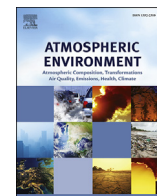


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## Long-term temporal trends and spatial patterns in the acid-base chemistry of lakes in the Adirondack region of New York in response to decreases in acidic deposition

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### H I G H L I G H T S

- Acid deposition is decreasing in the Adirondack region of New York.
- Acid neutralizing capacity in lakes is increasing with decreasing acid deposition.
- Lake classes most impacted by acidification show greatest recovery.
- Toxic dissolved inorganic aluminum decreases with lake recovery.
- Increases in dissolved organic matter or “browning” accompanies lake recovery.

### A R T I C L E I N F O

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### A B S T R A C T

We examined the response of lake water chemistry in the Adirondack Mountains of New York State, USA to decreases in acid deposition. Striking declines in the concentrations and fluxes of sulfate and hydrogen ion in wet deposition have been observed since the late 1970s, while significant decreases in nitrate have been evident since the early 2000s. Decreases in estimated dry sulfur and nitrate deposition have also occurred in the Adirondacks, but with no change in dry to wet deposition ratios. These patterns follow long-term decreases in anthropogenic emissions of sulfur dioxide and nitrogen oxides in the U.S. over the same interval. All of the 48 lakes monitored through the Adirondack Long-Term Monitoring program since 1992 have exhibited significant declines in sulfate concentrations, consistent with reductions in atmospheric deposition of sulfur. Nitrate concentrations have also significantly diminished at variable rates in many (33 of 48) lakes. Decreases in concentrations of sulfate plus nitrate (48 of 48) in lakes have driven widespread increases in acid neutralizing capacity (ANC; 42 of 48) and lab pH (33 of 48), and decreases in the toxic fraction, inorganic monomeric Al (45 of 48). Coincident with decreases in acid deposition, concentrations of dissolved organic carbon (DOC) have also increased in some (29 of 48) lakes. While recovery from elevated acid deposition is evident across Adirondack lakes, highly sensitive and impacted mounded seepages lakes and thin till drainage lakes are recovering most rapidly. Future research might focus on how much additional recovery could be achieved given the current deposition relative to future deposition anticipated under the Clean Power Plan, ecosystem effects of increased mobilization of dissolved organic matter, and the influence of changing climate on recovery from acidification.

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### 1. Introduction

Since the early 1970s, reductions in emissions of sulfur dioxide

(SO<sub>2</sub>) have driven remarkable decreases in atmospheric deposition of sulfate (SO<sub>4</sub><sup>2-</sup>) and hydrogen ion (H<sup>+</sup>) across eastern North America (National Emission Inventory; [www.epa.gov/air-emissions-inventories](http://www.epa.gov/air-emissions-inventories); Lehmann et al., 2005). Likewise, decreases in emissions of nitrogen oxides (NO<sub>x</sub>) initiated in the mid 1990s and early 2000s have diminished atmospheric nitrate (NO<sub>3</sub><sup>-</sup>) deposition in the years that have followed (Driscoll et al., 2010). Regulation of

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emissions and subsequent decreases in deposition of acidic air pollutants are reversing the acidification of sensitive freshwaters (Greaver et al., 2012; Strock et al., 2014). With the exception of the non-glaciated southeastern U.S., declines in atmospheric  $\text{SO}_4^{2-}$  deposition to montane forest watersheds of Europe and eastern North America have resulted in decreases in surface water concentrations of  $\text{SO}_4^{2-}$  (Evans et al., 2001; Kahl et al., 2004; Rice et al., 2014). Despite distinct decreases in acid deposition, the acid-base response of surface waters has been highly variable across these regions (Evans et al., 2001; Kahl et al., 2004; Warby et al., 2005; Waller et al., 2012).

Several landscape factors constrain the recovery of acid neutralizing capacity (ANC) in surface waters following decreases in acid deposition (Driscoll et al., 2001). Pools of exchangeable basic cations (particularly calcium) have been lost from soil cation exchange sites associated with historical leaching by strong acid anions from elevated acid deposition (Likens et al., 1996; Warby et al., 2009). Depletion of available basic cations limits the ability of soil to neutralize ambient inputs of acid deposition. Many surface waters have also shown compensatory increases in naturally occurring dissolved organic matter (DOM), apparently in response to decreases in acid deposition and/or changing climate (Monteith et al., 2007; Driscoll et al., 2007; Clark et al., 2010). Dissolved organic matter functions as organic acids with both characteristic strong acid and weak acid functional groups (Fakhraei and Driscoll, 2015). Increased supply of DOM with strongly acidic functional groups acidifies waters, offsetting potential increases in ANC. Finally, perhaps the most important watershed factor limiting ANC recovery is the  $\text{SO}_4^{2-}$  adsorption capacity of soils (Galloway et al., 1983). In areas with soils high in amorphous iron and aluminum oxides and  $\text{SO}_4^{2-}$  adsorption capacity (Johnson and Todd, 1983; Johnson, 1984), such as the non-glaciated region of the southeastern U.S., historical atmospheric  $\text{SO}_4^{2-}$  deposition has been retained in soil. As atmospheric  $\text{SO}_4^{2-}$  deposition decreases, legacy  $\text{SO}_4^{2-}$  previously retained in soil can be released to surface waters delaying recovery. Rice et al. (2014) found spatial and temporal patterns in the  $\text{SO}_4^{2-}$  source/sink behavior of watersheds in the Southeast, with  $\text{SO}_4^{2-}$  retention decreasing with time in response to decreases in atmospheric S deposition and increasing from north to south. In the glaciated northeast U.S., soil  $\text{SO}_4^{2-}$  adsorption/desorption is considerably less important in regulating the acid-base chemistry than in the Southeast (Galloway et al., 1983; Rochelle and Church, 1987).

Effects of elevated acid deposition have been evident for decades in the Adirondack region of New York, USA. The Adirondacks is a largely forested (24,000 km<sup>2</sup>) with approximately 2770 lakes (>2000 m<sup>2</sup> surface area). Generally shallow surficial deposits and bedrock geology have produced soils with inherently low pools of available nutrient cations and surface waters that are sensitive to acid deposition (Driscoll et al., 1991). A survey of 1469 Adirondack lakes conducted in 1984–87 found chronic acidity (ANC < 0  $\mu\text{eq/L}$ ) in 27% of lakes. An additional 21% had summer ANC values between 0 and 50  $\mu\text{eq/L}$  and could experience decreases in ANC near or below 0  $\mu\text{eq/L}$  during high discharge, such as snowmelt or precipitation events (Kretser et al., 1989).

Starting in 1982, long-term trends and seasonal patterns in chemical characteristics were evaluated for 17 lakes in the Adirondack region of New York, which has become the Adirondack Long-Term Monitoring (ALTM) program (Driscoll et al., 2003). Thirty-five lakes were added to the ALTM in 1992, for a total of 52 sites. Four of these lakes were treated with  $\text{CaCO}_3$  to neutralize acidity and were not considered in our analysis of water chemistry trends. The ALTM lakes have been classified in terms of their acid sensitivity on the basis of surficial geology and hydrologic flowpaths (Baker et al., 1990; Driscoll and van Dreason, 1993). In this

paper, we update trends in atmospheric deposition and resulting changes in the acid-base status of ALTM lakes and among lake classes, and evaluate mechanisms affecting these trends. We hypothesize that recent decreases in acid deposition will be manifested by decreases in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations in Adirondack lakes resulting in increases in ANC, with lake-watersheds with shallow hydrologic flowpaths exhibiting the most rapid response in ANC.

## 2. Methods

Wet deposition has been monitored at the Huntington Forest (HF) in the central Adirondacks (NY 20; 43° 58' N, 74° 13' W) since 1978 and at Whiteface Mountain (WM) in the eastern high peaks area (NY 98; 44° 24' N, 73° 52' W) since 1984, through the National Atmospheric Deposition Program (NADP). Note that among the six NADP sites in the Adirondacks, HF and WM have the longest records. Precipitation collections are made weekly and are measured for major solutes (nadp.sws.uiuc.edu). At the HF, atmospheric chemistry has also been monitored since 2003 through the U.S. Environmental Protection Agency Clean Air Status and Trends Network (CASTNET; [www.epa.gov/castnet](http://www.epa.gov/castnet); HWF187), which includes particulate  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , and  $\text{SO}_2$  and nitric acid vapor. Atmospheric concentrations of these constituents are coupled with modeled deposition velocity to estimate dry deposition. Dry deposition velocity estimates are made from the Multi-Layer Model (MLM), a dry deposition model. Missing deposition velocities have been replaced with historical averages. Dry deposition of  $\text{SO}_2$  and particulate  $\text{SO}_4^{2-}$  are summed to estimate dry S deposition and dry deposition of nitric acid vapor and particulate  $\text{NO}_3^-$  are summed to estimate dry  $\text{NO}_3^-$  deposition.

