between upland and wetland stream water concentrations were evident for MeHg. Concentrations of MeHg in upland stream waters showed little temporal variation and often were near the analytical detection limit. In contrast, large variations with a strong seasonal component were observed for stream MeHg concentrations draining wetlands. Minimum MeHg concentrations in wetland streams were observed during the winter months. MeHg concentrations

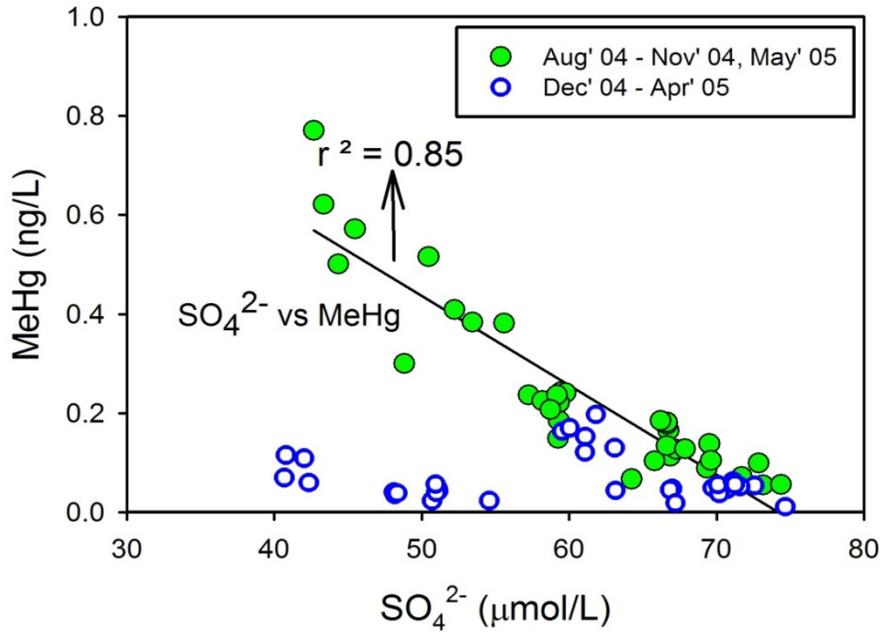
increased during late spring with the onset of warmer temperatures and peaked during summer. Concentrations of MeHg increased almost three-fold in the wetland streams from 0.1 ng/L during the non-growing season to 0.3 ng/L during the growing season. Comparatively, MeHg concentrations in upland stream water were much lower during both seasons (0.02-0.04 ng/L).

Wetland stream water SO_4^{2-} concentrations were consistently lower than upland streams, indicating reducing conditions and SO_4^{2-} retention in wetlands. Dissimilatory sulfate-reducing bacteria are linked to MeHg production in wetlands (Gilmour et al. 1992, Benoit et al. 2003). The greater difference between upland and wetland stream water SO_4^{2-} concentrations was consistent with the observation of higher MeHg concentrations draining wetlands during summer months (Figure 12). Note that low SO_4^{2-} concentrations in both upland and wetland streams resulting from snowmelt and high flow rather than reducing conditions during March, April, and November did not coincide with increases in MeHg in stream water.

The increase in MeHg concentrations in wetland stream waters coincided with a decrease in SO_4^{2-} . A significant negative relationship existed between MeHg and SO_4^{2-} concentrations during the growing season ($r^2 = 0.28$, $P < 0.0001$), which was not evident for the nongrowing season ($r^2 = 0.01$, $P = 0.12$). Decreases in SO_4^{2-} concentrations during the growing season in wetlands is often attributed to dissimilatory SO_4^{2-} reduction (Bailey et al. 1995, Fitzhugh et al. 1999) (Figure 12), and has been linked to MeHg production (Branfireun et al. 1999, Gilmour et al. 1998 and 1992). A weak but positive relation was found for DOC and MeHg concentrations during the growing ($r^2 = 0.20$, $P < 0.05$) and nongrowing seasons ($r^2 = 0.17$, $P < 0.05$). The slopes of the regressions were similar for the two seasons (Figure 13), with the intercept being greater for the growing season.

