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

**Final Report Summary**

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

## *Final Report Summary*

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## Preferred Citation

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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](http://nyserda.ny.gov/publications)

## Abstract

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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 [ $\text{SO}_4^{2-}$ ] and nitrate [ $\text{NO}_3^-$ ]) 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  $\text{SO}_4^{2-}$  in surface waters is being affected by the contribution of internal sulfur (S) sources (i.e., organic S, S-bearing minerals,  $\text{SO}_4^{2-}$  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  $\text{NO}_3^-$  in surface waters show marked annual variation with the amount of  $\text{NO}_3^-$  generation in the late summer/early fall appearing to be a major factor in determining the amount of  $\text{NO}_3^-$  loss during the period of snow melt, which is the period that dominates the amount of  $\text{NO}_3^-$  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  $\text{SO}_4^{2-}$  reduction and hence those periods with high biotic activity generate the most MeHg and result in low  $\text{SO}_4^{2-}$  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

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

## Acknowledgments

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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.

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# 1 Introduction

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## 1.1 Changes in Atmospheric Deposition in the Adirondacks

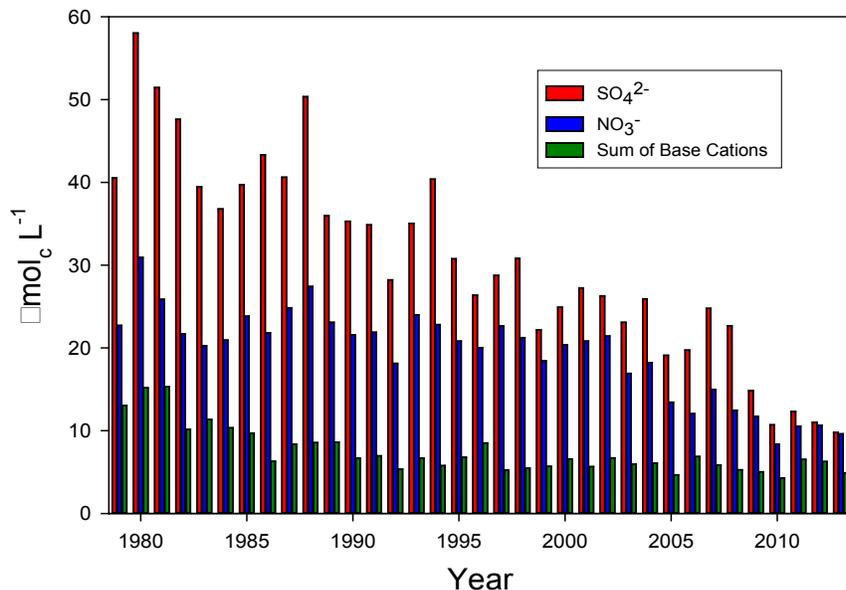
The Adirondack Mountains in New York State (USA) have been a focal region for research on the deleterious impacts of acidic deposition (“acid rain”) since observations in the 1970s and 1980s showed a substantial decline in the fisheries (Kretser et al. 1989a and 1989b; Driscoll et al. 1991a and 1991b). 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 ( $\text{SO}_4^{2-}$ ) ( $-1.0 \mu\text{mol}_c \text{L}^{-1} \text{yr}^{-1}$ ;  $p < .0001$ ;  $r^2 = 0.76$ ) and nitrate ( $\text{NO}_3^-$ ) ( $-0.44 \mu\text{mol}_c \text{L}^{-1} \text{yr}^{-1}$ ;  $p < .0001$ ;  $r^2 = 0.72$ ), coincident with decreases in emissions.

Another important component of atmospheric nitrogen inputs is ammonium ( $\text{NH}_4^+$ ). The emissions of ammonium are poorly estimated but thought to be relatively constant since the early 1990s (USA EPA, 1999). The proportion of  $\text{NH}_4^+$  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  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$