ALTM lakes are situated adjacent to largely forested watersheds, with predominantly hardwood or mixed conifer vegetation. A classification system was developed based on surficial geology and hydrologic flowpaths to characterize the sensitivity of Adirondack lakes to acid deposition (Baker et al., 1990). Drainage lakes in watersheds with largely shallow deposits of glacial till (thin till watersheds; <5% of the watershed containing thick, i.e., > 3 m depth, deposits of glacial till) are sensitive to acid deposition and, historically have been chronically acidic (ANC < 0  $\mu\text{eq/L}$ ). Twenty-seven ALTM lakes are included in the thin till drainage class. Lakes situated in watersheds with moderate deposits of deep glacial till (5–25% of the watershed contains thick deposits of glacial till) generally have positive but low ANC and are susceptible to short-term acidification associated with snow melt or storm events. This medium till drainage class includes 11 ALTM lakes. Watersheds with either more than 25% of the watershed with thick deposits of glacial till or stratified drift or deposits of calcite drain to lakes which are insensitive to acid deposition. Two of the ALTM lakes have calcite in the basin and three are in the thick till drainage class. The Adirondacks also have mounded seepage lakes, which receive most of their water from shallow hydrologic flow paths or directly from precipitation. Within the ALTM program there are five mounded seepage lakes.

Lake water samples are collected monthly and analyzed for major solutes (Driscoll et al., 2003). A helicopter is used to sample waters from remote drainage (n = 15) and seepage lakes (n = 5). Collections are made using a plastic Kemmerer sampler approximately 0.5 m beneath the surface over the deepest portion of the lake. When the lake surface is inaccessible (i.e., during ice development and break-up), samples are obtained at the shoreline for seepage lakes or the outlets of drainage lakes. Drainage lakes accessed by land (n = 28) are sampled at the outlet. Water samples are collected directly or are transferred into 1-L high-density polyethylene bottles, that have been acid-washed and distilled water

**Table 1**

Long-term trends in concentrations of chemical constituents in wet deposition at Huntington Forest (1978–2014) and Whiteface Mountain (1984–2014) in the Adirondacks. These changes are indicated as slopes of significant ( $p < 0.05$ ) concentration change (in  $\mu\text{eq/L}\cdot\text{yr}$ ).  $C_B$  is the sum of basic cations. Non-significant trends are indicated as NS.

Site	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{Cl}^-$	$C_B$	$\text{NH}_4^+$	$\text{H}^+$
Huntington Forest	-1.13	-0.49	-0.05	-0.16	-0.08	-1.20
Whiteface Mountain	-1.08	-0.45	-0.04	-0.06	NS	-1.26

rinsed. All samples are kept on ice after collection until transported to the Adirondack Lakes Survey Corporation (ALSC) laboratory in Ray Brook, NY. Driscoll and van Dreaseon (1993) summarized the field and analytical methods used. Driscoll et al. (2003) provide lake and watershed characteristics. Site descriptions and data are available ([www.adirondacklakessurvey.org](http://www.adirondacklakessurvey.org)).

We used the nonparametric seasonal Kendall Tau (SKT) test to detect monotonic trends (generally increasing or decreasing over time) in solute concentrations in precipitation and lake water (Hirsch and Slack, 1984). The SKT was run for measured observations of precipitation chemistry at HF and WM, and lake chemistry of the original 16 ALTM lakes (1982–2013) and overall 48 ALTM lakes that were not limed (1992–2013). The SKT test is a robust time-series procedure for data that are non-normal and characterized by seasonal patterns. This approach corrects data with moderate levels of serial correlation and accommodates missing observations. A  $p < 0.05$  was used as a significance level for all analysis.

### 3. Results

#### 3.1. Atmospheric deposition trends

The chemistry of precipitation has been changing in recent decades across the eastern U.S. in response to air quality management (Lehmann et al., 2005; Driscoll et al., 2010). The HF and WM have both shown marked decreases in concentrations of most solutes in wet deposition, with the exception of ammonium ( $\text{NH}_4^+$ )

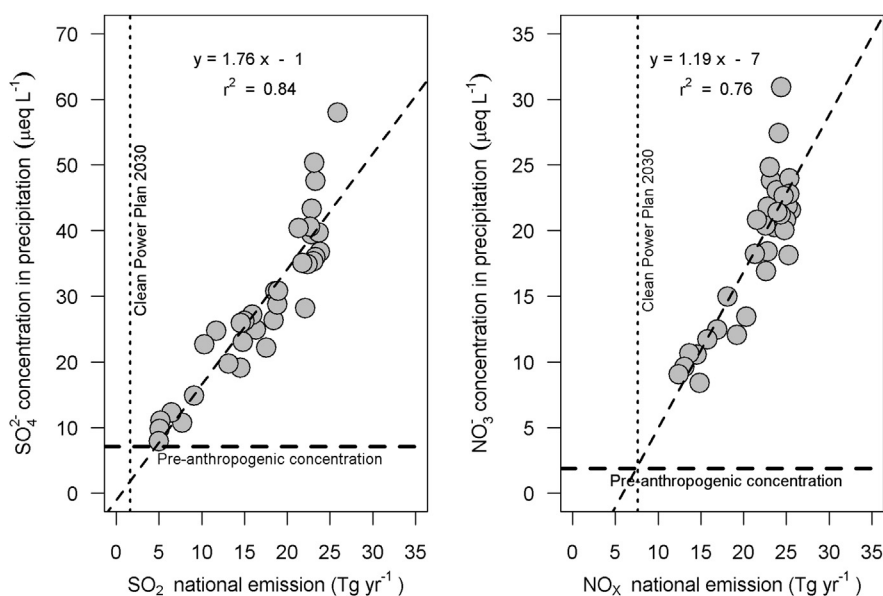
which has not changed at WM and decreased only slightly at HF (Table 1). Annual volume-weighted concentrations of  $\text{SO}_4^{2-}$  at HF ( $r^2 = 0.84$ ) and WF ( $r^2 = 0.83$ ) were positively correlated with total anthropogenic U.S. annual emissions of anthropogenic  $\text{SO}_2$  (National Emission Inventory: [www3.epa.gov/ttn/chieff/net/2014inventory.html](http://www3.epa.gov/ttn/chieff/net/2014inventory.html)) (Fig. 1). A similar pattern is evident between concentrations of  $\text{NO}_3^-$  in precipitation and total anthropogenic emissions of  $\text{NO}_x$  in the U.S., although the relationship is somewhat weaker ( $r^2 = 0.76$  at HF,  $r^2 = 0.75$  at WM; Fig. 1) and the magnitude of  $\text{NO}_x$  emission decreases and precipitation  $\text{NO}_3^-$  are less than for S.

Also coincident with decreases in  $\text{SO}_2$  and  $\text{NO}_x$  emissions have been similar but temporally more variable decreases in wet deposition and estimated dry deposition of S and  $\text{NO}_3^-$  to HF (Fig. 2). Based on NADP wet deposition measurements and U.S. EPA CAST-NET dry deposition estimates since 2003, wet deposition represents 92% of total S deposition and 91% of total  $\text{NO}_3^-$  deposition to HF. Note that some forms of dry deposition, in particular oxidized N, are not routinely monitored, so these values are likely underestimates of total dry deposition.

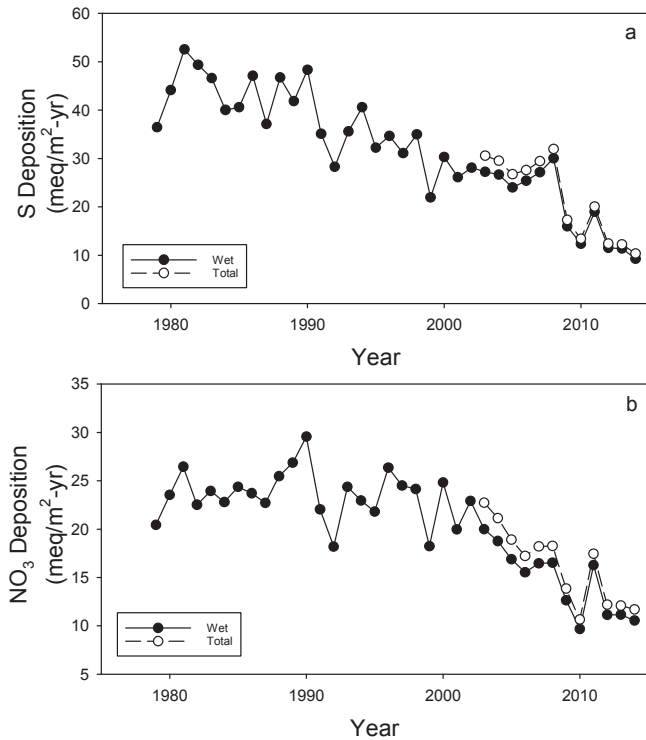
Although both wet and estimated dry S and  $\text{NO}_3^-$  deposition have decreased in response to emission controls, the dry to wet deposition ratios have remained constant (dry S/wet S =  $0.09 \pm 0.021$ ; dry  $\text{NO}_3^-$ /wet  $\text{NO}_3^-$  =  $0.10 \pm 0.018$ ).

