

## INFLUENCE OF CLIMATE ON LONG-TERM RECOVERY OF ADIRONDACK MOUNTAIN LAKEWATER CHEMISTRY FROM ATMOSPHERIC DEPOSITION OF SULFUR AND NITROGEN

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**ACKNOWLEDGMENTS:** *This research was supported by the New York State Energy Research and Development Authority (NYSERDA) through a contract with E&S Environmental Chemistry and conducted under the direction of Greg Lampman. This manuscript has not been reviewed by NYSERDA and no official endorsement is implied.*

### KEYWORDS

*Lakewater chemistry, climate, atmospheric deposition, acidification recovery, Adirondack Mountains*

### ABSTRACT

In this study, we assessed temporal patterns and long-term trends in nitrate ( $\text{NO}_3^-$ ), two forms of aluminum (inorganic,  $\text{Al}_i$ , and organic,  $\text{Al}_o$ ), and dissolved organic carbon (DOC) concentrations in the water of 29 Adirondack Mountain, New York lakes, and the potential effects of ambient weather conditions (i.e., climatic variation) on these patterns and trends.

CLOUDS LIT BY PRE-DAWN LIGHT REFLECTED IN OTTER BAY, RAQUETTE LAKE, HAMILTON CO., ADIRONDACK PARK & FOREST PRESERVE, NY

Long-term trends of decreasing lakewater  $\text{NO}_3^-$  and  $\text{Al}_i$  concentrations and increasing DOC were observed for all seasons and lakes. A model selection exercise identified a suite of climatic variables that were most consistently associated with interannual variability and long-term patterns in lake chemistry, in addition to deposition of N (which influences lake  $\text{NO}_3^-$ ) and S (which more strongly influences lake  $\text{Al}_i$  and DOC). These included the last date of recorded snowpack, maximum depth of late season snowpack, date of maximum snow depth, and seasonal average maximum air temperature. Although the presence of long-term trends is clear, there was also much variation within and among lakes and across seasons. Multiple regression modeling that included deposition and climate metrics failed to explain the majority of the observed variation in lake  $\text{NO}_3^-$  for many of the study lakes, while DOC and  $\text{Al}_i$  models were slightly more predictive. We conclude that climatic variation likely shapes temporal patterns and trends in lake chemistry in the Adirondacks, but further analysis is needed to tease apart causal factors and their interactions. Regardless, assessments of surface water chemical recovery from prior acidification in the Adirondack Mountains and elsewhere should consider aspects of climate.

## INTRODUCTION

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Lakes and streams in the Adirondack Mountains, New York are highly sensitive to, and affected by, water acidification caused by atmospheric deposition of acidifying sulfur (S) and nitrogen (N) compounds (Driscoll et al. 2001, Driscoll et al. 2003a, Lawrence et al. 2008, Lawrence et al. 2011). Atmospheric S and N deposition (collectively acidic deposition) in the Adirondack region increased throughout much of the twentieth century, reaching peak values during the 1970s to 1990s (Sullivan 2015). Since that time, acidic deposition has declined substantially.

Decreasing atmospheric deposition of S and N over the past two to three decades in the Adirondack Mountains, in response to rules and legislation pertaining to emissions controls, has contributed to partial chemical recovery of previously acidified lakes. In some cases, biological recovery of Adirondack lakes also has been documented (Sutherland et al. 2015). However, some lakes still are acidified, especially during periods of high precipitation and snowmelt (Civerolo et al. 2011, Lawrence et al. 2013). Coincident with chemical recovery, as reflected in increases in measured acid neutralizing capacity (ANC) and pH, dissolved organic carbon (DOC) also has increased. This has been attributed to increased solubility of DOC with higher pH and perhaps to changes in carbon (C) dynamics associated with warming climate (Fenner and Freeman 2011, Lawrence et al. 2013).

In addition to the well-established effects of atmospheric S and N deposition on lakewater acid-base chemistry, aspects of climate also affect the chemistry of lakes and streams (Eimers et al. 2004, Evans 2005). However, relatively little work has been done to evaluate the ways in which climatic controls on lakewater chemistry interact with lakewater recovery from acidification. Effects of climate on water quality are important areas of research, given the likelihood and magnitude of expected future regional and global climate change (Intergovernmental Panel on Climate Change [IPCC] 2007, Kernan et al. 2010).

Increased variability is projected to be an important part of climate change. This enhanced climatic variability may increase storm intensity and alter runoff patterns (Karl et al. 2009), both of which will affect the leaching of  $\text{NO}_3^-$ , DOC, and Al (Baron et al. 2013). Intra- and inter-annual variation in climate-related variables and long-term changes in climate can have substantial effects on the acid-base and nutrient dynamics of soils and surface waters. Soil and air temperature, precipitation amounts and patterns, and snowpack development and melting all influence key biogeochemical processes and cycles (Sullivan 2015). Acid- and nutrient-sensitive terrestrial and aquatic receptors are expected to respond to climatic factors. These responses can complicate interpretation of acidification or chemical recovery in response to changing levels of acidic atmospheric deposition, but are seldom explicitly considered in assessments of acidification/recovery of surface waters or soils.

Climate warming and associated change in evapotranspiration and moisture availability affect a host of biogeochemical processes and cycles. These include weathering, mineralization, and nitrification (Dalias et al. 2002, Campbell et al. 2009, Wu and Driscoll 2010). Air temperature has a large influence on snowpack development, snowmelt hydrology, and soil freeze-thaw cycles. The snowpack influences winter soil temperature and availability of water for runoff throughout the early portion of the growing season. Burns et al. (2007) and Hodgkins and Dudley (2006) documented earlier snowmelt in the northeastern United States in recent years. There apparently also has been an increase in winter rain (Hodgkins et al. 2003, Huntington 2003) and an increase in large rainstorms (Murdoch et al. 2000). Climate model predictions suggest, on average, the likelihood of a future reduction in snowfall, a smaller snowpack, and a lesser role for snowmelt in the hydrologic cycle of north temperate regions such as are found in northern New York (Burns et al. 2007, Intergovernmental Panel on Climate Change (IPCC) 2007). Diminished snowpack and earlier snowmelt would be expected to decrease stream flow and increase surface water temperature during summer, with potential impacts on cold-water fish (Mohseni et al. 2003). Reductions in snowpack also can enhance soil freezing (Tierney et al. 2001, Brown and DeGaetano 2011, Burns et al. 2011, Campbell et al. 2014), and fine root damage, with consequent increase in  $\text{NO}_3^-$  leaching (Fitzhugh et al. 2003). Other mechanisms, in addition to decreased snowpack, can further decrease stream flow. For example, increased evapotranspiration associated with a warming climate decreased annual runoff by an estimated 11% to 13% in a mountainous basin in New England (Huntington 2003).