Figure 12. Relationship between SO_4^{2-} concentrations and MeHg concentrations as a function of season (growing versus dormant) at Archer Creek

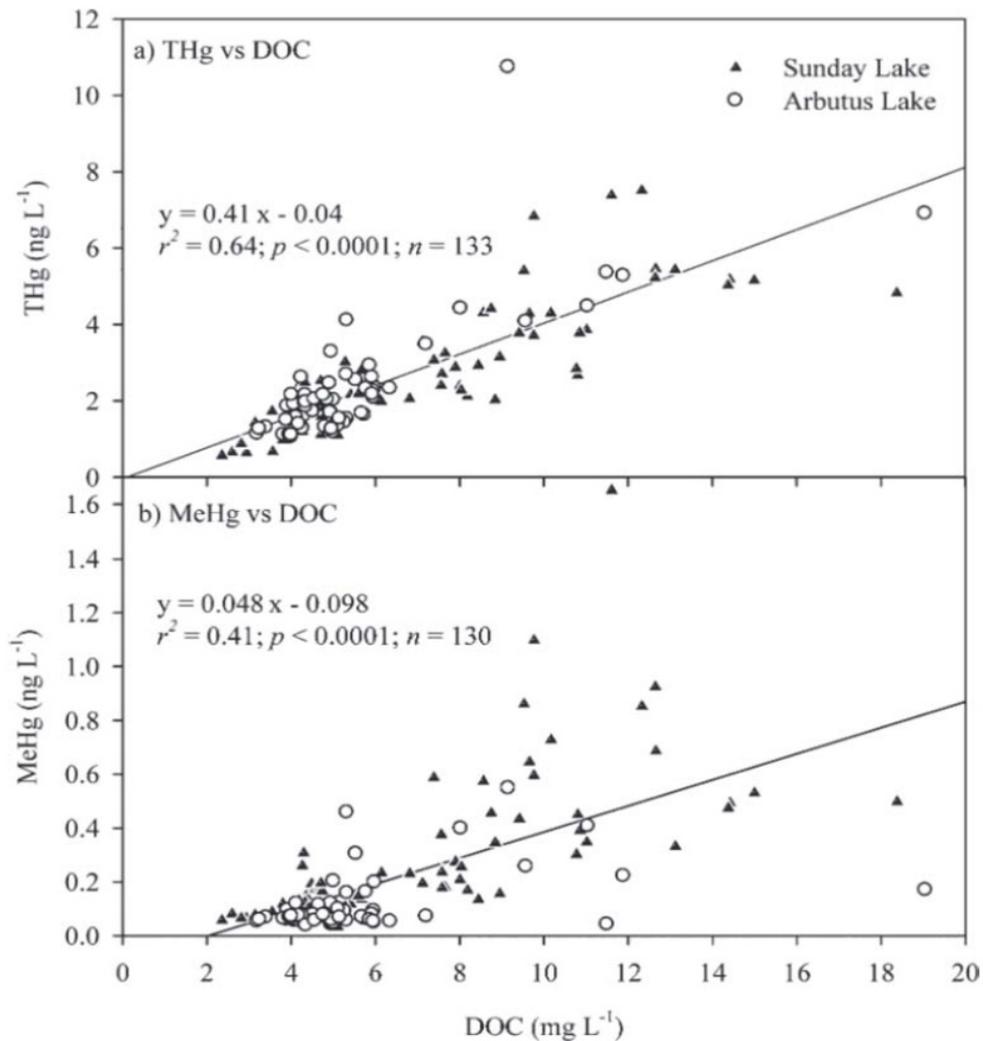
Data from Selvendiran et al. 2008.



The Hg mass balance for HF showed that coupled with atmospheric deposition (previously discussed), soil evasion ($6.5 \mu\text{g m}^{-2} \text{yr}^{-1}$) was the most important Hg export mechanism, exceeding Hg fluxes in lateral and vertical drainage from soil ($2.8 \mu\text{g m}^{-2} \text{yr}^{-1}$). Marked seasonal variation in the transfers of Hg is largely mediated by annual canopy development of the forest ecosystem. The upland hardwood forest ecosystem was a net sink for atmospheric Hg deposition.

Figure 13. Relationships between DOC concentrations and total Hg and MeHg concentrations in Arbutus Lake and Sunday Pond in the Adirondack Mountains

Reprinted from Selvendiran et al. 2009.