#### 3.2. Lake sulfate, nitrate and chloride trends

As observed for atmospheric deposition, there have been marked changes in the chemical composition and acid-base status of Adirondack Lakes in recent years (Figs. 3 and 4). We show time-series patterns of chemical concentrations in Fig. 3 for Big Moose Lake, a thin till drainage lake, to illustrate the response of an acid-sensitive lake to decreases in acid deposition over the longer period of record (Fig. 3; 1982–2015). Since 1982, all the original ALTM lakes have experienced significant ( $p < 0.05$ ) decreases in  $\text{SO}_4^{2-}$  concentrations, at a mean rate of decline ( $\pm$ standard deviation) of  $2.35 \pm 0.39 \mu\text{eq/L}\cdot\text{yr}$  (Fig. 4a). Similar decreases in  $\text{SO}_4^{2-}$  concentrations were evident for the 48 ALTM lakes sampled since 1992 (Fig. 4b). Although the rate of  $\text{SO}_4^{2-}$  decline was more variable



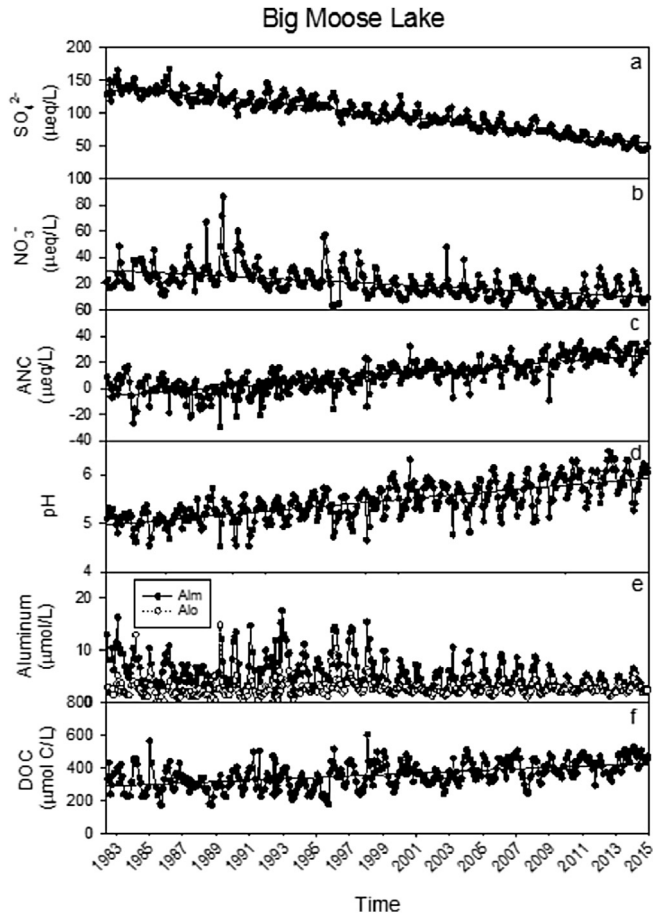
**Fig. 1.** Relationships between U.S. human emissions of sulfur dioxide (a) and nitrogen oxides (b) and annual volume-weighted concentrations of sulfate and nitrate, respectively, in wet deposition, at Huntington Forest (NY20) in the central Adirondacks. Also shown are estimates of pre-industrial concentrations (after Galloway et al., 1982) and projections of emissions in 2030 anticipated under the Clean Power Plan (USEPA, 2015).



**Fig. 2.** Time-series of annual wet and estimated total S deposition (a) and nitrate deposition (b) at Huntington Forest in the central Adirondacks. Wet deposition is from the National Atmospheric Deposition Program (NADP; NY 20). Dry deposition is estimated from observations from the U.S. EPA CASTNET program at Huntington Forest. Estimated total deposition is the sum of annual wet and estimated dry deposition.

( $-0.99$  to  $-4.00$   $\mu\text{eq/L-yr}$ ) for all ALTM lakes over the more recent interval (1992–2013) than for the 16 lakes with the longer record, the mean rate of concentration decrease was similar ( $-2.55 \pm 0.67$   $\mu\text{eq/L-yr}$  vs.  $-2.35 \pm 0.39$   $\mu\text{eq/L-yr}$ ). There were no significant differences in rates of  $\text{SO}_4^{2-}$  decline among drainage lake classes (thin till  $-2.67 \pm 0.60$   $\mu\text{eq/L-yr}$ ; medium till  $-2.54 \pm 0.57$   $\mu\text{eq/L-yr}$ ; thick till and carbonate influenced  $-2.87 \pm 0.71$   $\mu\text{eq/L-yr}$ ). However, rates of  $\text{SO}_4^{2-}$  for seepage lakes were significantly lower ( $-1.55 \pm 0.45$   $\mu\text{eq/L-yr}$ ) than drainage lakes, which likely reflects differences in the direct pathway of inputs to the lake surface and the near-lake zone for seepage lakes in comparison to the watershed inputs which include additional dry S deposition associated with the canopy and the greater concentrating effect of evapotranspiration in forest drainage lake-watersheds.

Decreases in concentrations of  $\text{NO}_3^-$  were also evident in many of the ALTM lakes, but at variable rates (Figs. 4 and 5). Eleven of the original 16 sites exhibited significant decreases in  $\text{NO}_3^-$  (mean value  $-0.38$   $\mu\text{eq/L-yr}$ , range  $-0.14$  to  $-0.68$   $\mu\text{eq/L-yr}$ ). Thirty-three of the 48 ALTM lakes (1992–2013) showed decreases in  $\text{NO}_3^-$ , with no lakes exhibiting increases. A few lakes with low  $\text{NO}_3^-$  had low but significant decreases in concentrations. For lakes exhibiting significant decreases in  $\text{NO}_3^-$ , the rate of decrease generally increased with increasing  $\text{NO}_3^-$  concentration. Adirondack seepage lakes were characterized by low  $\text{NO}_3^-$  ( $6.2 \pm 9.2$   $\mu\text{eq/L}$ ). As a result, these lake types are marginally N growth limited and projected to become increasing N limited under anticipated future decreases in atmospheric N deposition (Gerson et al., 2016). Three of five seepage lakes exhibited small but significant  $\text{NO}_3^-$  decreases ( $-0.044 \pm 0.013$   $\mu\text{eq/L-yr}$ ). For drainage lakes, rates of  $\text{NO}_3^-$  decline increased from deep to shallow watershed till depth (thick till and carbonate 2 of 5

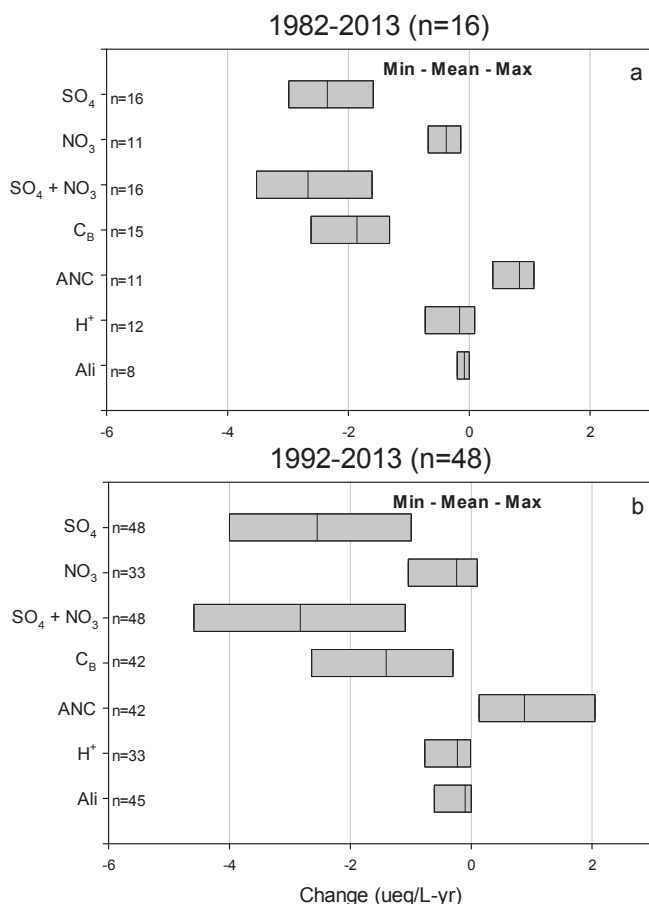


**Fig. 3.** Time-series of monthly concentrations of sulfate (a), nitrate (b), acid neutralizing capacity (c), pH (d), monomeric and organic monomeric aluminum (e) and dissolved organic carbon (f) for Big Moose Lake (1982–2013). Inorganic monomeric aluminum is the difference between monomeric and organic monomeric aluminum. A statistically significant slope from time series analysis is shown for all analytes with a solid line, except Al. There is a significant decrease in monomeric and inorganic monomeric Al concentrations. Big Moose Lake is a thin till drainage lake part of the Adirondack Long-Term Monitoring program. Changes in its chemical concentrations are indicative of the recovery of impacted lakes from acid deposition in the region.

lakes decreasing at  $-0.046 \pm 0.026$   $\mu\text{eq/L-yr}$ ; medium till 9 of 11 lakes decreasing at  $-0.24 \pm 0.22$   $\mu\text{eq/L-yr}$ ; thin till 19 of 27 lakes decreasing at  $-0.41 \pm 0.28$   $\mu\text{eq/L-yr}$ ). These observations suggest that decreases in  $\text{NO}_3^-$  leaching are most prominent in drainage lake watersheds with shallow hydrologic flowpaths.