Projected effects of ongoing and future climate change include increased magnitude and frequency of extreme weather-related events, such as drought and flood, with likely more substantial effects of extreme events on future ecosystem biogeochemistry as compared with anticipated changes in average conditions (Dale et al. 2001, Jentsch et al. 2007). Acid-sensitive surface waters in New York may experience more pronounced episodes of acidification driven by large rain events, including those preceded by drought.



Throughout most of the year, the main cause of acidification of most acid-sensitive Adirondack Mountain streams and lakes is S (Sullivan et al. 1997). At the peak of spring snowmelt, however, the  $\text{NO}_3^-$  concentration can be nearly as high or just as high as the sulfate ( $\text{SO}_4^{2-}$ ) concentration (Sullivan et al. 1997). The seasonal shift in the relative importance of S and N as drivers of surface water acidity is likely related to the seasonal dynamics of plant and microbial growth and hydrological cycles associated with snowpack accumulation and melting.

Change over time in the amount of organic acidity also complicates evaluation of surface water recovery from acidification. Concentrations of DOC generally have increased over the past 10 to 15 years (Driscoll et al. 2003b, Evans et al. 2006, Monteith et al. 2007). This is likely a response to both decreased acidic deposition and changing climate (Hudson et al. 2003, Evans et al. 2006, Monteith et al. 2007, Worall and Burt 2007, Clair et al. 2008, Burns et al. 2011, Clair et al. 2011). These changes in DOC are important because DOC plays important roles in a variety of ecosystem processes, including episodic acidification, Al toxicity, mercury (Hg) methylation and transport, light penetration into the water column, water temperature, and lakewater stratification (Snucins and Gunn 2000). In addition, increased DOC and associated strong organic acid anions limit the ANC recovery of acidified surface waters (Lawrence et al. 2007).

Lakewater monitoring data collected within the Adirondack Long Term Monitoring (ALTM) (Civerolo et al. 2011) program provide an opportunity to investigate lakewater acidification, recovery, and their interactions with climate. The goal of this study was to use these monitoring data to investigate linkages among climate-related variables and the chemical recovery of acidified Adirondack lakes. The focus was on changes in the concentrations of  $\text{NO}_3^-$ , DOC, and Al, especially during the spring season. These parameters are known to be climate-sensitive and collectively exert substantial control on the toxicity of runoff chemistry to fish and other aquatic life (Lawrence et al. 2013, Fuss et al. 2015, Durán et al. 2016). We analyzed the chemistry reflected in long term monitoring data collected in the ALTM program over a 20-year period. Analyses were considered in the context of trends, and associated residuals, in water chemistry in response to changes in N and S deposition, with an effort to isolate climatic effects from those caused by changes in acidic deposition.

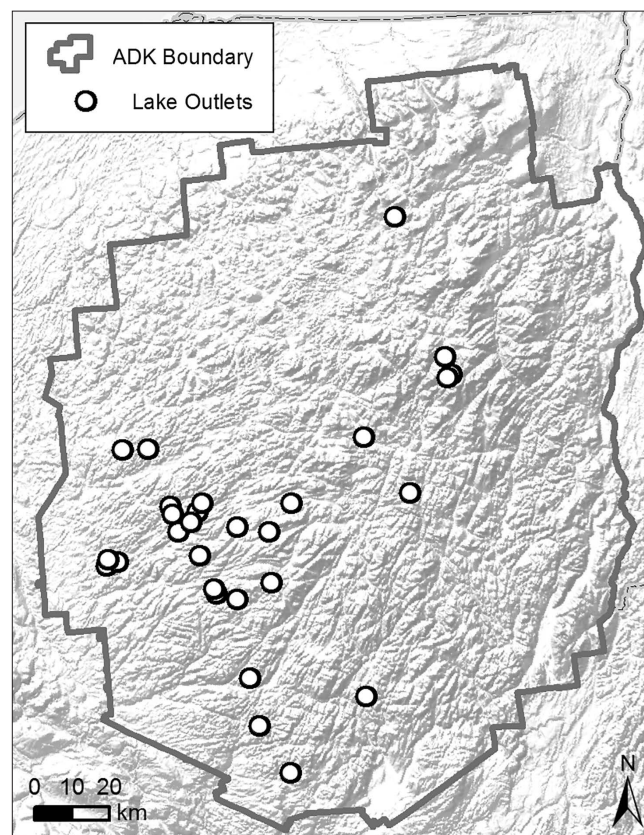
## METHODS

### Lake Selection

During the two-decade study period (1993 to 2012), the ALTM monitored the chemistry of 52 Adirondack lakes. Water samples were collected approximately monthly and analyzed for major ion chemistry (Civerolo et al. 2011). A subset of the monitored lakes was selected for inclusion in the study reported here. In an attempt to develop a set of relatively homogenous sites, lakes were removed from consideration for this study from the full set of 52 ALTM lakes if they exhibited any of the following characteristics:

- Seepage hydrologic type
- Thick till watershed
- Influenced by carbonate geology
- History of liming
- Significant amount of shoreline development
- Watershed area greater than 100 km<sup>2</sup>
- Watershed contains another nested study lake

Analyses presented here primarily relied on data from 29 ALTM lakes that remained after screening using the above criteria (Figure 1). This allowed focus on a subset of the more acid-sensitive, thin-tilled drainage lakes in the study region that had not been strongly affected by human disturbance within the respective watersheds (cf., Driscoll et al. 1991). Lake names and locations are given in the Appendix, A1.



**Figure 1.** Lake locations. Geographical coordinates are given in Table A1-1. Base Layer Credits: Environmental Systems Research Institute, U.S. Geological Survey, and National Oceanographic and Atmospheric Administration.

## Lakewater Chemistry

Lakewater chemistry results for Al ( $Al_i$  and organic monomeric Al [ $Al_o$ ]), DOC, and dissolved  $NO_3^-$  were obtained from the Adirondack Lakes Survey Corporation's (ALSC) ALTM database. Available monthly samples from December 1992 through December 2012 were used for analyses that are reported here.

## Climate Data

Monthly estimates of precipitation and air temperature for the period December 1992 through December 2012 were obtained from the PRISM database (Daly et al. 2008) to represent climatic conditions during this 20-year period. Total monthly precipitation (ppt), minimum daily temperature (tmin), maximum daily temperature (tmax), and mean daily temperature (tmean; (tmin + tmax)/2) were attributed to each study lake as an average of all 30 arc-second (~800 m) grid cells contained within the associated watershed.

Data collected by the Northeast Regional Climate Center (NRCC) were used to characterize annual winter snowpack development and the timing of snowmelt. Two NRCC sites located within the Adirondack Park boundary were used to assign an NRCC site to each study watershed based on a nearest neighbor approach. Snow-related metrics derived from the NRCC data included maximum late season snowpack, day of year of maximum late season snowpack, day of year of last recorded snowpack, and number of days between maximum late season snowpack and last date of recorded snowpack.