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

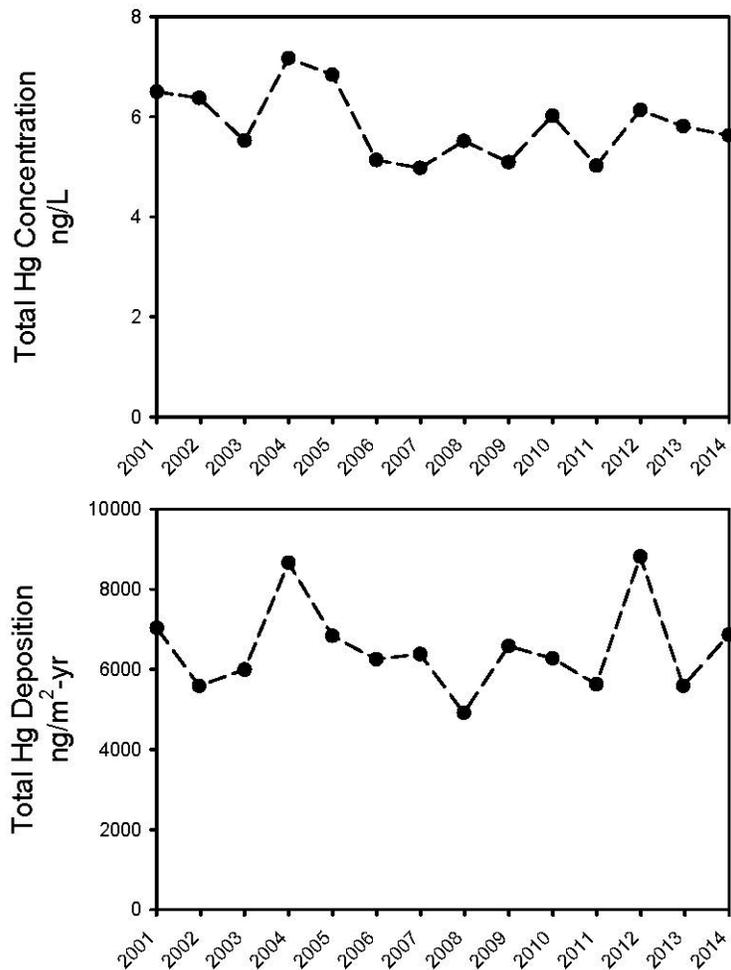
Northern forest ecosystems, including the Adirondacks, are sensitive to atmospheric mercury (Hg) deposition (Evers et al. 2007). Atmospheric deposition is the predominant input of Hg to remote watersheds like the Adirondacks (Fitzgerald et al. 1998; Driscoll et al. 2013). The inputs and fate of

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 ( $\text{ng}/\text{m}^2$ ) 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**

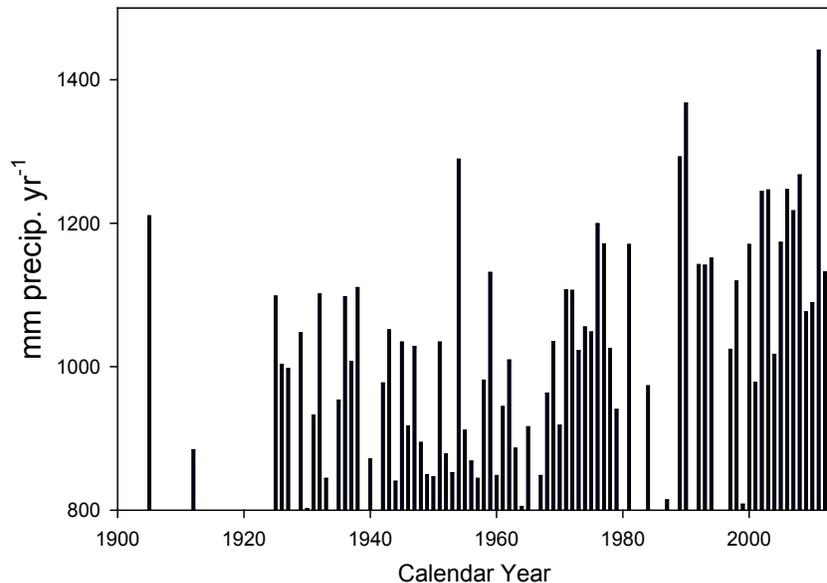
These results from the lake ice records are consistent with other studies in the northeast U.S. that have shown significant warming in recent decades (Campbell et al. 2011, Frumhoff et al. 2007, Hayhoe et al. 2007). NOAA meteorological data were analyzed for Newcomb, NY. The weather station at Newcomb 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  $2.8 \text{ mm yr}^{-1}$  (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).

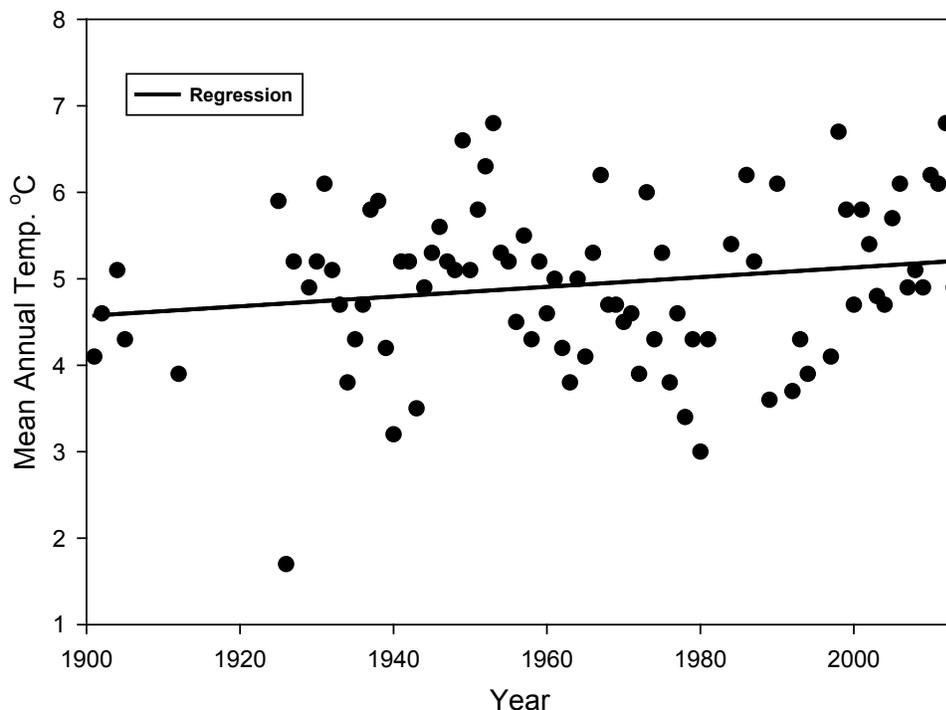
**Figure 3. Annual precipitation change at the Tupper Lake NOAA (Station ID 308631) site in the central Adirondack Mountains of New York State**