All of the 16 original ALTM lakes exhibited significant decreases in  $\text{SO}_4^{2-} + \text{NO}_3^-$ , with a mean value of  $-2.67 \pm 0.57$   $\mu\text{eq/L-yr}$ . Likewise all 48 sites showed significant decreases in  $\text{SO}_4^{2-} + \text{NO}_3^-$ , with a mean value of  $-2.83 \pm 0.79$   $\mu\text{eq/L-yr}$  over the shorter interval. As observed for individual strong acid anions, concentrations and rates of decrease of  $\text{SO}_4^{2-} + \text{NO}_3^-$  were lower in seepage lakes than drainage lakes ( $\text{SO}_4^{2-} + \text{NO}_3^-$ :  $60.5 \pm 31$   $\mu\text{eq/L}$ ;  $-1.64 \pm 0.45$   $\mu\text{eq/L-yr}$ , respectively). Slight differences in decreases in  $\text{SO}_4^{2-} + \text{NO}_3^-$  were apparent across the classes of drainage lakes with thin till lakes showing slightly greater rates of decline associated with their higher decreases in  $\text{NO}_3^-$  ( $-3.05 \pm 0.73$   $\mu\text{eq/L-yr}$ ).

Concentrations of chloride ( $\text{Cl}^-$ ) were generally low across ALTM lakes ( $9.0 \pm 3.8$   $\mu\text{eq/L}$ ). Despite these low concentrations, we observed widespread decreases in lake  $\text{Cl}^-$  (for observations both starting since 1982 and 1992). Thirty-four of 48 lakes showed significant decreases in lake  $\text{Cl}^-$ , with three lakes exhibiting significant increases. Note the rate of lake  $\text{Cl}^-$  decreases were low



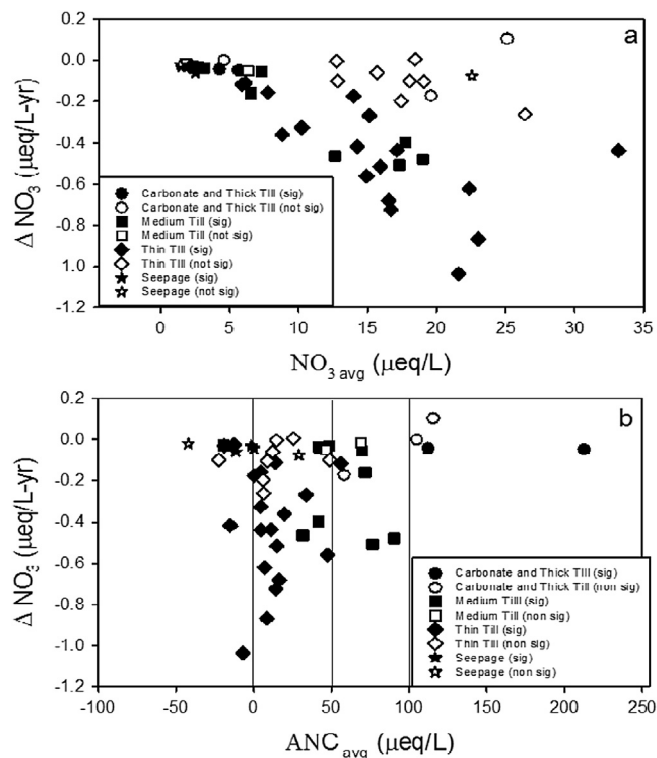
**Fig. 4.** Long-term trends in concentrations of chemical constituents in 16 lakes from 1982 to 2013 (a) and 48 lakes from 1992 to 2013 (b) of the Adirondack Long-Term Monitoring (ALTM) program. The number of lakes showing significant ( $p < 0.05$ ) trends and changes in minimum, mean and maximum concentrations are shown. Rates of concentration change are expressed as  $\mu\text{eq/L-yr}$ , except for inorganic monomeric aluminum (Ali) which is shown as  $\mu\text{mol/L-yr}$ .

( $-0.074 \pm 0.11 \mu\text{eq/L-yr}$ ) compared to the decreases in  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$ . Decreases in lake  $\text{Cl}^-$  could likely be associated with observed decreases in  $\text{Cl}^-$  in wet deposition (Table 1), which have been reported elsewhere and attributed to controls on emissions from electric utilities (Lovett et al., 2005).

### 3.3. Trends in lake basic cations

The original 16 ALTM lakes, all exhibited significant declines in  $\text{C}_B$  (mean rate  $-1.86 \pm 0.38 \mu\text{eq/L-yr}$ ), except the mounded seepage lake Little Echo Pond. Forty-two of the 48 ALTM lakes have also shown significant decreases in  $\text{C}_B$  coinciding with decreases in  $\text{SO}_4^{2-} + \text{NO}_3^-$  since 1992, with the thin till drainage lakes (mean value  $-1.29 \pm 0.46 \mu\text{eq/L-yr}$ ) and mounded seepage lakes (mean value  $-1.02 \pm 0.26 \mu\text{eq/L-yr}$ ) showing lower rates of decline than medium (mean value  $-1.59 \pm 0.63 \mu\text{eq/L-yr}$ ) and thick till and carbonate drainage lakes (mean value  $-1.94 \pm 0.49 \mu\text{eq/L-yr}$ ; Fig. 6).

Concentrations of individual basic cations (i.e.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ) had highly significant decreasing trends, except for  $\text{Na}^+$  for which several lakes had small increasing trends ( $n = 11$ ). Note that these increasing trends for  $\text{Na}^+$  run counter to the widespread decreasing trends for  $\text{Cl}^-$  (discussed above), suggesting that increased human contamination or road salting is not a factor in most ALTM lakes. Overall decreases in  $\text{C}_B$  were largely due to decreases in  $\text{Ca}^{2+}$ , which is the dominant cation in most Adirondack surface waters (44 of 48



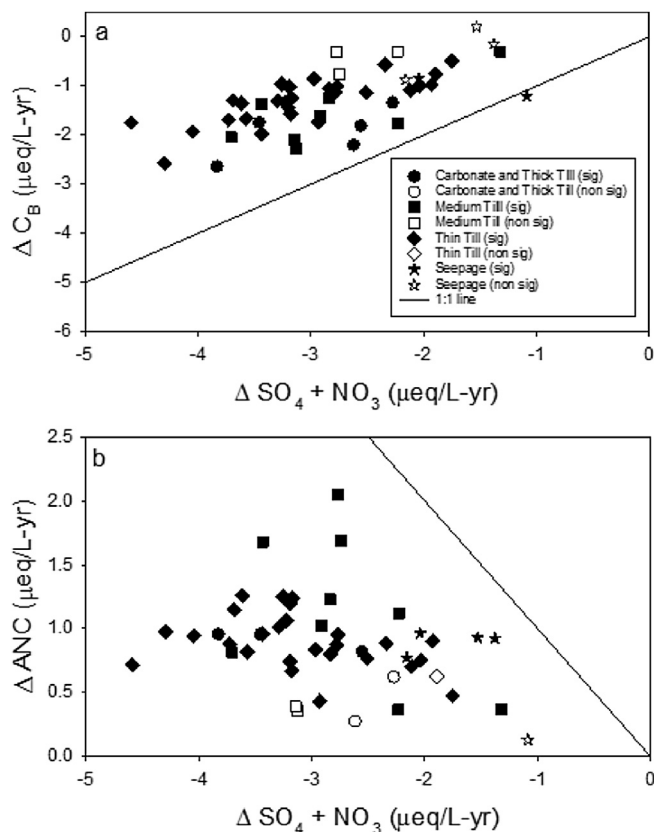
**Fig. 5.** Changes in nitrate concentrations in Adirondack Long Term Monitoring (ALTM) program lakes (1992–2013) as a function of mean lake nitrate concentration (a) and acid neutralizing capacity (b). Shown are values for different lake classes. Significant relationships ( $p < 0.05$ ) for lakes are shown with filled symbols and non-significant relationships are indicated by open symbols. Vertical lines are shown in b for ANC values of 0, 50 and 100  $\mu\text{eq/L}$  for perspective.

sites with significant decreases at a mean rate of decline  $-1.04 \pm 0.40 \mu\text{eq/L-yr}$ .