## N and S Deposition

Seasonal precipitation-weighted mean inorganic N and sulfate ( $SO_4^{2-}$ ) precipitation concentration data for the years 1993 to 2012 were obtained from National Atmospheric Deposition Program/National Trends Network (NADP/NTN) measurements at Huntington Forest in the Adirondack Mountains (Site NY20). Measured data summarized by season at Huntington Forest were required to have valid samples for at least 60% of the summary period for inclusion in this analysis. An average of the two most recent seasons of data was used to interpolate for one season (the winter of 1994) because of low data completeness. Seasonal S and N wet deposition estimates were determined by multiplying the seasonal precipitation-weighted mean inorganic N (both oxidized and reduced forms) and  $SO_4^{2-}$  concentrations by seasonal PRISM precipitation totals calculated as the watershed average for each lake. Dry deposition is less certain and was not considered. Estimates by Schwede and Lear (2014) suggest that the ratios of dry to total N and S deposition may have decreased in recent years.

## Data Analysis

Average seasonal  $NO_3^-$ ,  $Al_i$ , and DOC concentrations in lakewater and the ratio between  $Al_i$  and  $Al_o$  provided the basis for analysis of long-term trends and inter-annual variation in water chemistry shown here. Seasons were defined as, winter: December-February, spring: March-May, summer: June-August, fall: September-November. For each study lake, trends in seasonal lakewater chemistry over the period 1993 to 2012 were determined using the Mann-Kendall test and Theil-Sen's slope estimator. Theil-Sen slopes were considered to be significant at  $p < 0.1$ .

**Table 1.** Variables available for building regression models used to predict seasonal Adirondack lake chemistry.

PREDICTOR
Atmospheric N Deposition
Atmospheric S Deposition <sup>a</sup>
Precipitation N Concentration
Precipitation $SO_4^{2-}$ Concentration <sup>b</sup>
Precipitation Amount
Average Maximum Temperature
Last Date of Recorded Snowpack
Max Depth of Late Season Snowpack
Day of Maximum Snow Depth
Days from Maximum Snow to Last Date of Recorded Snowpack

- a. Atmospheric S deposition not used for  $NO_3^-$  predictions  
 b. Precipitation  $SO_4^{2-}$  concentration not used for  $NO_3^-$  predictions

Two sets of multiple regression models were developed to predict seasonal  $NO_3^-$ ,  $Al_i$ ,  $Al_i:Al_o$ , and DOC concentrations and their residual values for each lake. The two sets of predictor variables used in this analysis were: 1) seasonal N and/or seasonal S deposition (predictor set 1); and 2) seasonal climate-related variables (including timing of snowpack development, average seasonal maximum temperature and total seasonal precipitation) and seasonal N and S concentrations in precipitation (predictor set 2; Table 1). Models were derived from stepwise linear regression to converge on a "best" model based on lowest Akaike Information Criterion (step AIC) (Venables and Ripley 2002). This resulted in a total of 928 models derived from 4 response variables, 2 sets of predictors, 4 seasons, and 29 study lakes. This matrix provided the basis for developing an improved understanding of how aspects of climatic variability may influence Adirondack lake chemistry along with the well-known effects associated with changing levels of atmospheric N and S deposition. Although many models were generated, only two models (based on predictor sets 1 and 2 described above) were established and compared for a given response variable, season, and study lake. These models were compared to determine the extent to which climate-related variables (included in predictor set 2) were

able to further explain the variation in lake chemistry response over the 20-year monitoring period, beyond what was possible using deposition variables alone (predictor set 1). The  $r^2$  statistic was used for the comparison instead of AIC because 1) the requirement of AIC improvement was inherent to the step AIC process used for model selection, and 2) values of  $r^2$  can be useful for describing the magnitude of variance explained. Building individual lake models allowed us to evaluate the consistency with which a given climate variable was (or was not) selected during the stepwise process. This provided an indication of the transferability of results to other lakes with similar characteristics to those included in this study.

Individual lake and watershed characteristics were extracted from the ALTM lake characteristics database (Nathan Houck, ALSC, personal communication, June 2014) and were used where possible to explain lake-to-lake differences in model fit. These attributes included lake elevation, maximum lake depth, mean lake depth, lake volume, lake surface area (SA), watershed area (WA), SA:WA ratio, and lake retention time. Such variables might correlate with watershed sensitivity to acidification (Sullivan 2015).

Trends in lake chemistry were evaluated for the full set of study lakes and for two subsets of lakes that were grouped according to reference period (average of the period 1993 to 1995) lakewater chemistry. These subsets were labeled “low” or “high” based on having values below or above the median seasonal reference period chemistry given in Table 2. For each of the 29 study lakes, trends in water chemistry between 1993 and 2012 were detrended as described in the Appendix, A2. These analyses reflected inter-annual differences in water chemistry that might be attributable to climate variation.

**Table 2.** Thresholds for designation of high/low lakewater median chemistry values ( $\mu\text{mol/L}$ ) based on the median seasonal average over the period 1993-1995.

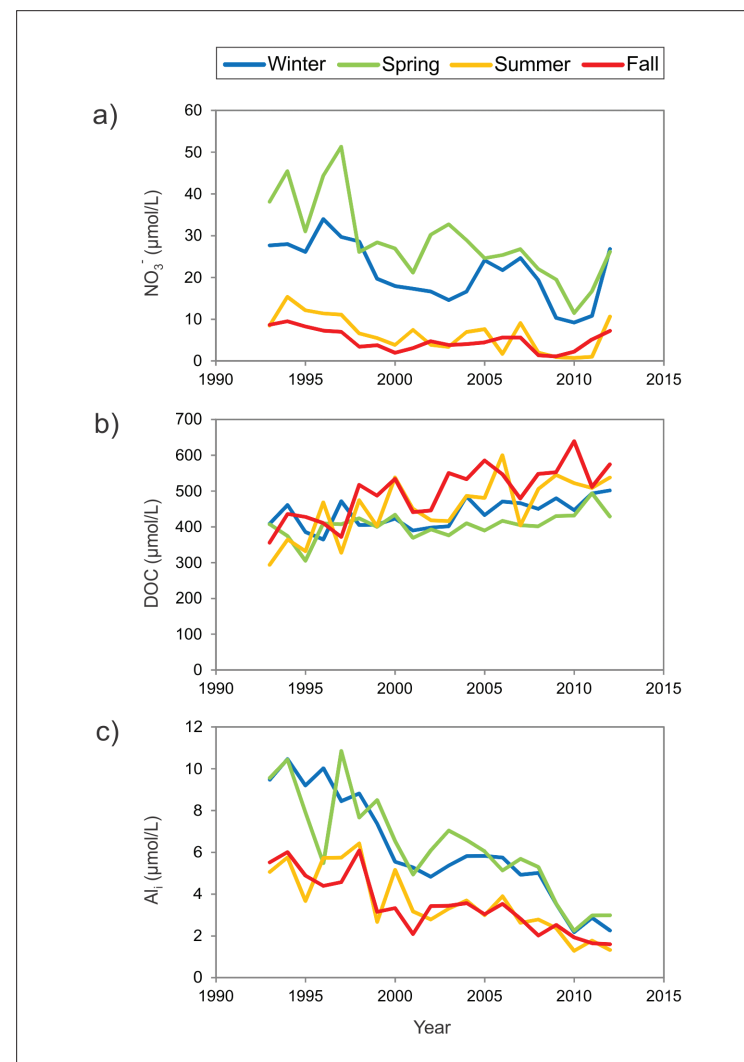
SEASON	$\text{NO}_3^-$	DOC	$\text{Al}_i$	$\text{Al}_o$
Winter	18	357	4.5	2.6
Spring	28	304	4.9	2.7
Summer	8	319	1.5	1.7
Fall	5	351	1.3	1.8