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



**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.

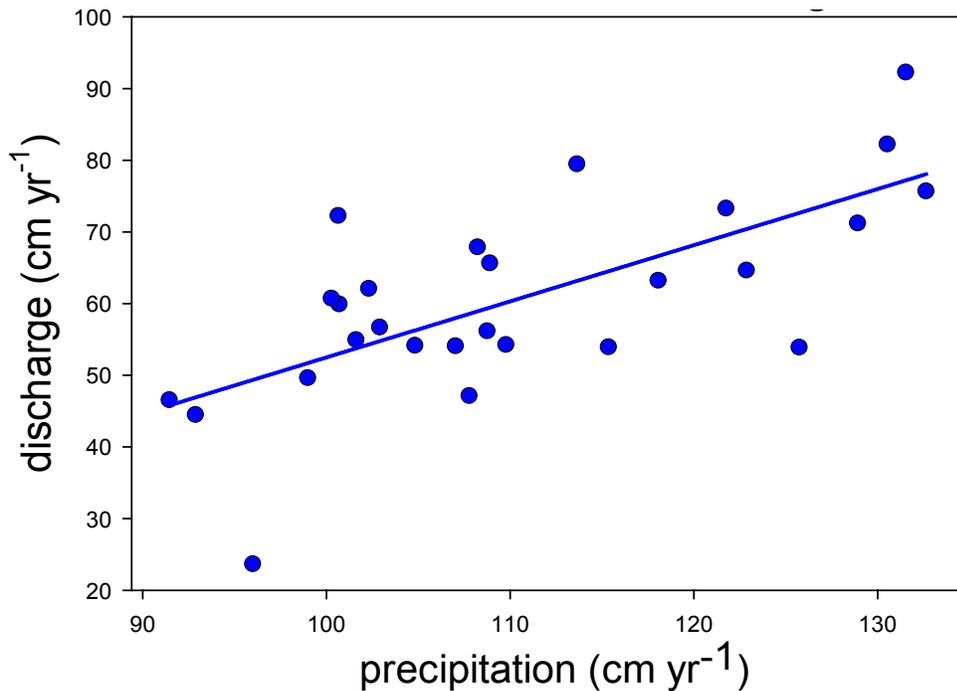
### 1.3.3 Discharge

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)  $\text{cm yr}^{-1}$  (45% evapotranspiration), respectively. The calculated evapotranspiration values of the Arbutus Lake Watershed are very similar to those for the HBEF (45 to 60  $\text{cm yr}^{-1}$ ) (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

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### 2.1 Sulfur

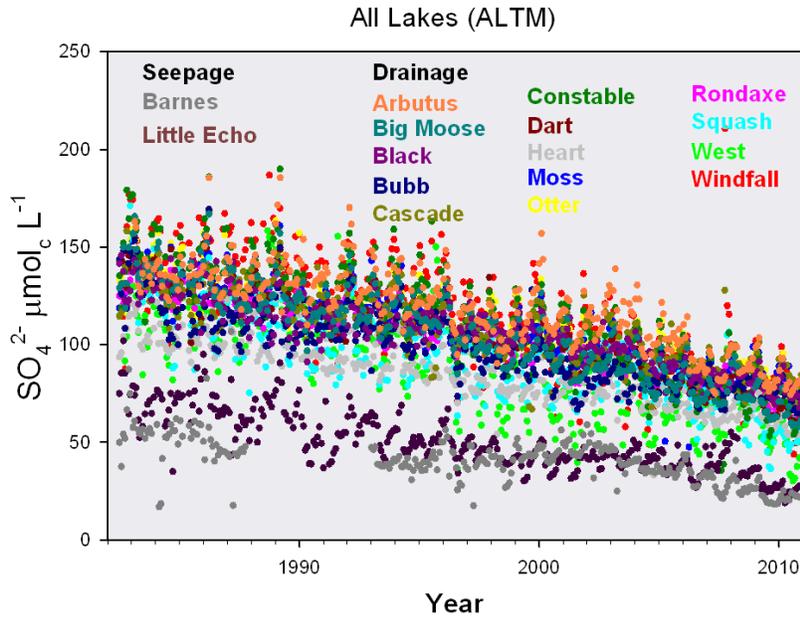
The decrease in the atmospheric emissions of S, and the resultant decrease in both wet and dry deposition, is clearly reflected in decreases in  $\text{SO}_4^{2-}$  concentrations in surface waters. This decrease is shown in the Adirondack Long-Term Monitoring (ALTM) program that originally started with 17 lakes in 1982 to monitor concentrations of major solutes including  $\text{SO}_4^{2-}$  (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  $\text{SO}_4^{2-}$  concentrations (Figure 6). Although there has been a decline in  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  desorption). The relative amount of internal  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  source can be shown by examining both chemical and isotopic changes over a hydrograph for a storm event (Figure 8). The stream  $\text{SO}_4^{2-}$  concentrations increased with increased discharge at Archer Creek at the HF while the S and O isotope ratios of  $\text{SO}_4^{2-}$  are lower in the middle of the storm suggesting that this  $\text{SO}_4^{2-}$  was derived from reduced sulfide minerals (Mitchell et al. 2006). These studies indicate that the biogeochemical regulation of  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  mobilization to soil, ground, and surface waters are depicted in Figure 9.