### 3.4. Trends in lake acid neutralizing capacity, pH, Al and DOC

Eleven of the 16 original ALTM lakes had significant increasing trends of ANC (Fig. 4) from 1982 to 2013. Those lakes showing a significant increasing ANC trends were mostly in the thin till drainage class (7) and had a mean rate of increase of  $0.83 \pm 0.22 \mu\text{eq/L-yr}$ , ranging from 0.39 to 1.07  $\mu\text{eq/L-yr}$ . Forty-two of the 48 ALTM lakes had significant trends of increasing ANC for the period 1992–2013 ( $0.95 \pm 0.32 \mu\text{eq/L-yr}$ ). Surprisingly, rates of ANC increase for lakes showing significant trends did not differ among lake classes or mean ANC (Fig. 7a). Twenty-six of the 27 thin till drainage lakes had increases in ANC at a mean rate of  $0.89 \pm 0.22 \mu\text{eq/L-yr}$ . Nine of 11 medium till drainage lakes exhibited increases in ANC at a mean rate of  $1.15 \pm 0.58 \mu\text{eq/L-yr}$ . Three of the five thick till and carbonate drainage lakes exhibited increases in ANC at a mean rate of  $0.91 \pm 0.077 \mu\text{eq/L-yr}$ . Four of the five seepage lakes had significant increases in ANC of  $0.90 \pm 0.084 \mu\text{eq/L-yr}$ .

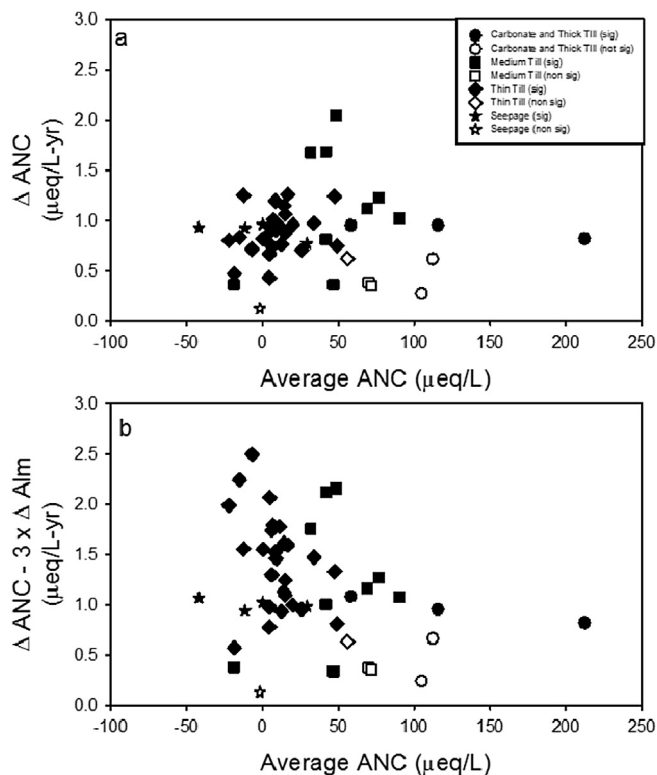
Increases in ANC and decreases in  $\text{C}_B$  in Adirondack lakes are largely driven by decreases in concentrations of  $\text{SO}_4^{2-} + \text{NO}_3^-$ . As a result, an important metric of surface water recovery from acid deposition is the unit increase in ANC in response to unit decreases in concentrations of strong acid anions (Fig. 6). The stoichiometric responses of decreases in  $\text{C}_B$  ( $\Delta\text{C}_B/\Delta(\text{SO}_4^{2-} + \text{NO}_3^-)$ ) and increases in ANC ( $\Delta\text{ANC}/\Delta(\text{SO}_4^{2-} + \text{NO}_3^-)$ ) for a unit decrease in  $\text{SO}_4^{2-} + \text{NO}_3^-$  were calculated for different ALTM lake classes (1992–2013; Fig. 6; Table 2). There have been consistent decreases in  $\text{C}_B$  with unit



**Fig. 6.** Long-term trends in concentrations of the sum of base cations ( $C_B$ ; a) and acid neutralizing capacity (ANC; b) with changes in  $SO_4^{2-} + NO_3^-$  for Adirondack Long Term Monitoring lakes over 1992–2013. Shown are values for different lake classes. Significant relationships ( $p < 0.05$ ) are shown with filled symbols and non-significant relationships are indicated by open symbols. Shown are 1:1 lines which are indicative of a stoichiometric relationship.

decreases in  $SO_4^{2-} + NO_3^-$  (Fig. 6a). We observed decreases in the sum of basic cations ( $C_B$ ) that were less than stoichiometric with declines in  $SO_4^{2-} + NO_3^-$  in most ALTM lakes (Figs. 4 and 6). Lakes experiencing the greatest changes in  $SO_4^{2-} + NO_3^-$  have generally shown the largest decreases in  $C_B$ . The more insensitive classes (8 of 11 significant medium till sites ( $\Delta C_B/\Delta(SO_4^{2-} + NO_3^-) = 0.54 \pm 0.19$ ); all thick till and calcite sites ( $\Delta C_B/\Delta(SO_4^{2-} + NO_3^-) = 0.67 \pm 0.13$ )) generally had larger decreases in  $C_B$  per unit decrease in  $SO_4^{2-} + NO_3^-$  (Fig. 6a). In comparison, all thin till drainage lakes exhibited significant relationships of decreasing  $C_B$  with decreasing  $SO_4^{2-} + NO_3^-$  ( $\Delta C_B/\Delta(SO_4^{2-} + NO_3^-) = 0.42 \pm 0.09$ ), but at lower values than drainage lakes in medium till, thick till or calcite watersheds (Table 2). This pattern is consistent with the greater rate of base cation supply for lake-watersheds with thicker surficial deposits or calcite than thin till lake-watersheds. A significant relationship between decreases in  $C_B$  with decreasing  $SO_4^{2-} + NO_3^-$  was only evident for two of the five mounded seepage lakes.

The increases in ANC to equivalent decreases in  $SO_4^{2-} + NO_3^-$  ( $\Delta ANC/\Delta(SO_4^{2-} + NO_3^-)$ ) mirrors the patterns for  $\Delta C_B/\Delta(SO_4^{2-} + NO_3^-)$  for most sites in the different lake classes (Fig. 6b). The mounded seepage lakes exhibited a less than stoichiometric response, but a relatively high increase in ANC for unit decreases in  $SO_4^{2-} + NO_3^-$  ( $\Delta ANC/\Delta(SO_4^{2-} + NO_3^-) = -0.53 \pm 0.14$ ). The absolute increase in ANC for mounded seepage lakes is not particularly large compared to drainage lake classes due to relatively low increases in concentrations of  $SO_4^{2-} + NO_3^-$ . Nevertheless, this strong relative response is likely due to hydrologic inputs largely occurring from



**Fig. 7.** Long term trends in acid neutralizing capacity (a) and increases acid neutralizing capacity less decreases monomeric Al ( $\Delta ANC - 3 \times \Delta Alm$ ) (b) with mean lake ANC for different classes of Adirondack Long-Term Monitoring lakes (1992–2013). Significant relationships ( $p < 0.05$ ) are shown with filled symbols and non-significant relationships are indicated by open symbols.

direct precipitation and shallow near-shore flowpaths, resulting in limited contact with surficial materials. As a result mounded seepage lakes are very sensitive and relatively responsive to changes in atmospheric deposition. Four out of five mounded seepage lakes show a significant increase in ANC coinciding with a significant decrease in  $SO_4^{2-} + NO_3^-$ .

Twenty-six of the thin till drainage lakes had significant increases in ANC with decreases in  $SO_4^{2-} + NO_3^-$ . The thin till drainage lakes exhibited a mean 0.30 equivalent increase in ANC for every equivalent unit decrease in  $SO_4^{2-} + NO_3^-$  ( $\Delta ANC/\Delta(SO_4^{2-} + NO_3^-) = -0.30 \pm 0.08$ ). There are three mechanisms restricting increases in ANC per unit decrease in  $SO_4^{2-} + NO_3^-$  in chronically acidic thin till lakes: limited supply of  $C_B$  from soil to drainage waters, marked decreases in the mobilization of Al and relatively large increases in the supply of naturally occurring dissolved organic matter (discussed below).