## RESULTS AND DISCUSSION

### Long-Term Lake Chemistry Trends

The 10 most acid-sensitive lakes in the study, as reflected in measured ANC, showed strong patterns of decreasing  $\text{NO}_3^-$  and  $\text{Al}_i$  concentrations and increasing DOC concentrations over time during all seasons (Figure 2). Comparable analyses for the 10 lakes having highest ANC showed smaller changes and generally lower concentrations (data not shown).

**Figure 2.** Lakewater monitoring mean annual results for a)  $\text{NO}_3^-$ , b) DOC, and c)  $\text{Al}_i$  concentrations over time, by season, for the 10 study lakes having lowest ANC.



Most study lakes showed changes over time in the concentrations of  $\text{NO}_3^-$ , DOC, and  $\text{Al}_i$  and in the ratio of  $\text{Al}_i$  to  $\text{Al}_o$ . Many of these trends were statistically significant, as summarized in Table 3. In general,  $\text{NO}_3^-$  and  $\text{Al}_i$  concentrations decreased, DOC increased, and the ratio of  $\text{Al}_i$ : $\text{Al}_o$  decreased during the study period. Increases in DOC and  $\text{Al}_o$  and decreases in  $\text{Al}_i$  and  $\text{NO}_3^-$  concentrations have been shown for many Adirondack lakes in previous studies (Driscoll et al. 2003b, Lawrence et al. 2013).

**Table 3.** Number of lakes (n=29) that showed a significant or non-significant seasonal increase/decrease in  $\text{NO}_3^-$ , DOC,  $\text{Al}_i$ , or  $\text{Al}_i:\text{Al}_o$  during the period 1993 to 2012 according to Theil-Sen slope. One lake showed no trend in  $\text{Al}_i:\text{Al}_o$  during the winter season. It is not represented in this summary of trends.

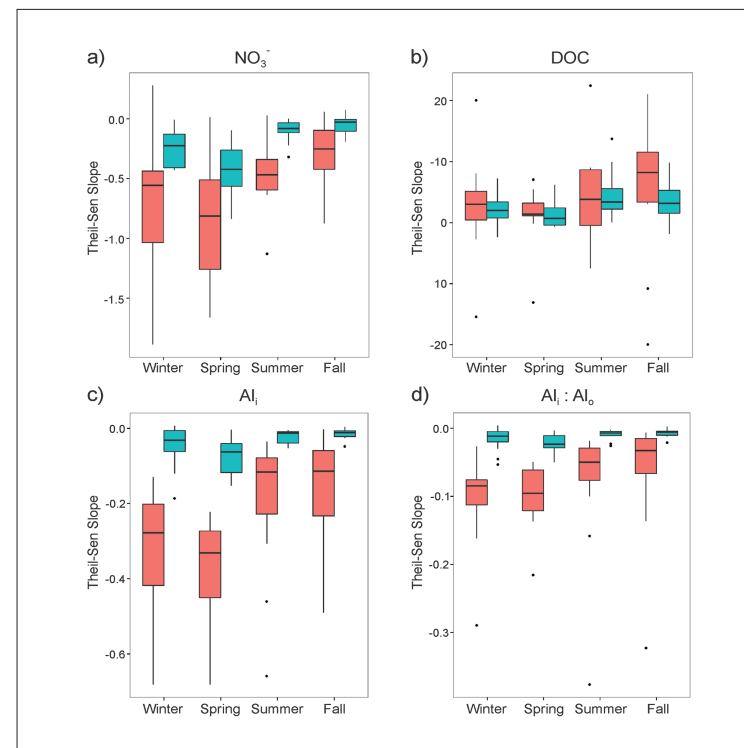
PARAMETER	TREND	SIGNIFICANCE (P < 0.05)	SEASON			
			WINTER	SPRING	SUMMER	FALL
$\text{NO}_3^-$	Increase	Significant	0	0	0	0
		Non-significant	1	1	2	4
	Decrease	Significant	13	15	13	11
		Non-significant	15	13	14	14
DOC	Increase	Significant	10	8	11	18
		Non-significant	12	14	14	7
	Decrease	Significant	2	1	0	2
		Non-significant	5	6	4	2
$\text{Al}_i$	Increase	Significant	0	0	0	0
		Non-significant	1	0	0	1
	Decrease	Significant	19	26	21	21
		Non-significant	9	3	8	7
$\text{Al}_i:\text{Al}_o$	Increase	Significant	0	0	0	0
		Non-significant	1	0	0	1
	Decrease	Significant	19	23	19	22
		Non-significant	8	6	10	6

Median seasonal lake  $\text{NO}_3^-$  concentrations during the reference period (1993-1995) were highest during spring (28  $\mu\text{mol/L}$ ) and winter (18  $\mu\text{mol/L}$ ) and lowest (8 and 5  $\mu\text{mol/L}$ ) during summer and fall, respectively (Table 2). Seasonal lake  $\text{NO}_3^-$  concentrations during the period 1993 to 2012 showed decreasing trends for nearly all lakes (Figure 3a). Negative trends in  $\text{NO}_3^-$  concentration were largest during spring and smallest during fall. The median lake  $\text{NO}_3^-$  concentration during spring decreased by one-third during the study period. The  $\text{NO}_3^-$  concentrations decreased more rapidly for lakes that had relatively high reference period  $\text{NO}_3^-$  concentration as compared with lakes having relatively low reference period  $\text{NO}_3^-$  concentration. Low  $\text{NO}_3^-$  values during fall might be attributable, at least in part, to heterotrophic N uptake in response to litterfall (Goodale et al. 2009).

Seasonal lake DOC concentrations changed from the reference period to 2012, showing increasing trends for most study lakes (Figure 3b). There were only slight differences in the rate of increase over time among lakes that had relatively high reference period DOC concentration as compared with lakes that had relatively low reference period DOC concentration.

Nearly all trends in seasonal lake  $\text{Al}_i$  concentration showed decreases from the reference period during the study (Figure 3c). Decreasing trends were larger for lakes that had relatively high reference period  $\text{Al}_i$  concentration as compared with lakes having relatively low reference period  $\text{Al}_i$  concentration.