**Figure 6. Declines in  $\text{SO}_4^{2-}$  concentrations for 16 (14 drainage and 2 seepage lakes) of the 17 original Adirondack Long-Term Monitoring Lakes (ALTM) from 1984 through 2010**

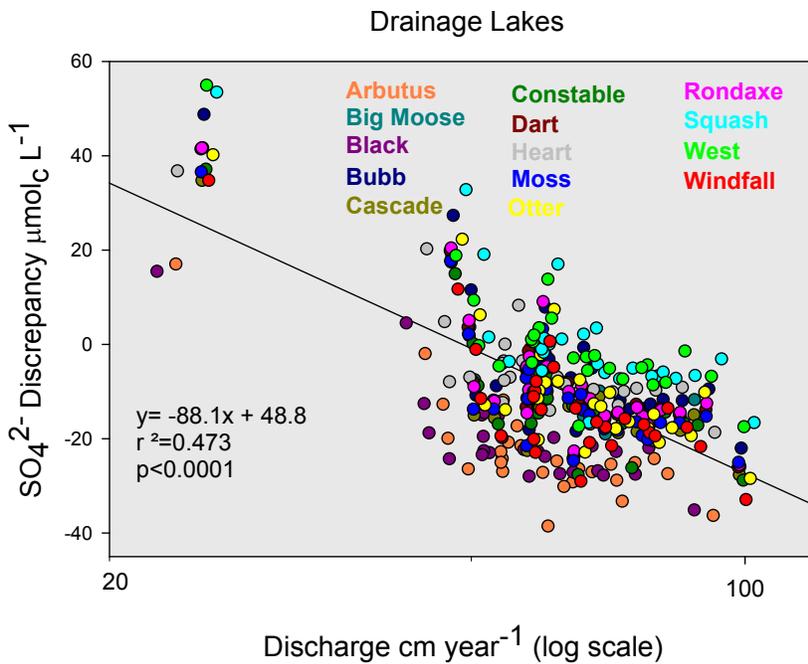
Mean change:  $-2.14 \mu\text{mol}_c \text{L}^{-1} \text{yr}^{-1}$ ;  $p < 0.00001$  for each lake