Our stoichiometric analysis for thick till and calcite impacted drainage lakes indicate that a unit decrease in  $SO_4^{2-} + NO_3^-$  resulted in a somewhat less than equivalent decrease in  $C_B$  leaching ( $\Delta C_B/\Delta(SO_4^{2-} + NO_3^-) = 0.67 \pm 0.13$ ), with moderate rates of ANC increase ( $\Delta ANC/\Delta(SO_4^{2-} + NO_3^-) = -0.28 \pm 0.04$ ). This limited ANC response might be expected for more base rich watersheds with thick surficial deposits or calcite. Surprisingly, medium till sites exhibited relatively large increases in ANC per unit decrease in  $SO_4^{2-} + NO_3^-$  ( $\Delta ANC/\Delta(SO_4^{2-} + NO_3^-) = -0.42 \pm 0.19$ ), with nine of 11 sites showing a significant response. There was considerable variability in the stoichiometric response for this class of lake watersheds. Three medium till sites had the greatest rates of ANC increase of all the ALTM sites (i.e., Limekiln, Little Hope, Big Hope) from 1992 to 2013. It is not evident why these lakes had high rates of ANC

**Table 2**

The stoichiometry of decreases in  $C_B$  ( $\Delta C_B/\Delta(\text{SO}_4^{2-} + \text{NO}_3^-)$ ) and increases in ANC ( $\Delta \text{ANC}/\Delta(\text{SO}_4^{2-} + \text{NO}_3^-)$ ) in response to equivalent decreases in  $\text{SO}_4^{2-} + \text{NO}_3^-$  in Adirondack Long-Term Monitoring lakes for 1992–2013 in comparison with surface waters from other regions. The number of significant relationships ( $p < 0.05$ ) is shown in parenthesis for Adirondack lake classes.

Site	$\Delta C_B/\Delta(\text{SO}_4^{2-} + \text{NO}_3^-)$	$\Delta \text{ANC}/\Delta(\text{SO}_4^{2-} + \text{NO}_3^-)$	Reference
Adirondacks			This study
Perched seepage (5)	0.76 (2)	−0.53 (4)	
Thin till (27)	0.42 (27)	−0.30 (26)	
Medium (11)	0.54 (8)	−0.42 (9)	
Thick till/calcite (5)	0.67 (5)	−0.28 (3)	
New England	0.84	−0.06	(Kahl et al., 2004)
Appalachian	0.94	−0.22	(Kahl et al., 2004)
Upper Midwest	0.42	−0.32	(Kahl et al., 2004)
Europe	0.5	−0.5	(Evans et al., 2001)

increase. However, these three lakes also had modest rates of decreases in concentrations of  $C_B$  (two with non-significant decreases), likely contributing to high rates of ANC increase.

We also observed significant decreases in  $\text{H}^+$  concentrations in 12 of the 16 original ALTM lakes (Fig. 3a). Not surprisingly, rates of  $\text{H}^+$  decrease were highly variable. The mounded seepage lake, Little Echo Pond ( $-0.73 \mu\text{eq/L-yr}$ ), and thin till drainage lakes (mean value  $0.15 \pm 0.21 \mu\text{eq/L-yr}$ ; except West Pond which increased) had the greatest rates of  $\text{H}^+$  decrease. Over the shorter record, 33 of 48 ALTM lakes had significant decreases in  $\text{H}^+$ . As with the longer record, decreases in concentrations of  $\text{H}^+$  were greatest for thin till drainage (24 of 27 decreasing at  $0.23 \pm 0.20 \mu\text{eq/L-yr}$ ) and the mounded seepage (4 of 5 decreasing  $0.46 \pm 0.31 \mu\text{eq/L-yr}$ ) lake classes.

Changes in Al concentrations largely occurred with the Al<sub>i</sub> fraction, which is considered to be the toxic form of total monomeric Al (Driscoll et al., 1980). Moreover, although significant decreases in Al<sub>i</sub> were widely evident, large concentration changes were restricted to chronically acidic thin till drainage lakes. Five of eight lakes in the thin till drainage class of the original ALTM lakes had significant decreases in concentrations of Al<sub>i</sub>. These rates of decline were highly variable, ranging from  $-0.20$  to  $0.00 \mu\text{mol/L-yr}$ . For the recent record of ALTM lakes (1992–2013), 45 of 48 lakes had significant decreasing trends in Al<sub>i</sub> concentrations, but most noteworthy were marked decreases Al<sub>i</sub> in all of the 26 thin till lakes ( $-0.17 \pm 0.16 \mu\text{mol/L-yr}$ ).

Aluminum is an underappreciated pH buffering process (Driscoll and Postek, 1996). To evaluate the potential for Al buffering, we coupled rates of equivalent decreases of monomeric Al with increases in ANC ( $\Delta \text{ANC} - 3^* \Delta \text{Alm}$ ). We use monomeric Al (Alm) in this metric because both inorganic (Al<sub>i</sub>) and organic (Al<sub>o</sub>) forms of monomeric Al undergo hydrolysis (Fakhraei and Driscoll, 2015). We observed no significant difference in increases in ANC across the sundry lake classes or across the range of ANC values in study lakes (Fig. 7a). However, when Al buffering is considered ( $\Delta \text{ANC} - 3^* \Delta \text{Alm}$ ), the role of Al mobilization and hydrolysis in the acid-base chemistry to thin till drainage lakes becomes clearly evident (Fig. 7b). In these acid-sensitive watersheds, much of the decrease in strong acid leaching associated with decreases in acid deposition is manifested through decreases in Al leaching, particularly the toxic Al<sub>i</sub> fraction. Aluminum buffering is not important in seepage lakes because their hydrologic flowpaths do not allow for the mobilization of Al from soil (Driscoll and Newton, 1985). Likewise lakes in medium till and thick till and calcite classes have higher ANC and do not experience elevated concentrations of Alm. Decreases in Al<sub>i</sub> may be one of the most important aspects of decreases in acid deposition because of its adverse effects on aquatic biota at elevated concentrations (Driscoll et al., 2001).

Significant increases in DOC were experienced in 10 of the 16 original ALTM lakes at a mean rate of  $4.5 \pm 3.8 \mu\text{mol C/L-yr}$ , with two of the lakes showing decreases in DOC. Similarly 29 of 48 lakes

(1992–2013) had significant increases in DOC, while two exhibited decreasing trends. One of the lakes, Little Hope Pond, appears to be an outlier as it experienced a relatively rapid rate of DOC decline ( $-10.4 \mu\text{mol C/L-yr}$ ).

## 4. Discussion

### 4.1. Emissions and atmospheric deposition trends

Sulfate and  $\text{NO}_3^-$  concentrations in precipitation and in wet and dry deposition have decreased markedly in Adirondack over the last two decades as a result of declines in  $\text{SO}_2$  and  $\text{NO}_x$  emissions (Figs. 1 and 2). These patterns demonstrate the strong linkage between regulatory programs of emission controls, including the Clean Air Act, the  $\text{NO}_x$  Budget Program, the Clean Air Interstate Rule and the Cross State Air Pollution Rule (Driscoll et al., 2010), and decreases in acid deposition. Indeed the most recent annual volume-weighted  $\text{SO}_4^{2-}$  concentration in precipitation at HF ( $7.9 \mu\text{eq/L}$  in 2014) and WM ( $9.7 \mu\text{eq/L}$  in 2014) are approaching values previously suggested by Galloway et al. (1982) as “background” precipitation concentrations (e.g.,  $7.1 \mu\text{eq/L}$  in Alaska) based on measurements at remote locations. Using the empirical relationship between total U.S.  $\text{SO}_2$  emissions and precipitation  $\text{SO}_4^{2-}$  concentrations at HF (Fig. 1), we might anticipate future concentrations to decrease well below current values if emissions decrease to levels anticipated for the U.S. Environmental Protection Agency Clean Power Plan in 2030 (USEPA, 2015, Fig. 1). In contrast to  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  deposition in the Adirondacks has changed little over time and as a result has become a more prominent component of acid deposition. Ammonia emissions are not regulated and although emissions of  $\text{NH}_3$  are uncertain they probably have been relatively constant in the Northeast in recent years. However, like  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  is acidifying deposition, as it can oxidize and contribute to soil and surface water acidification.

Estimates from CASTNET (Fig. 2) suggest that dry deposition is a minor component of total acid deposition to this remote region far removed from major emission sources. It has been suggested that dry deposition velocity estimates of  $\text{SO}_2$  and  $\text{HNO}_3$  from CASTNET are generally lower than those used by the Canadian network (CAPMoN) (Schwede et al., 2011), and recent hybrid model/measurement efforts to estimate total deposition (Schwede and Lear, 2014). However, it is noteworthy that despite large decreases in  $\text{SO}_2$  and  $\text{NO}_x$  emissions and both wet and dry deposition of oxidized forms of sulfur and nitrogen, their ratios (dry to wet) have remained relatively constant over the period of observation.