**Figure 3.** Seasonal trends (Theil-Sen slope) in the lakewater concentrations of a)  $\text{NO}_3^-$ , b) DOC, c)  $\text{Al}_i$  and d) the  $\text{Al}_i$  to  $\text{Al}_o$  ratio over the period of study. Results for lakes with “low” reference period concentration are coded blue; results for “high” reference period concentration are coded red. Positive values indicate increasing trends; negative values indicate decreasing trends. Values of the Theil-Sen slope reflect the magnitudes of the trends over time.



Nearly all trends in the seasonal  $\text{Al}_i:\text{Al}_o$  concentration ratios showed decreases from the reference period (Figure 3d). Thus,  $\text{Al}_i$  concentration decreased over time in these lakes to constitute a lesser percentage of the total monomeric Al. Decreasing trends were larger for lakes with relatively high initial  $\text{Al}_i:\text{Al}_o$  as compared with lakes having relatively low initial  $\text{Al}_i:\text{Al}_o$ . These patterns reflect a marked decrease over time in the likely toxicity of Al to aquatic biota in these lakes.

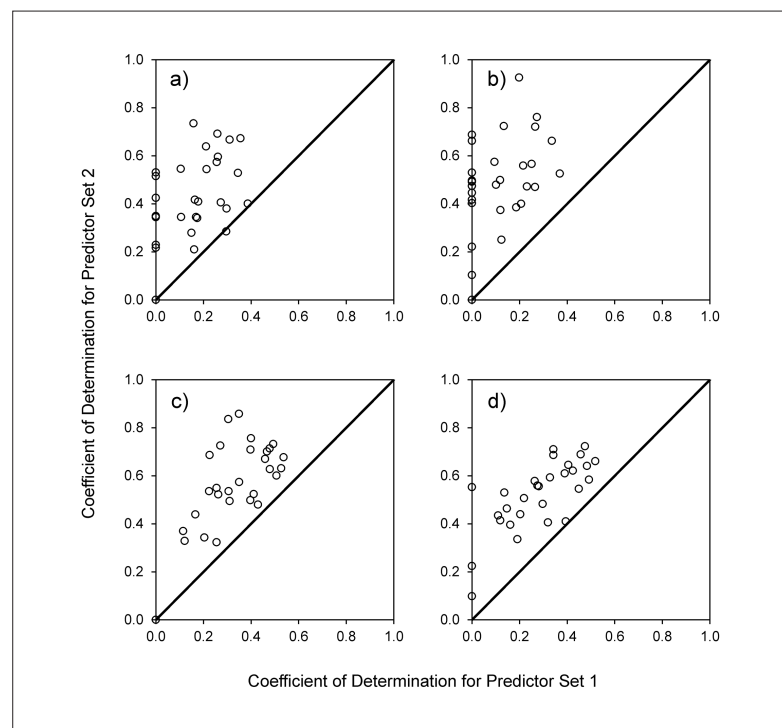
### PREDICTING SEASONAL LAKE $\text{NO}_3^-$ CONCENTRATION

Models poorly predicted  $\text{NO}_3^-$  concentration based on N deposition (predictor set 1), although explanatory power was slightly higher for the spring season. Nitrogen deposition in all cases was positively related to lake  $\text{NO}_3^-$  concentration across the period of study. Models that included climate-related variables predictor set 2) had marginally higher explanatory power, but these models typically left about half of the seasonal variance in lake  $\text{NO}_3^-$



unexplained (Figure 4). The concentration of N in precipitation was selected in 17 of 29 lake models to predict both spring and summer lake  $\text{NO}_3^-$  concentration, whereas fall and winter  $\text{NO}_3^-$  concentrations more often were related to seasonal precipitation amount (Table 4). The climate variables were of varying importance. Average maximum air temperature was included in nearly three-quarters (21 of 29) of the models to predict spring  $\text{NO}_3^-$  concentration, but the timing of late season peak snowpack generally was not a significant predictor of  $\text{NO}_3^-$  concentration, with the exception of the summer season (Table 4). The number of days from late season peak snowpack to last date of recorded snowpack almost never was selected as an important predictor of  $\text{NO}_3^-$  concentration. This finding is perhaps not surprising; analysis of long-term monitoring data from southern Norway that suggested that reduced snowpack, and its effects on soil temperature, can either increase or decrease N leaching, depending on interactions with N deposition, soil freezing, and winter discharge (Stuanes et al. 2008). Although Groffman et al. (2011) showed that snowpack removal and associated soil freezing events during winter can stimulate N leaching, our results suggest that a transition to lower late winter snowpack and warmer spring air temperatures may contribute to lower lakewater  $\text{NO}_3^-$  and  $\text{Al}_i$  concentrations, perhaps due to a reduction in the magnitude of episodic events and increased biological uptake.

**Figure 4.** Relationship between coefficient of determination ( $r^2$ ) derived from predictor set 1 and from predictor set 2 for estimating spring season a)  $\text{NO}_3^-$ , b) DOC, c)  $\text{Al}_i$ , and d) the ratio of  $\text{Al}_i$  to  $\text{Al}_e$ .



**Table 4.** Number of individual lake models based on predictor set 2 that included climate-related variables or precipitation N concentration for predicting seasonal lake  $\text{NO}_3^-$  concentration over the period 1993 to 2012.

SEASON	LAST DATE OF RECORDED SNOWPACK	MAXIMUM DEPTH OF LATE SEASON SNOWPACK	DAY OF MAXIMUM SNOW DEPTH	DAYS FROM MAXIMUM SNOW TO LAST DATE OF RECORDED SNOWPACK	SEASONAL PRECIP N CONCENTRATION	SEASONAL PRECIP AMOUNT	SEASONAL AVERAGE MAXIMUM AIR TEMP	NONE OF THE VARIABLES WERE SELECTED
Fall	10	5	2	-	9	20	16	2
Spring	8	6	6	2	17	6	21	1
Summer	16	15	10	-	17	9	10	4
Winter	6	6	6	-	9	21	7	4

Potential effects of time lags on the deposition terms were investigated for predicting lake  $\text{NO}_3^-$  concentration. These generally did not improve model fits (Appendix, A3). Fuss et al. (2015) found similarity between whole-year trends (1982-2011) in stream ANC and year-to-year trends during the snowmelt season at Hubbard Brook Experimental Forest (HBEF) in New Hampshire, demonstrating consistency between recovery from chronic acidification during base flow and abatement of acidification during snowmelt. Nevertheless,  $\text{NO}_3^-$  concentrations declined more rapidly across the study period during the snowmelt season compared with the whole-year trend in  $\text{NO}_3^-$  concentration. Fuss et al. (2015) attributed this observation to the observed decrease in  $\text{NO}_3^-$  deposition during the monitoring period.