3 Role of Future Changes in Climate and Atmospheric Deposition on the Biogeochemical Responses

An important shift is occurring in the biogeochemical regulation of watersheds in the Adirondack Mountains. Paleolimnological analyses of diatom, chrysophyte, and cladoceran assemblages in lake sediments have suggested that acidification of lakes began in the early 1900s and that lakes became acidic in the 1930s and 1950s with the timing of acidification being a function of lake type and level of acidic deposition (Cumming et al. 1991 and 1992). More recent paleolimnological studies have shown that some of the lakes are recovering from acidification and this recovery has been accelerated by the implementation of the U.S. Acid Rain Program in 1995. The recovery from acidification is a direct function of the decreases in atmospheric emission and deposition of acidifying compounds (e.g., Figure 1). Not all paleolimnological indicator taxa have returned to preacidification numbers and there is some suggestion that the increase of certain taxa (e.g., the chrysophyte, *Synura echinulata*) may be due to recent warming in the Adirondacks (Arseneau et al, 2011, Cumming et al, 2011).

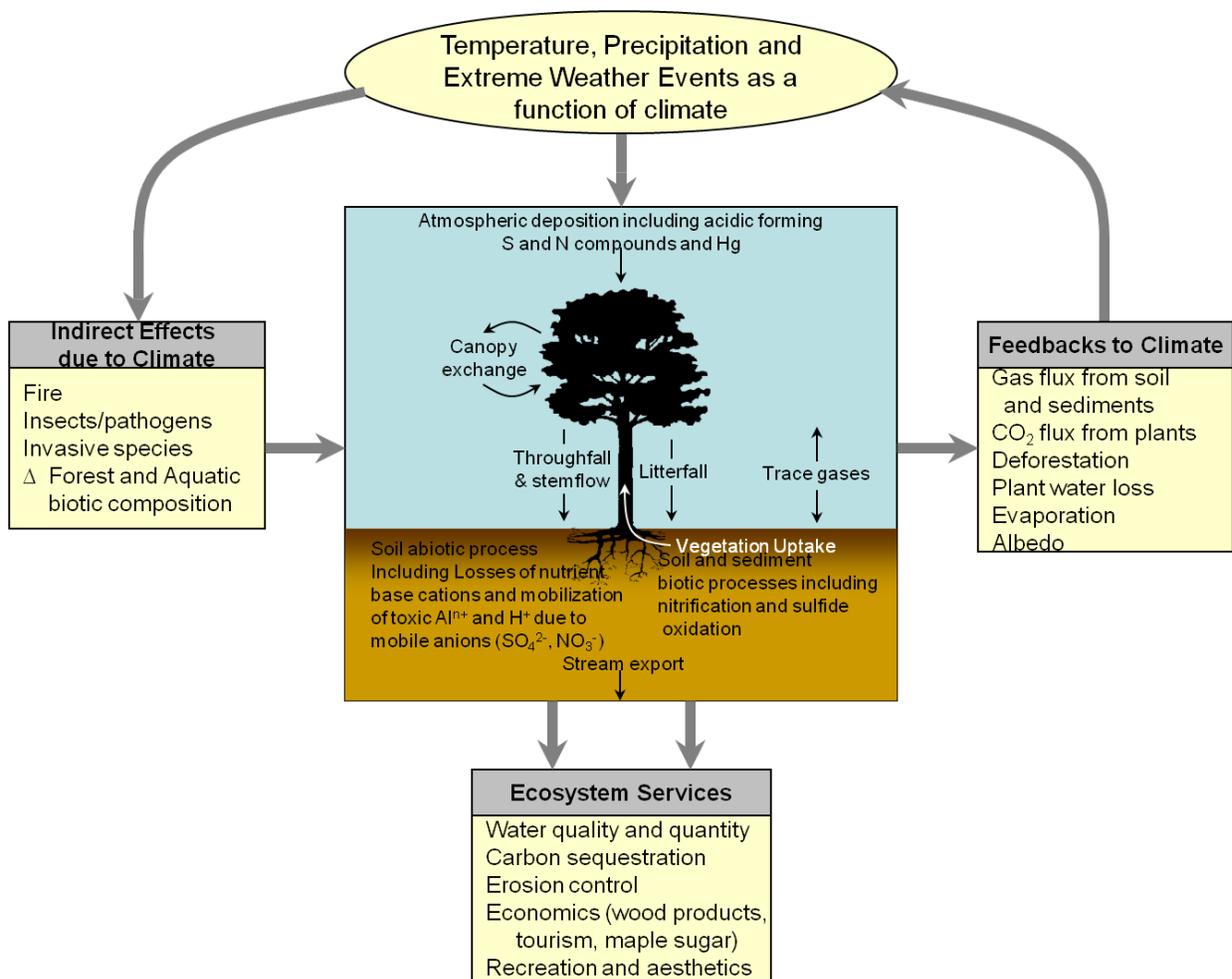
Along with work by other investigators in the Adirondacks, our study has suggested that the inputs of acidic deposition (especially S) have shown marked decreases, and chemical recovery of surface waters has been quantified with increases in ANC. The chemical recovery of soils, however, is going to be much slower because acid sensitive soils have lost nutrient base cations and the recovery of these soils will be a long process and possibly not occur within the next century. Also it appears that the biological recovery of surface waters and soils has also been notably slower than for chemical recovery although the data on biological recovery are substantially less. It is noteworthy, in marked contrast to the decrease in acidic deposition, the atmospheric inputs of mercury in the Adirondacks have not shown any significant decrease.