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**

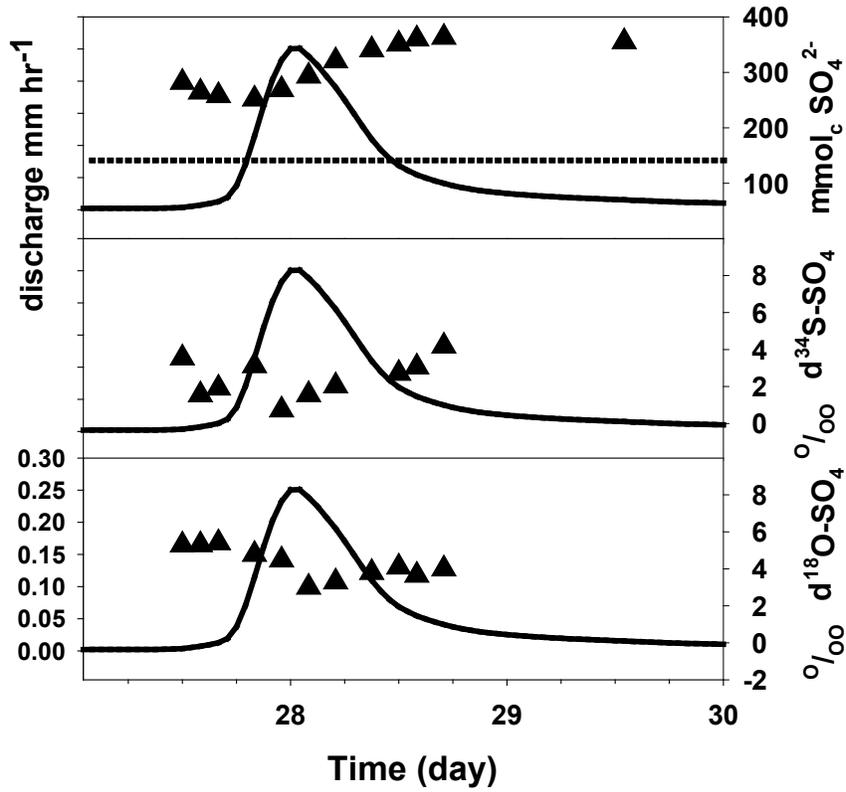
From Mitchell et al. 2013



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

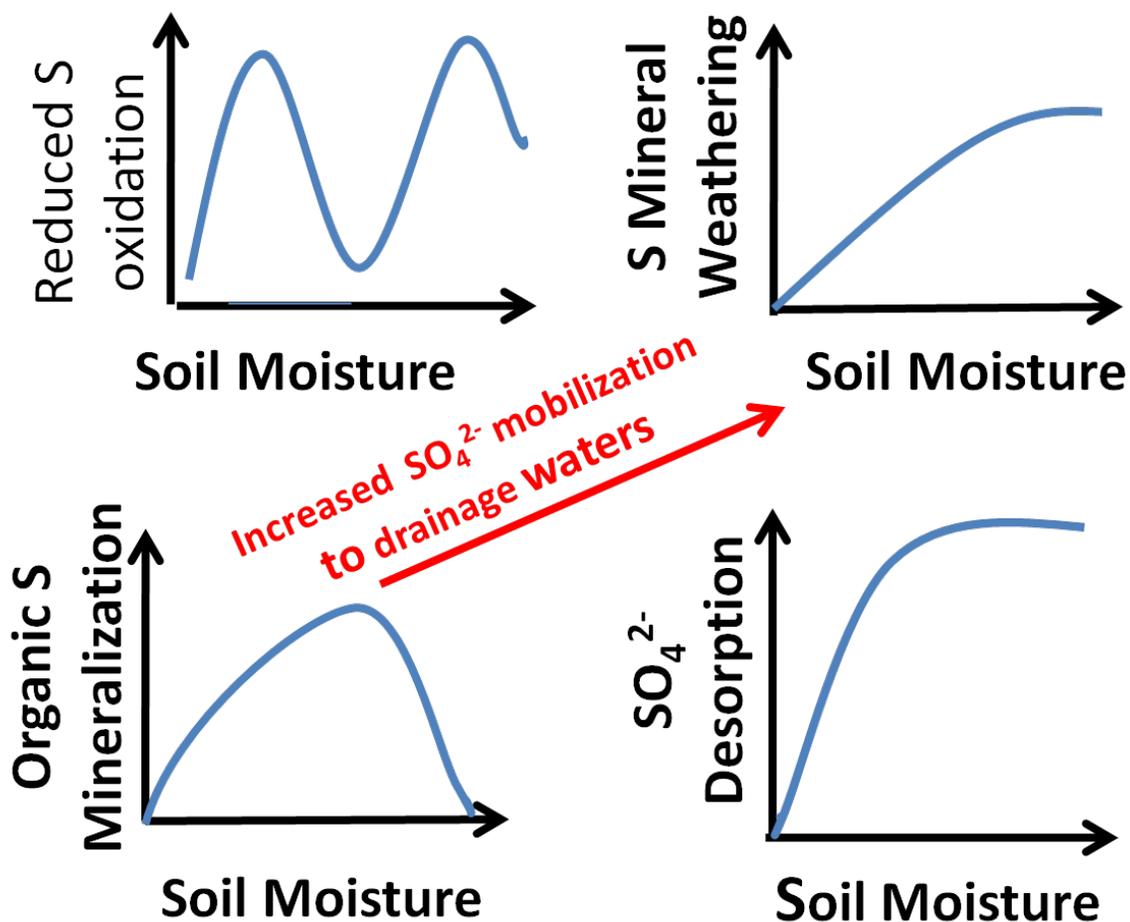
The increase in  $\text{SO}_4^{2-}$  concentration is shown peaking at the greatest discharge being derived from the oxidation of previously reduced sulfide with characteristic lower  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values of  $\text{SO}_4^{2-}$ .

*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  $\text{SO}_4^{2-}$**

Conceptual diagram showing the relationships between water availability and  $\text{SO}_4^{2-}$  generation from various internal S sources in a watershed. All four internal S sources are predicted to show increases in  $\text{SO}_4^{2-}$  mobilization with greater water availability as predicted with climate change in the Northeast US. Most cases show a monotonic increase in  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  concentrations have become lower and  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  concentrations in October to December were excellent predictors of January to May  $\text{NO}_3^-$  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  $\text{NO}_3^-$  concentrations**