#### SIGNS OF CLIMATE VARIABLES SELECTED FOR THE FULL $\text{NO}_3^-$ MODEL (PREDICTOR SET 2)

Despite the limited improvement in predictive ability, the signs of the coefficients in  $\text{NO}_3^-$  models for individual lakes suggested potential effects of weather and climatic variability in regulating lake  $\text{NO}_3^-$  concentrations. Nearly all non-winter models (32 of 34) that selected last date of recorded snowpack showed a positive relationship between last date of recorded snowpack and lake  $\text{NO}_3^-$  concentration. This suggests that longer snow seasons may have resulted in higher lake  $\text{NO}_3^-$  concentrations during the subsequent spring, summer, and fall seasons. Relatively low-elevation study plots at HBEF that showed less snow, more soil freezing during winter, and more freeze/thaw cycles had lower N mineralization than plots located at higher elevation (Durán et al. 2016). This finding is consistent with analyses showing long-term decreases in N mineralization and inorganic N concentrations in stream water in concert with warming temperature and decreased annual snow accumulation (Bernal et al. 2012, Yanai et al. 2013, Durán et al. 2016).

A longer snow season, and associated shorter growing season, should promote less N uptake by vegetation, with proportionately more  $\text{NO}_3^-$  available for leaching. In contrast, parameter coefficients between maximum late season depth of snowpack and lake  $\text{NO}_3^-$  concentrations were typically negative (24 of 32). The timing of snowmelt may be more important than the depth of the snowpack as an influence on seasonal lake  $\text{NO}_3^-$  concentration. Seasonal

precipitation amount generally showed a positive relationship with lake  $\text{NO}_3^-$  concentration for the same season, perhaps reflecting increased  $\text{NO}_3^-$  flushing through shallow soils. Warmer air temperature generally was negatively related to lake  $\text{NO}_3^-$  concentration for all seasons. This may reflect increased biological uptake within the lakes or tributary watersheds during warmer years.

### PREDICTING SEASONAL LAKE DOC CONCENTRATION

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Inclusion of climate-related variables increased  $r^2$  in about two-thirds (20 of 29) of the individual lake models for each season, often explaining an additional 20% to 30% of the variation in seasonal DOC concentration (Figure 4; Appendix, A4). For the model that included both precipitation concentration of N and  $\text{SO}_4^{2-}$  and climate-related variables (predictor set 2), precipitation, average maximum air temperature, and last date of recorded snowpack were the most frequently selected climate-related variables to predict DOC. Temperature was related positively to DOC concentration for fall and spring season models, but generally (8 of 10 models) was related negatively for the summer season. Last date of recorded snowpack generally (7 of 10 models) was related positively to spring DOC concentration, but negatively related during the other seasons.

Porcal et al. (2009) reviewed the biogeochemistry of DOC and its interactions with climate change. They concluded that increasing temperature and changes in runoff are likely to cause changes in the quality and quantity of DOC export from terrestrial ecosystems to surface waters above and beyond any changes that might be attributable to acidification processes. Increased water temperature will also cause changes in DOC processing in lakewater. Change in lakewater DOC concentration has been shown to impact recovery from acidification. For example, Erlandsson et al. (2010) examined the effects of increasing lake DOC on acidification recovery for 66 lakes in southern Sweden. Study lakes generally were small, had low ANC and previously had been acidified by acidic atmospheric deposition. About 75% of the study lakes showed increased DOC between 1990 and 2008. The increase in DOC retarded pH recovery by 0.13 pH units (median for all lakes) and by more than a full pH unit for individual lakes.

### PREDICTING SEASONAL LAKE $\text{Al}_i$ CONCENTRATION

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Model fits for predicting lake  $\text{Al}_i$  concentration based on predictor set 1 showed that deposition of S was selected as an explanatory predictor in more than 75% of the individual lake models for each season and was always positively correlated with  $\text{Al}_i$ . Deposition of N was selected less often. However, N deposition was a significant predictor in nearly three-quarters of spring models and was always negatively related to  $\text{Al}_i$  for this season. Precipitation amount was a significant predictor for about one-third to one-half of the winter, summer, and fall models developed to predict lake  $\text{Al}_i$  concentration and was always positively related to lake  $\text{Al}_i$  concentration for these seasons.

Inclusion of climate-related variables in addition to N and S concentration in precipitation increased  $r^2$  in the majority of individual lake models for each season, often explaining an

additional 10 – 25% of the variation in seasonal  $\text{Al}_i$  concentration and in the ratio of  $\text{Al}_i$  to  $\text{Al}_o$  (Figure 4; Appendix, A4). For the full model (predictor set 2), precipitation and average maximum air temperature were the most frequently selected climate-related variables. For spring and summer seasons, temperature was negatively related to  $\text{Al}_i$  concentration for all lake models in which it was selected. For fall and winter, temperature was negatively related to  $\text{Al}_i$  concentration for almost all lake models in which it was selected (fall: 14 of 16; winter: 12 of 13).

Snow-related variables were selected for about one-third of the study lakes to predict  $\text{Al}_i$  concentration for most seasons. Relationships between snow-related variables and  $\text{Al}_i$  concentration were mixed (some positive and some negative). One exception was that maximum late season snow depth was positively correlated with spring  $\text{Al}_i$  concentration in all nine of the models in which it was selected.

### CONCLUSIONS

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Acid-sensitive Adirondack study lakes have experienced trends of decreasing concentrations of  $\text{NO}_3^-$  and  $\text{Al}_i$ , and increasing concentrations of DOC across all seasons, over the past two decades. Although such trends and patterns are thought to be consistent with decreasing emissions and deposition of S and N, a considerable amount of year-to-year variation in lake chemistry cannot be explained by deposition patterns alone. At least some of this variance is likely attributable to interannual variability in weather conditions, including seasonal temperature fluctuations and the timing and amounts of rainfall, snowpack, and snowmelt. However, the scale at which we typically measure these basic climatic drivers of watershed processes is much coarser, both spatially and temporally, than the local meteorological conditions that occur in each watershed-lake system. For this reason, and because these factors may interact in complex and path-dependent ways – such as the interplay between spring heat accumulation, rainfall events, and snowpack conditions in determining the timing of snowmelt – their roles as drivers of watershed processes may not be readily captured by statistical models. Instead, simulation models that focus on the temperature and moisture sensitivity of these processes, both in the watershed and in surface waters, and that can incorporate stochastic and/or non-linear dynamics may be better suited to this purpose and may provide better mechanistic understanding as well as prediction of future trends/patterns of surface water chemistry under conditions of a changing climate. Our analyses suggest a suite of specific climatic variables to consider, and raise the question of whether increasing variance in weather conditions, as has been widely observed across northeastern North America, could drive increasing seasonal and interannual variance in watershed processes affecting  $\text{NO}_3^-$ ,  $\text{Al}_i$ , and DOC export, in conjunction with deposition trends. Overall, climate may play an important role in recovery of Adirondack lakewater from past acidification, and such climatic influence on chemical recovery may become more pronounced in the future, as the Adirondack climate changes further and likely becomes warmer, wetter, and more variable. Further study is needed to understand and predict how such climatic changes will interact with deposition and other factors shaping watershed processes and lake water chemistry.