### 4.2. Patterns of lake-watershed response to changing atmospheric deposition

Rates of  $\text{SO}_4^{2-}$  decrease have not been uniform in ALTM lakes in our reports over the measurement interval. The rates of  $\text{SO}_4^{2-}$

concentration decreases were moderate when they were first documented for the Adirondacks in the 1980s ( $-2.33 \pm 0.67 \mu\text{eq/L-yr}$ ; Driscoll and van Dreason, 1993). Rates decreased in the 1990s ( $-2.75 \mu\text{eq/L-yr}$ ; Driscoll et al., 2003) likely due to large decreases in atmospheric  $\text{SO}_4^{2-}$  deposition as a result of  $\text{SO}_2$  emission regulations associated with the 1990 Amendments of the Clean Air Act. The overall rate of  $\text{SO}_4^{2-}$  decrease slowed somewhat as the monitoring was extended to 2004 ( $-2.16 \pm 0.81 \mu\text{eq/L-yr}$ ) (Driscoll et al., 2007), but current values have increased again, likely due to decreases in  $\text{SO}_4^{2-}$  associated with the Clean Air Interstate Rule coupled with a downturn in the economy (less energy demand) and fuel switching associated with relatively cheap and abundant natural gas. Strock et al. (2014) also found greater rates of decreases in  $\text{SO}_4^{2-}$  concentrations in Adirondack and New England lakes in the 2000s than the 1990s. The rate of decreases in lake  $\text{SO}_4^{2-}$  has been relatively spatially uniform across the Adirondacks ( $-1.59$  to  $-2.99 \mu\text{eq/L-yr}$ ) suggesting that decreases in  $\text{SO}_2$  emissions and atmospheric  $\text{SO}_4^{2-}$  deposition are an important driver of this trend. However, there is some variability in rates of decrease in  $\text{SO}_4^{2-}$  concentrations among ALTM lake-watersheds which is likely due to spatial patterns in atmospheric  $\text{SO}_4^{2-}$  deposition across the Adirondacks (Driscoll et al., 1991), coupled with landscape variation in biogeochemical processes, including vegetation and landcover (wetlands), soils and surficial geology, and in-lake processes.

Rates of decrease in  $\text{SO}_4^{2-}$  concentrations we observe for Adirondack lakes are generally consistent with spatial patterns observed across eastern North America (Strock et al., 2014). A regional analysis of surface water chemistry trends was conducted through the 1990s to characterize the response to changes in atmospheric deposition (Kahl et al., 2004). Rates of  $\text{SO}_4^{2-}$  decrease were greatest in lakes of the Upper Midwest ( $-3.36 \mu\text{eq/L-yr}$ ), with values decreasing eastward in Appalachian streams ( $-2.27 \mu\text{eq/L-yr}$ ) and New England lakes ( $-1.77 \mu\text{eq/L-yr}$ ), consistent with a spatial gradient of  $\text{SO}_2$  emissions and  $\text{SO}_4^{2-}$  deposition (Driscoll et al., 2001). In contrast, streams draining the unglaciated Ridge and Blue Ridge Provinces of the southeastern U.S. generally experienced increasing  $\text{SO}_4^{2-}$  concentrations as watersheds approached steady-state with respect to retention of  $\text{SO}_4^{2-}$  by highly weathered soils. The decreases in  $\text{SO}_4^{2-}$  for Adirondack lakes ( $-2.26 \mu\text{eq/L-yr}$ ) reported by Kahl et al. (2004) were somewhat lower than our values, likely due to the earlier period over which their time-series analysis were conducted.

Rates of  $\text{SO}_4^{2-}$  decline observed for the Adirondacks are comparable to median estimates for surface waters in Europe ( $-1.92 \mu\text{eq/L-yr}$ ). European values ranged from lower rates of  $\text{SO}_4^{2-}$  decline in surface waters of the United Kingdom ( $-1.10 \mu\text{eq/L-yr}$ ) and Italy ( $-1.00 \mu\text{eq/L-yr}$ ), regions experiencing lower acid deposition, to greater decreases in areas of historically elevated deposition such as the Czech Republic ( $-3.47 \mu\text{eq/L-yr}$ ) and Slovakia ( $-4.17 \mu\text{eq/L-yr}$ ; Evans et al., 2001).

Widespread decreases in  $\text{NO}_3^-$  in drainage lakes across the Adirondacks, may be suggestive of a regional driver (or combination of drivers) of N change (e.g., decreases in N deposition,  $\text{CO}_2$  fertilization, climate change). Other investigations of forest mountain watersheds in the Northeast have reported decreases in surface water  $\text{NO}_3^-$  concentrations (Goodale and Aber, 2001; Kahl et al., 2004; Yanai et al., 2013). Interestingly, this pattern of decreasing  $\text{NO}_3^-$  concentrations runs counter to theoretical expectations that watersheds should be approaching a condition of N saturation (Aber et al., 1989). As discussed, regional decreases in emissions of  $\text{NO}_x$  and atmospheric  $\text{NO}_3^-$  deposition likely contribute to the widespread decreases in lake  $\text{NO}_3^-$  concentrations (Fig. 2). Researchers have also speculated that fertilization of forests associated with increases in atmospheric  $\text{CO}_2$  and climate change may be driving increases in watershed N retention and contributing to

long-term decreases in surface water  $\text{NO}_3^-$  (Aber et al., 2002; Duran et al., 2016; Oren et al., 2001; Pourmohktarian et al., 2012).

Increases in ANC observed in Adirondack lakes can be largely attributed to decreases in  $\text{SO}_4^{2-} + \text{NO}_3^-$  concentrations, resulting from decreases in acid deposition. It is encouraging that many acid-impacted lakes are experiencing increases in ANC. This pattern is indicative of the success of emission control strategies to mitigate surface water acidification. However, at current rates of ANC increase and with the generally slow biological response to chemical changes, it will likely be decades before acid-impacted Adirondack lakes support a diverse biological community (Driscoll et al., 2001, 2003; Fakhraei et al., 2014; Baldigo et al., 2016 this issue), although biological recovery has been noted in some Adirondack lakes (Josephson et al., 2014). The rate and extent of aquatic biological recovery may depend on the extent acidification of lakes during the most severe conditions in the 1980–90s (Fakhraei et al., 2014). Those lakes that were strongly impaired (e.g. chronically acidic with ANC less than  $0 \mu\text{eq/L}$ ) will likely recover more slowly than lakes with less severe acidification.

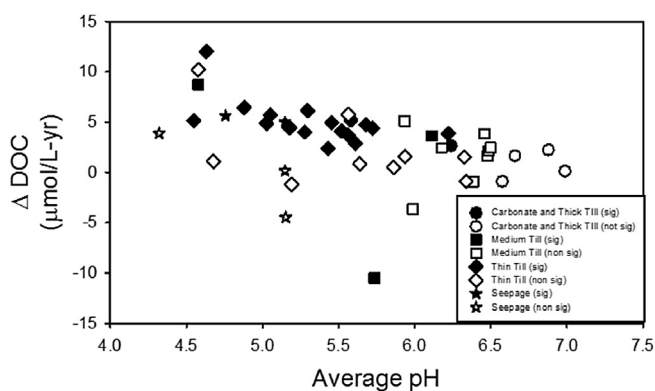
We use a stoichiometric approach to compare recovery of Adirondack lakes from decreases in acid deposition for the Adirondacks with other regions (Table 2). Lakes in the Upper Midwest of the U.S. have exhibited a mixture of decreased  $\text{C}_B$  leaching and ANC increase per unit decrease  $\text{SO}_4^{2-} + \text{NO}_3^-$  (Kahl et al., 2004). This pattern may be due to the relatively large number of seepage lakes monitored in this region. Lakes in New England and Appalachian streams largely responded to a unit decreases in  $\text{SO}_4^{2-} + \text{NO}_3^-$  from acid deposition through decreases in leaching of  $\text{C}_B$ , with little increase in ANC. For European surface waters from a variety of countries, unit decreases  $\text{SO}_4^{2-} + \text{NO}_3^-$  resulting in both increases in ANC and decreases in  $\text{C}_B$  leaching (Evans et al., 2001).

#### 4.3. Future research directions

One the most intriguing observations from the ALTM program is the increased mobilization of DOM or “browning” of many Adirondack lakes. Several processes potentially contribute to increases in lake DOC (Clark et al., 2010). Monteith et al. (2007) observed that increases in DOC in surface waters of Northern Europe and North America appears to be consistent with decreases in acid deposition. Increases in pH decrease the partitioning of DOC to soil surfaces (Ussiri and Johnson, 2004). Other investigators have suggested that increases in DOC may be the result of a “salt effect” manifested through decreases in ionic strength due to decreases in acid deposition (Tipping and Hurley, 1988; Filius et al., 2000). Researchers have also hypothesized that changing climate is driving increases in DOC (Clark et al., 2010), likely associated with increases in precipitation quantity and increasing water flows during high discharge events along shallow flowpaths. Although there is considerable variability in DOC trends with many lakes not showing significant trends, we observe that in general the rate of increases in DOC increases with decreases in mean lake pH (Fig. 8). This pattern suggests that ANC recovery in chronically acidic or low ANC waters will be limited due to increases in the mobilization of naturally occurring organic acids (Fakhraei and Driscoll, 2015).