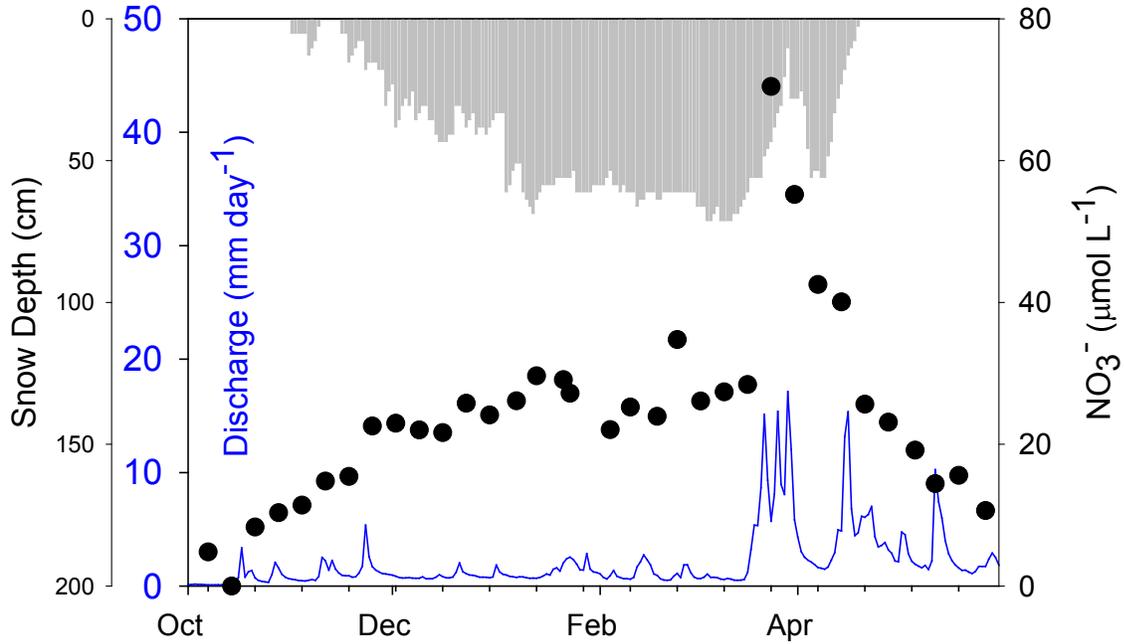
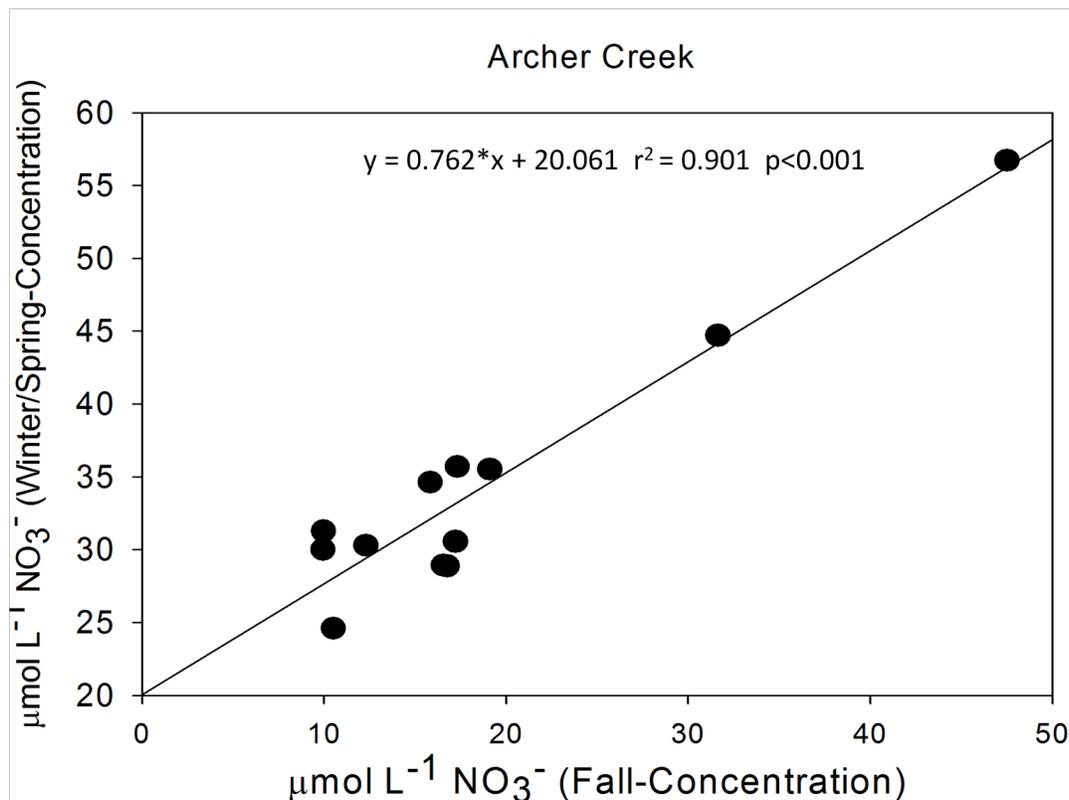


Figure 11. Relationship between annual winter/spring  $\text{NO}_3^-$  concentrations and fall  $\text{NO}_3^-$  concentrations at Archer Creek



One of the most intriguing questions of watershed N dynamics is what is regulating the long-term temporal patterns in  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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