Recent studies including those cited in this report clearly show that climatic factors (especially precipitation inputs and temperature increases) have changed and these changes are affecting the biogeochemical relationships of key elements such as sulfur, nitrogen, and mercury. For example, our study has shown how the losses of SO_4^{2-} (Figure 9) and NO_3^- (Figure 10) to surface waters are dependent on climatic factors such as temperature and precipitation in the Adirondacks. Hence in the future these

climatic factors (Jenkins, 2010, Horton et al. 2014) will be of greater importance in regulating the biogeochemical response of Adirondack ecosystems. Evaluating these climatic roles concomitantly with evaluating changes in atmospheric deposition is a major challenge for scientists and policymakers. This task is made even more difficult because of the impact of other extrinsic factors such as invasion of exotic species including pathogens and alteration of plant and animal communities as depicted in Figure 14.

Figure 14. Interactions between acidic deposition and climate change in affecting forested watersheds including other extrinsic factors important for forest ecosystem processes such as ecological services

Diagram derived from Campbell et al. 2009.



4 References

- Aber J D, Goodale CL, Ollinger SV, et al. 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? *Bioscience* 53: 375-389.
- Aber JD, Melillo JM, Nadelhoffer KJ, et al. 1991. Factors controlling nitrogen cycling and nitrogen saturation in northern temperate forest ecosystems. *Ecological Applications* 1: 303-315.
- Arseneau KMA, Driscoll CT, Brager LM, et al. 2011. Recent evidence of biological recovery from acidification in the Adirondacks (New York, USA): a multiproxy paleolimnological investigation of Big Moose Lake. *Canadian Journal of Fisheries and Aquatic Sciences* 68(4): 575-592.
- Bailey SW, Driscoll CT, Hornbeck JW. 1995. Acid-base chemistry and aluminum transport in an acidic watershed and pond in New Hampshire. *Biogeochemistry* 28: 69-91.
- Bailey AS, Hornbeck JW, Campbell JL, et al. 2003. Hydrometeorological Database for Hubbard Brook Experimental Forest: 1955 - 2000. General Technical Report NE-305. 36 p. United States Department of Agriculture Forest Service, Northeastern Research Station.
- Beier CM, Stella JC, Dovciak M, et al. 2012. Local climatic drivers of changes in phenology at a boreal-temperate ecotone in eastern North America. *Climate Change* 115: 399-417.
- Benoit JM, Gilmour C, Heyes A, et al. 2003. Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. Pages 262-297 in Y. Chai and O. C. Braids, editors. *Biogeochemistry of Environmentally Important Trace Elements*. Washington, DC. American Chemical Society.
- Binkley D, Ice GG, Kaye J, et al. 2004. Nitrogen and Phosphorus Concentrations in Forest Streams of the United States. *J Am Water Res Assoc* 40: 1277-1291.
- Branfireun BA, Roulet NT, Kelly CA, et al. 1999. In situ sulphate stimulation of mercury methylation in a boreal peatland: Toward a link between acid rain and methylmercury contamination in remote environments (Paper 1999GB900033). *Global Biogeochemical Cycles* 13: 8.
- Campbell JL, Driscoll, CT, Pourmokhtarian A, et al. 2011. Streamflow responses to past and projected future changes in climate at the Hubbard Brook Experimental Forest, New Hampshire, USA. *Water Resources Research*. 47: W02514.
- Campbell JL, Rustad LD, Boyer EW, et al. 2009. Consequences of climate change for biogeochemical cycling in forests of northeastern North America. *Canadian Journal of Forest Research* 39: 264-284.
- Casson NJ, Eimers MC, Battles JM. 2010. The contribution of rain-on-snow events to nitrate export in the forested landscape of south-central Ontario, Canada. *Hydrological Processes* 24: 1985-1993.
- Christopher SF, Page BD, Campbell JL, et al. 2006. Contrasting stream water NO₃⁻ and Ca²⁺ in two nearly adjacent catchments: the role of soil Ca and forest vegetation. *Global Change Biology* 12: 364-381.