**APPENDIX**

**A1. Study Lakes**

**Table A1-1.** Geographical coordinates used for study lake watershed delineation.

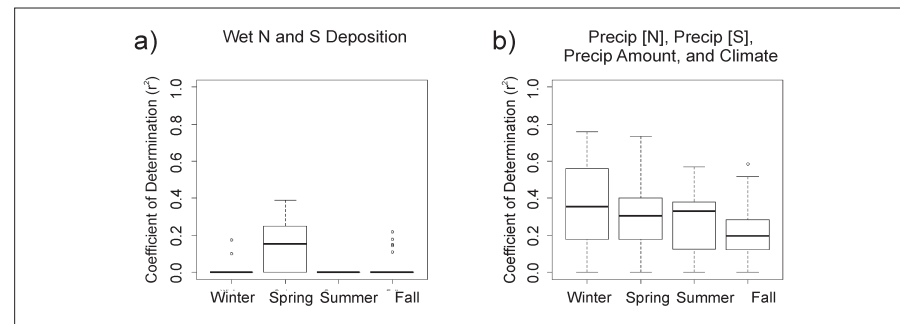
ALSC ID	NAME	LONGITUDE	LATITUDE	AVERAGE CONCENTRATIONS (YEAR 2012)		
				ANC (µEQ/L)	AL <sub>i</sub> (µG/L)	DOC (MG/L)
050684	Arbutus Lake	-74.235372	43.982392	85.08	0.96	5
050707	Avalanche Lake	-73.969179	44.130568	19.96	95	7.55
040874	Brooktrout Lake	-74.662437	43.599765	10.26	15.15	2.71
040748	Bubb Lake Stream	-74.846234	43.774862	63.36	4.06	3.3
040777	Constable Pond Stream	-74.806816	43.830486	19.32	52.28	6.33
070859	G Lake	-74.636452	43.418756	23.3	22.44	2.69
040706	Grass Pond	-75.065535	43.690196	45.76	26.68	3.9
020264	Heart Lake	-73.966994	44.180522	62.01	1.42	2.44
040852	Indian Lake	-74.761374	43.623443	9.35	41.14	5.92
050259	Jockeybush Pond	-74.585328	43.301965	19.22	15.11	2.57
040826	Limekiln Lake	-74.812473	43.712844	51.81	4.15	3.53
020058	Little Hope Pond	-74.126223	44.515876	73.47	8.67	9.42
050649	Long Pond	-74.478263	43.838068	1.07	58.02	13.45
040186	Loon Hollow Pond	-75.044739	43.961068	-6.14	119.76	4.44
040887	Lost Pond	-74.559294	43.645916	26.15	54.23	7.51
020265	Marcy Dam Pond	-73.951633	44.159125	28.58	31.71	3.72
040707	Middle Branch Lake	-75.101434	43.697903	70.72	7.6	4.49
040704	Middle Settlement Lake	-75.099838	43.683321	24.18	10.46	3.43
040746	Moss Lake	-74.853141	43.780948	98.46	6.85	3.8
050577	Nate Pond	-74.093870	43.858929	82.71	3.44	5.29
070728	Otter Lake	-74.504126	43.184549	25.35	16.25	2.97
060329	Queer Lake	-74.806921	43.813130	26.27	8.21	3.49
060315A	Raquette Lake Reservoir	-74.651020	43.795080	50.15	37.51	8.62
060313	Sagamore Lake	-74.628583	43.765465	57.98	22.5	7.72
040754	Squash Pond	-74.888931	43.824532	-13.29	116.38	7.81
040850	Squaw Lake	-74.738567	43.636251	34.8	1.92	3.24
040753	West Pond Stream	-74.882819	43.812237	7.31	41.45	9.02
050215	Willis Lake	-74.246423	43.371388	97.36	2.52	8.5
040210	Willys Lake	-74.956716	43.971981	1.62	45.96	2.89

**A2. De-trending for Analysis of Inter-Annual Variation**

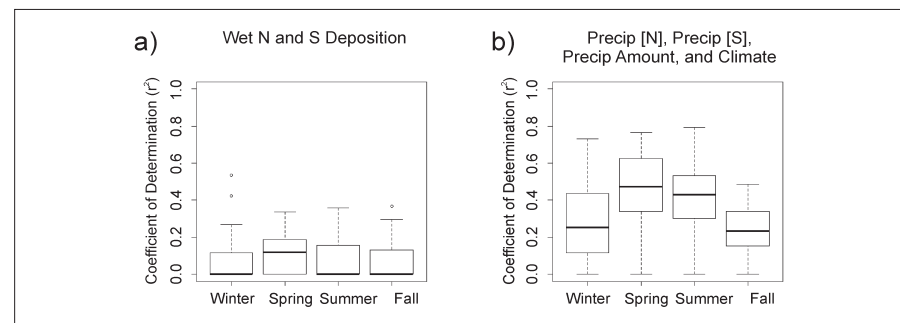
For some analyses reported here, lake chemistry data were de-trended in an attempt to remove apparent long-term responses to decreases in N and S deposition, thereby allowing for analysis of inter-annual differences in lake chemistry that are potentially associated with variables related to climate. For each study lake, trends in seasonal lakewater chemistry over the period 1993 to 2012 were determined using the Mann-Kendall test and Theil-Sen's slope estimator. Theil-Sen slopes were considered to be significant at  $p < 0.1$ . Individual lake chemistry time-series data showing significant slopes were de-trended using linear least squares regression. For lakes that did not show a significant negative trend in key water chemistry variables, the mean of the data was subtracted from each data point to develop analogous residual datasets reflecting deviation from the central tendency of the data.

Predictions of residual lake  $\text{NO}_3^-$  concentrations using wet N deposition only were very poor for all seasons except spring (Figure A2-1a). Inclusion of climate variables yielded a substantial improvement in residual predictions (Figure A2-1b). Inclusion of climate variables also resulted in improved predictions of residual DOC (Figure A2-2) and  $\text{Al}_i$  (Figure A2-3).

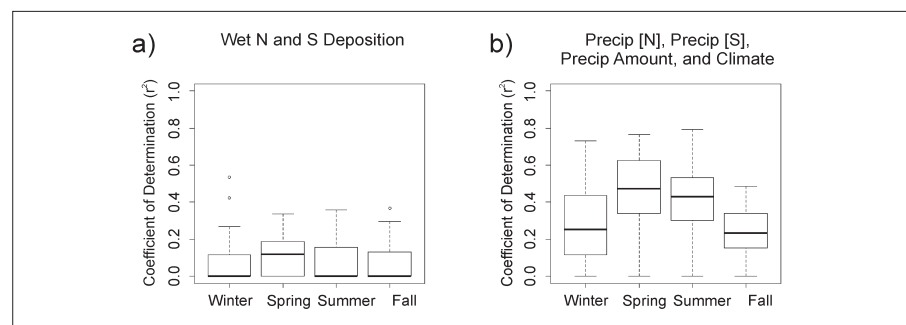
**Figure A2-1.** Distribution across study lakes of the  $r^2$  value for predicting residual lake  $\text{NO}_3^-$  concentration, using a) wet N and S deposition and b) concentration of inorganic N in precipitation, plus precipitation amount, plus climate variables.