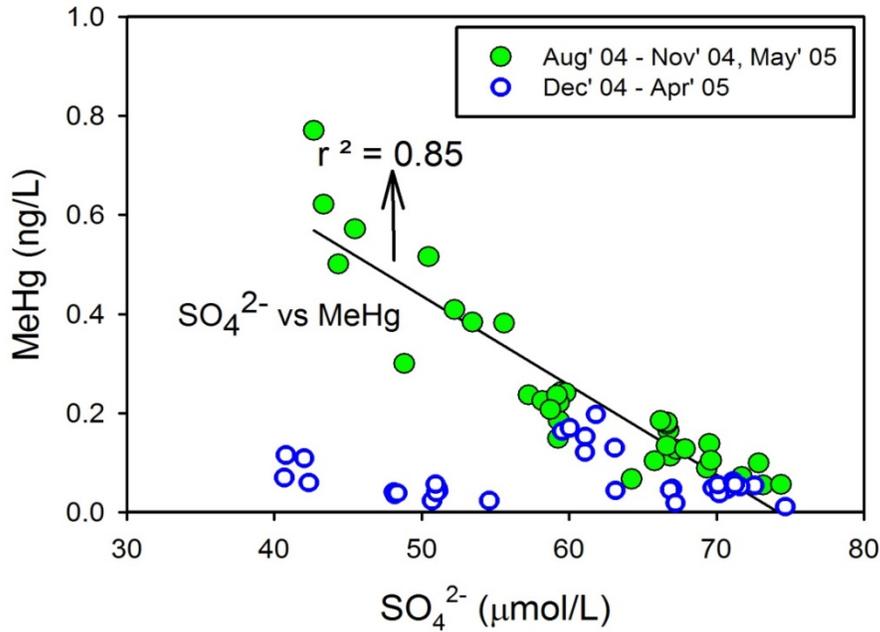
increased during late spring with the onset of warmer temperatures and peaked during summer. Concentrations of MeHg increased almost three-fold in the wetland streams from 0.1 ng/L during the non-growing season to 0.3 ng/L during the growing season. Comparatively, MeHg concentrations in upland stream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

Wetland stream water  $\text{SO}_4^{2-}$  concentrations were consistently lower than upland streams, indicating reducing conditions and  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  concentrations was consistent with the observation of higher MeHg concentrations draining wetlands during summer months (Figure 12). Note that low  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$ . A significant negative relationship existed between MeHg and  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  concentrations during the growing season in wetlands is often attributed to dissimilatory  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  concentrations and MeHg concentrations as a function of season (growing versus dormant) at Archer Creek**