- Cumming BF, Davey KA, Smol JP, et al. 1991. When Did Acid-Sensitive Adirondack Lakes (New York, USA) Begin to Acidify and Are They Still Acidifying? *Canadian Journal of Fisheries and Aquatic Sciences*, 1994, 51(7): 1550-1568.
- Cumming BF, Smol JP, Kingston JC, et al. 1992. How much acidification has occurred in Adirondack region lakes (New York, USA) since preindustrial times? *Can. J. Fish. Aquat. Sci.* 49(1): 128-141.
- Cumming BF, Smol JP, Kingston JC, et al. 2011. Recent evidence of biological recovery from acidification in the Adirondacks (New York, USA): a multiproxy paleolimnological investigation of Big Moose Lake. *Canadian Journal of Fisheries and Aquatic Sciences* 68(4): 575-592.
- Dennis IF, Clair TA, Driscoll CT, et al. 2005. Distribution patterns of mercury in lakes and rivers of northeastern North America. *Ecotoxicology* 14: 113-123.
- Driscoll CT, Blette V, Yan C, et al. 1995. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack lakes. *Water, Air, and Soil Pollution* 80: 10.
- Driscoll CT, and van Drearon R. 1993. Seasonal and long-term temporal patterns in the chemistry of Adirondack Lakes. *Water, Air, and Soil Pollution* 67: 319-344.
- Driscoll CT, Driscoll KM, Roy KM, et al. 2007. Changes in the chemistry of lakes in the Adirondack region of New York following declines in acidic deposition. *Applied Geochemistry* 22: 1181-1188.
- Driscoll CT, Driscoll KM, Mitchell MJ, et al. 2009 p. 114-127. In: W.P. Porter, R.S. Whaley & J. D. Erickson (eds.). *Light from an Adirondack Prism: The Great Experiment in Conservation*. Syracuse, NY. Syracuse University Press
- Driscoll CT, Lawrence GB, Bulger AJ, et al. 2001. Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. *Bioscience* 51: 180-198.
- Driscoll CT, Mason RP, Chan HM, et al. 2013. Mercury as a global pollutant: Sources, pathways, and effects. *Environmental Science & Technology* 47: 4967-4983.
- Driscoll CT, Newton RM, Gubala CP, et al. 1991a. Adirondack Mountains. Pages 133-202 in D. F. Charles, editor. *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*. Springer-Verlag, New York.
- Driscoll CT, Newton RM, Gubala CP, et al. 1991b. D. Charles (ed.) *Acidic Deposition and Aquatic Ecosystems*. pp. 133-202. Springer-Verlag, New York.
- Eimers MC, Buttle JM, Watmough SA .2007. The contribution of rain-on-snow events to annual NO₃-N export at a forested catchment in central Ontario, Canada. *Applied Geochemistry* 22: 1105-1110.
- Eimers MC, Dillon PJ, Schiff SL. 2004a. A S isotope approach to determine the relative contribution of redox processes to net SO₄ export from upland and wetland dominated catchments. *Geochimica Et Cosmochimica Acta*, 68: 3665-3674.
- Eimers MC, Dillon PJ, Schiff SL. 2004b. Sulphate flux from an upland forested catchment in south-central Ontario, Canada. *Water, Air, and Soil Pollution* 152: 3-21.