**Figure A2-2.** Distribution across study lakes of the  $r^2$  value for predicting lake DOC residual, using a) wet N and S deposition and b) concentration of inorganic N and S in precipitation, plus precipitation amount, plus climate variables.



**Figure A2-3.** Distribution across study lakes of the  $r^2$  value for predicting lake  $\text{Al}_i$  residual, using a) wet N and S deposition and b) concentration of inorganic N and S in precipitation, plus precipitation amount, plus climate variables.



Inter-annual variation in lake chemistry was represented by residual lake concentrations of  $\text{NO}_3^-$ , DOC, and  $\text{Al}_i$  after de-trending to remove the presumed influence of long-term acidification recovery. Predictor variables representing long-term changes in N deposition were included in the final models less frequently for predicting residual lake  $\text{NO}_3^-$  concentration than for predicting measured lake  $\text{NO}_3^-$  concentration. This indicates that the inter-annual variation in lake  $\text{NO}_3^-$  concentration may be more closely associated with climate variables than with changes in N deposition or precipitation N concentration.

During spring, summer, and fall, models for predicting residual  $\text{NO}_3^-$  performed best for:

- smaller lakes (spring)
- smaller watershed area (spring)
- higher elevation (winter, summer)
- shorter retention time (fall)

These tend to be the more acid-sensitive watersheds (Sullivan 2015). Climate variables were associated with residual  $\text{NO}_3^-$  concentrations in the following manner:

- Nearly all non-winter models (26 of 28) that selected last date of recorded snowpack showed a positive relationship between last date of recorded snowpack and residual lake  $\text{NO}_3^-$  concentration, indicating that longer snow seasons resulted in higher residual  $\text{NO}_3^-$  in the spring, summer, and fall.
- Relationships between maximum late season depth of snowpack and residual  $\text{NO}_3^-$  were almost always negative (36 of 40).

- Seasonal precipitation amount was positively related to residual  $\text{NO}_3^-$  in winter, spring, and fall, but was negatively related in summer.
- Warmer air temperature was generally negatively related to residual  $\text{NO}_3^-$  for all seasons.

Last date of recorded snowpack and maximum late season depth of snowpack were selected in about one-third to one-half of the individual lake watershed models to predict both the spring and summer  $\text{NO}_3^-$  residual. Precipitation N concentration was rarely selected for predicting the  $\text{NO}_3^-$  residual for any season. However, seasonal precipitation amount was selected for about one-half to three-quarters of the models to predict the  $\text{NO}_3^-$  residual.

Inclusion of additional candidate climate variables improved model fits for predicting lake DOC concentration and residual DOC across all seasons. This indicates that both long-term trends and inter-annual variability in climate-related variables may have influence on lake DOC. Stuanes et al. (2008) found that seasonal variation in streamwater total organic carbon (TOC) at the Storgama catchment in southern Norway was mainly climatically controlled, whereas atmospheric S and N deposition better explained the long-term increase in streamwater TOC.

Models for predicting residual lake  $\text{Al}_i$  generally performed poorly for the spring season, when  $\text{Al}_i$  concentrations tended to be high. Some improvement was noted upon inclusion of the climatic variables. Fall season models generally outperformed models for other seasons provided that they included precipitation amount and/or other climate variables.

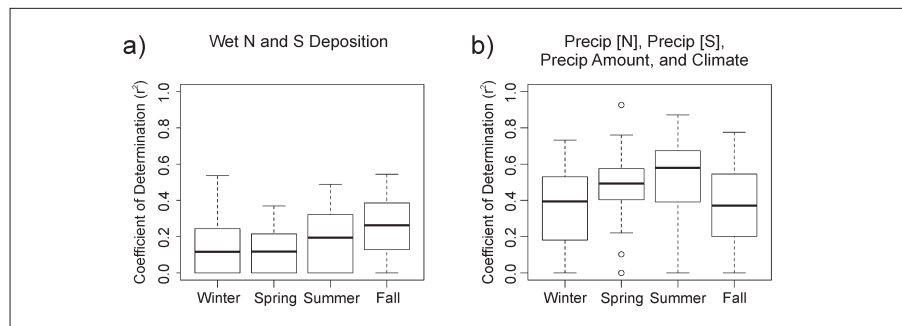
### A3. Effects of Time Lags in N Deposition

We tested the effect of introducing lags on the N deposition terms for predicting  $\text{NO}_3^-$  concentration based on predictor set 3. Four different lags were tested, whereby the seasonal lake  $\text{NO}_3^-$  concentrations were lagged behind the predictor variables describing N deposition (seasonal precipitation amount and N concentration in precipitation) from one to four seasons (e.g., winter season N deposition to predict spring lake  $\text{NO}_3^-$  concentrations [one season lag], winter season N deposition to predict summer lake  $\text{NO}_3^-$  concentrations [two season lag], etc.). For all seasons, lagging N deposition generally resulted in reduced ability to predict lake  $\text{NO}_3^-$  concentrations (with the exception of spring season with two lags, which showed marginal improvement among the lakes).

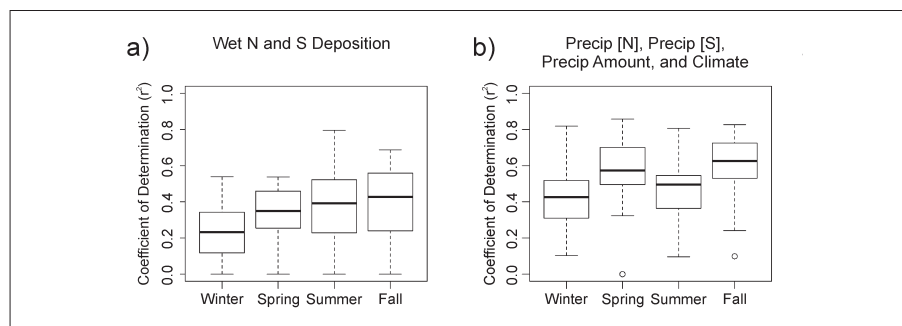
### A4. Predictions of DOC and $\text{Al}_i$ With and Without Variables.

Inclusion of climatic variables improved model fits for DOC (Figure A4-1) and  $\text{Al}_i$  (Figure A4-2) concentrations.

**Figure A4-1.** Distribution across study lakes of the  $r^2$  value for predicting lake DOC concentration, using a) wet N and S deposition, and b) precipitation, plus precipitation amount, plus climate variables.



**Figure A4-2.** Distribution across study lakes of the  $r^2$  value for predicting lake  $Al_i$  concentration, using a) wet N and S deposition and b) precipitation, plus precipitation amount, plus climate variables.



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