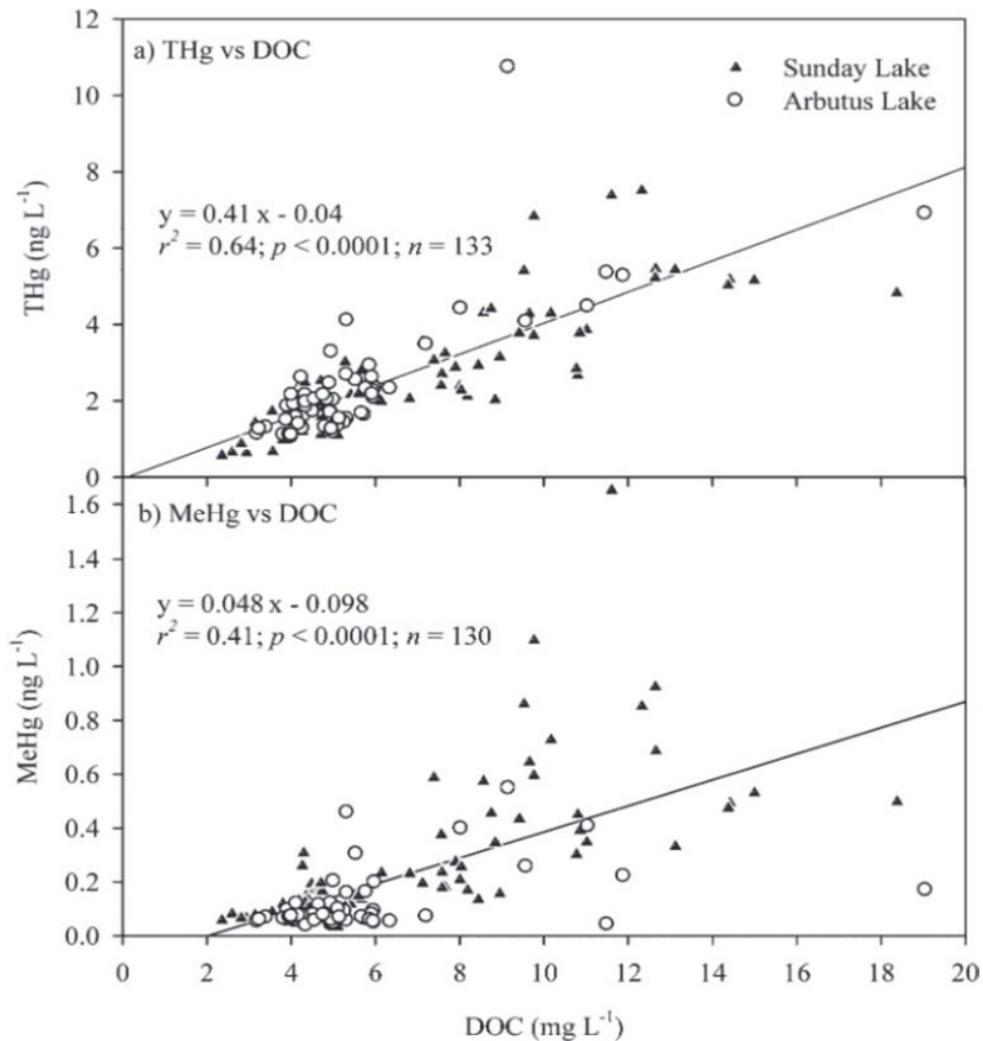
*Data from Selvendiran et al. 2008.*



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

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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).

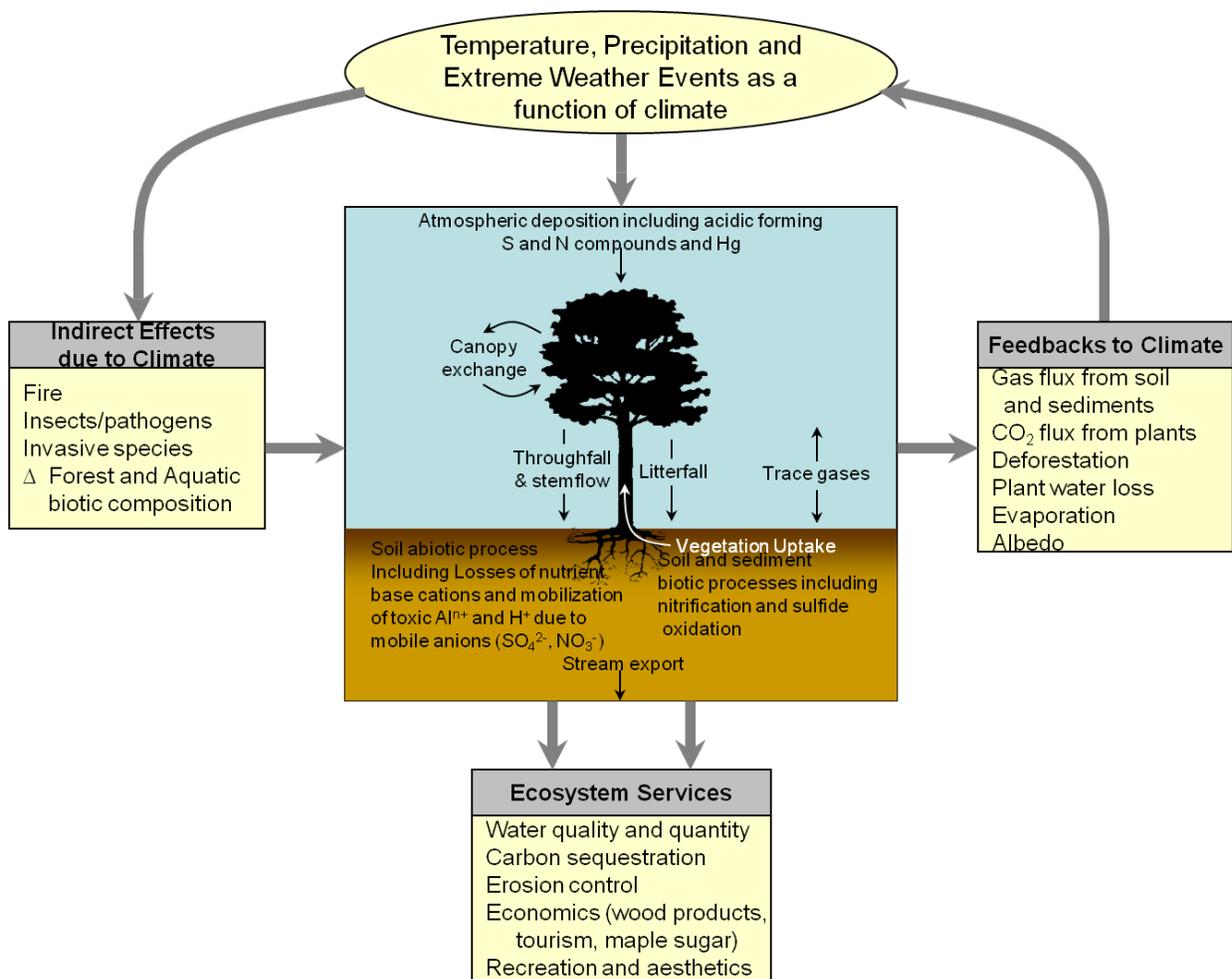
Along with work by other investigators in the Adirondacks, our study has suggested that the inputs of acidic deposition (especially S) have shown marked decreases, and chemical recovery of surface waters has been quantified with increases in ANC. The chemical recovery of soils, however, is going to be 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  $\text{SO}_4^{2-}$  (Figure 9) and  $\text{NO}_3^-$  (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.*



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