- Evers DC, Han Y-J, Driscoll CT et al. 2007. Biological mercury hotspots in the Northeastern United States and Southeastern Canada. *Bioscience* 57: 1-15.
- Fenn ME, Poth MA, Aber JD, et al. 1998. Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies. *Ecological Applications* 8: 28.
- Fitzgerald WF, Engstrom DR, Mason RP, et al. 1998. The case for atmospheric mercury contamination in remote areas. *Environmental Science & Technology* 32: 1-7.
- Fitzhugh R, Likens G, Driscoll C, et al. 2003. The role of soil freezing events in interannual patterns of stream chemistry at the Hubbard Brook Experimental Forest. *Environ Sci Tech* 37: 1575-1580.
- Fitzhugh RD, Furman T, Webb JR, et al. 1999. Longitudinal and seasonal patterns of stream acidity in a headwater catchment on the Appalachian Plateau, West Virginia, U.S.A. *Biogeochemistry* 47: 39-62.
- Fowler D, Smith R, Muller J et al. 2007. Long term trends in sulphur and nitrogen deposition in Europe and the cause of non-linearities. *Water Air Soil Pollut* 7: 41-47.
- Frumhoff PC, McCarthy JJ, Melillo JM, et al. 2007. *Confronting Climate Change in the U.S. Northeast: Science, Impacts, and Solutions*. Synthesis report of the Northeast Climate Impacts Assessment (NECIA). Cambridge, MA: Union of Concerned Scientists (UCS).
- Gilmour CC, Henry EA, Mitchell R. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Environmental Science & Technology* 26: 2281-2287.
- Gilmour CC, Riedel GS, Ederinton MC, et al. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry* 40: 327-345.
- Goodale CL, Aber JD, Vitousek PM. 2003. An unexpected nitrate decline in New Hampshire streams. *Ecosystems* 6: 75-86.
- Groffman PM, Driscoll CT, Fahey TJ, et al. 2001. Effects of mild winter freezing on soil nitrogen and carbon dynamics in a northern hardwood forest. *Biogeochemistry* 56: 191-213.
- Groffman PM, Hardy JP, Fisk MC, et al. 2009. Climate variation and soil carbon and nitrogen cycling processes in a northern hardwood forest. *Ecosystems* 12: 927-943.
- Hayhoe K, Wake CP, Huntington TG, et al. 2007. Past and future changes in climate and hydrological indicators in the US Northeast. *Climate Dynamics* 28: 381-407.
- Horton R, Bader D, Tryhorn L, et al. 2011. Climate Risks. *Annals of the New York Academy of Sciences* 1244: 15-48.
- Horton, R, Yohe G, W. Easterling W, et al., 2014: Ch. 16: Northeast. *Climate Change Impacts in the United States: The Third National Climate Assessment*, J. M. Melillo, Terese (T.C.) Richmond, and G. W. Yohe, Eds., U.S. Global Change Research Program, 16-1nn

- Huntington TG. 2003. Climate warming could reduce runoff significantly in New England. *Agric. For. Meteorol.* 117: 193-201.
- Huntington TG, Richardson AD, McGuire KJ, et al. 2009. Climate and hydrological changes in the northeastern United States: recent trends and implications for forested and aquatic ecosystems. *Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere* 39: 199-212.
- Jenkins, J. 2010. *Climate Change in the Adirondacks The Path to Sustainability*. Cornell University Press. 200 p.
- Kerr JG, Eimers MC, Creed IF, et al. 2012. The effect of seasonal drying on sulphate dynamics in streams across southeastern Canada and the northeastern USA. *Biogeochemistry* 111: 393-409.
- Kretser WJ, Gallagher J, Nicolette J. 1989a. An evaluation of fish communities and water chemistry. Ray Brook, NY. Adirondack Lakes Survey Corporation
- Kretser WJ, Gallagher WJ, Nicollette J. 1989b. Adirondack Lakes Study, 1984--1987. An evaluation of fish communities and water chemistry, summary report, Adirondack Lakes Surv. Corp.
- Kurian LM, Lautz LK, Mitchell MJ. 2013. Winter hydrology and concentrations in a forested watershed: a detailed field study in the Adirondack Mountains of New York. *Journal of the American Water Resources Association* 49: 264-283.
- Lovett GM, Timothy GM, Tear TH, et al. 2009. "Effects of Air Pollution on Ecosystems and Biological Diversity in the Eastern United States", *Year in Ecology and Conservation Biology* 1162: 99-135.
- Mitchell MJ. 2011. Nitrate Dynamics of Forested Watersheds: Spatial and Temporal Patterns in North America, Europe and Japan. *Journal of Forest Research* 16: 333-340.
- Mitchel et al. manuscript in prep
- Mitchell MJ and Driscoll CT (eds). 2004. Special Issue: Interrelationships between atmospheric deposition and landscape features of forest catchments in regulating surface water biogeochemistry. *Hydrological Processes*. 18: 2615-2755.
- Mitchell MJ, Driscoll CT, McHale PJ, et al. 2013. Lake/watershed sulfur budgets and their response to decreases in atmospheric sulfur deposition: Watershed and climate controls *Hydrological Processes* 27: 710-720.
- Mitchell M, Driscoll C, Murdoch P, et al. 1996. Climatic control of nitrate loss from forested watersheds in the northeast United States. *Environ Sci Tech* 30: 2609-2612.
- Mitchell MJ, Driscoll CT, Owen JS, et al. 2001. Nitrogen biogeochemistry of three hardwood ecosystems in the Adirondack Region of New York. *Biogeochemistry* 56: 41.
- Mitchell MJ, Foster NW, Shepard JP, et al. 1992. Nutrient cycling in Huntington Forest and Turkey Lakes deciduous stands: nitrogen and sulfur. *Canadian Journal of Forest Research* 22: 457-464.

- Mitchell MJ and Likens GE. 2011. Watershed Sulfur Biogeochemistry: Shift from Atmospheric Deposition Dominance to Climatic Regulation. *Environmental Science and Technology* 45: 5267-5271
- Mitchell MJ, Lovett G, Bailey S, et al. 2011. Comparisons of watershed sulfur budgets in southeast Canada and northeast US: new approaches and implications. *Biogeochemistry* 103: 181-207.
- Mitchell MJ, Piatek KB, Christopher S, et al. 2006. Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: a combined hydrological, chemical and isotopic approach. *Biogeochemistry* 78: 217-246.
- Rosenzweig C, Solecki W, DeGaetano A, et al. (Eds.). 2011. Responding to Climate Change in New York State: The ClimAID Integrated Assessment for Effective Climate Change Adaptation. Technical Report. Albany, New York. New York State Energy Research and Development Authority (NYSERDA) www.nysesda.ny.gov
- Selvendiran P, Driscoll CT, Bushey JT, et al. 2008. Wetland influence on mercury fate and transport in a temperate forested watershed. *Environmental Pollution* 154: 46-55.
- Selvendiran P, Driscoll CT, Montesdeoca MR, et al. 2009. Mercury dynamics and transport in two Adirondack Lakes. *Limnol. Oceanogr.* 54: 413-427.
- Stoddard JL. 1994. Long-term changes in watershed retention of nitrogen: its causes and consequences. Pages 223-284 in L. A. Baker, editor. *Environmental Chemistry of Lakes and Reservoirs*. Washington, D.C. American Chemical Society
- USA EPA. 1999. National Air Quality and Emissions Trends Report, 1999. <http://www.epa.gov/airtrends/aqtrnd99/>
- Vitousek PM, Aber JD, Howarth RW, et al. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications* 7: 737-750
- Yanai RD, Vadeboncoeur MA, Hamburg SP, et al. 2013. From missing source to missing sink: Long-term changes in the nitrogen budget of a northern hardwood forest. *Environmental Science & Technology* 47: 11440-11448.

NYSERDA, a public benefit corporation, offers objective information and analysis, innovative programs, technical expertise, and support to help New Yorkers increase energy efficiency, save money, use renewable energy, and reduce reliance on fossil fuels. NYSERDA professionals work to protect the environment and create clean-energy jobs. NYSERDA has been developing partnerships to advance innovative energy solutions in New York State since 1975.

To learn more about NYSERDA's programs and funding opportunities, visit nysesda.ny.gov or follow us on Twitter, Facebook, YouTube, or Instagram.

**New York State
Energy Research and
Development Authority**

17 Columbia Circle
Albany, NY 12203-6399

toll free: 866-NYSERDA
local: 518-862-1090
fax: 518-862-1091

info@nysesda.ny.gov
nysesda.ny.gov



State of New York

Andrew M. Cuomo, Governor

New York State Energy Research and Development Authority

Richard L. Kauffman, Chair | John B. Rhodes, President and CEO