Regardless of the mechanism, increases in dissolved organic matter has important implications for lake ecosystems. Dissolved organic matter regulates the attenuation of light and the thermal stratification of Adirondack lakes (Effler et al., 1985). Increases in DOM can extend and strengthen summer stratification, thus counteracting anticipated effects of climate warming. The nutrient dynamics of lakes recovering from decreases acid deposition will likely be strongly affected by increases in DOM due to the supply of associated phosphorus (Gerson et al., 2016). Finally, increases in DOM may serve as a complexing ligand for trace metals (e.g., Al,





**Fig. 8.** Long-term trends in concentrations of dissolved organic carbon in lakes of the Adirondack Long Term Monitoring (ALTM) program (1992–2013) as a function of mean lake pH. Shown are values for different lake classes. Significant relationships ( $p < 0.05$ ) are shown with filled symbols and non-significant relationships are indicated by open symbols.

Hg), likely enhancing transport but also potentially diminishing toxicity. Note however in this regard that we only observed increases in concentrations in organic monomeric Al in 6 of the 48 lakes. There is a critical need to better understand how the browning affects their structure and function of aquatic ecosystems.

While decreases in acid deposition is the major driver of the recovery of Adirondack lakes, coincident with this transformation is changing climate. Like much of the northeastern U.S., climate change in the Adirondacks is manifested through increases in air temperature, particularly since the 1980s, increases in precipitation, decreases in snowpack accumulation and earlier snowmelt with decreases in peak discharge in the spring (Campbell et al., 2009, 2011; Melillo et al., 2014). Regional hydrologic records of remote forest watersheds in the Northeast have shown long-term increases in annual discharge due to increases in precipitation coupled with decreases in evapotranspiration (Campbell et al., 2011). Climate is a fundamental controller of watershed biogeochemical processes and changing climate is undoubtedly affecting ecosystem structure and function (Campbell et al., 2009) and its response to decreases in acid deposition. It is likely that increases in precipitation and runoff are increasing the flushing S and N from watersheds that accumulated in soil during the earlier period of elevated atmospheric deposition and serving to facilitate recovery. As discussed above, increasing temperature and atmospheric concentrations of  $\text{CO}_2$  are likely enhancing tree growth which facilitates watershed N retention. Indeed, Duran et al. (2016) recently hypothesized that climate change is driving the “oligotrophication” of the Northern Forest based on long-term decreases in soil mineralization and nitrification that appear coupled with climatic indicators at the Hubbard Brook Experimental Forest, NH, driving enhanced watershed N retention and counteracting N saturation. Schaefer and Alber (2007) and Schaefer et al. (2009) indicate that increases in temperature increase rates of denitrification enhancing watershed N retention. It seems likely that decreases in ice cover and increases in lake temperature associated with climate change should increase the stratification period and facilitate in-lake processing of solutes (Kelly et al., 1987).

While changing climate is undoubtedly affecting lake-watershed biogeochemical processes and lake recovery from acid deposition, it is also likely changing the endpoints of biological recovery. The lower trophic level organisms are shifting in Adirondack lakes, in part due to recovery from acid deposition and in part due to climate change or other factors (Arseneau et al., 2011). Changes in the lower food chain, species introductions and

invasives, and well as changing habitat are altering Adirondack lake ecosystems towards a new future (Baldigo et al., 2016). So it is unlikely that aquatic communities emerging from the aftermath of acid deposition will be comparable to those before its advent. Clearly future studies need to focus on how the legacies of acid deposition affect the transition of ecosystems under changing climate and how changing climate facilitates or obscures recovery from acid deposition.

## 5. Conclusions

The Adirondacks have experienced marked decreases in both wet and dry S and  $\text{NO}_3^-$  deposition in response to decreases in  $\text{SO}_2$  and  $\text{NO}_x$  emissions, respectively, but no change in the dry to wet deposition ratios was evident. The magnitude of decreases in precipitation  $\text{SO}_4^{2-}$  is particularly noteworthy as concentrations approach “pre-industrial” values estimated from early measurements at remote locations. If the empirical relationships between  $\text{SO}_2$  emissions and precipitation  $\text{SO}_4^{2-}$  hold, concentrations might be expected to decrease further in the future due to decreases in emissions anticipated under the U.S. Environmental Protection Agency Clean Power Plan. Lake concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  and, to a lesser extent  $\text{NO}_3^-$ , have decreased in concert with decreases in atmospheric deposition. There has been widespread increases in lake ANC in response to decreases in acid deposition, with the rate of recovery similar across hydrologic lake classes. However, decreases in the acid sensitive thin till watershed class has shown marked decreases in the toxic inorganic fraction of Al<sub>m</sub>. There appears to have been compensatory increases in concentrations of dissolved organic matter in response to decreases in acid deposition, which acts as an organic acid offsetting increases in ANC and could affect physical and biogeochemical processes in the trajectory of recovering lake ecosystems.

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## References

- Aber, J.D., Nadelhoffer, K.J., Steudler, P., Melillo, J.M., 1989. Nitrogen saturation in northern forest ecosystems. *BioScience* 39, 378–386.
- Aber, J.D., Ollinger, S.V., Driscoll, C.T., Likens, G.E., Holmes, R.T., Freuder, R.J., Goodale, C.L., 2002. Inorganic N losses from a forested ecosystem in response to physical, chemical, biotic and climatic perturbances. *Ecosystems* 5, 648–658.
- Arseneau, K.M.A., Driscoll, C.T., Brager, L., Ross, K.A., Cumming, B.F., 2011. Recent evidence of biological recovery from acidification in the Adirondacks (NY, USA): a multi-proxy paleolimnological investigation of Big Moose Lake. *Can. J. Fish. Aquat. Sci.* 68, 575–592.
- Baker, J.P., Gherini, S.A., Christensen, S.W., Munson, R.K., Driscoll, C.T., Newton, R.M., Gallagher, J., Reckhow, K.H., Schofield, C.L., 1990. Adirondack Lakes Survey: an Interpretive Analysis of Fish Communities and Water Chemistry, 1984–87. Adirondack Lakes Survey Corporation. Ray Brook, NY.
- Baldigo, B.P., Roy, K.M., Driscoll, C.T., 2016. Response of fish assemblages to declining acidic deposition in Adirondack Mountain lakes 1984–2012. *Atmos. Environ.* <http://dx.doi.org/10.1016/j.atmosenv.2016.06.049>.
- Campbell, J.L., Driscoll, C.T., Pourmoghkhtarian, A., Hayhoe, K., 2011. Streamflow responses to past and projected future changes in climate at the Hubbard Brook Experimental Forest, New Hampshire, United States. *Water Resour. Res.* 47, 15. W02514.
- Campbell, J.L., Rustad, L.E., Boyer, E.W., Christopher, S.F., Driscoll, C.T., Fernandez, I.J., Goffman, P.M., Houle, D., Kiebusch, J., Magill, A.H., Mitchell, M.J., Ollinger, S.V., 2009. Consequences of climate change for biogeochemical cycling in forests of northeastern North America. *Can. J. For. Res.* 39, 264–284.

- Clark, J.M., Bottrell, S.H., Evans, C.D., Monteith, D.T., Bartlett, R., Rose, R., Newton, R.J., Chapman, P.J., 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Sci. Total Environ.* 408, 2768–2775.
- Driscoll, C.T., Baker, J.P., Bisogni, J.J., Schofield, C.L., 1980. Effect of aluminum speciation on fish in dilute acidified waters. *Nature* 284, 161–164.
- Driscoll, C.T., Cowling, E.B., Grennfelt, P., Galloway, J., Dennis, R., 2010. Integrated assessment of ecosystem effects of atmospheric deposition: lessons available to be learned. *EM Mag.* 6–13. November 2010.
- Driscoll, C.T., Driscoll, K.M., Roy, K.M., Dukett, J., 2007. Changes in the chemistry of lakes in the Adirondack region of New York following declines in acidic deposition. *Appl. Geochem* 22, 1181–1188.
- Driscoll, C.T., Driscoll, K.M., Roy, K.M., Mitchell, M.J., 2003. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environ. Sci. Technol.* 37, 2036–2042.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. *BioScience* 51, 180–198.
- Driscoll, C.T., Newton, R.M., 1985. Chemical characteristics of acid-sensitive lakes in the Adirondack Region of New York. *Environ. Sci. Technol.* 19, 1018–1024.
- Driscoll, C.T., Newton, R.M., Gubala, C.P., Baker, J.P., Christensen, S.W., 1991. Adirondack mountains. In: Charles, D.F. (Ed.), *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*. Springer-Verlag, New York, pp. 133–202.
- Driscoll, C.T., Postek, K.M., 1996. The chemistry of aluminum in surface waters. In: Sposito, G. (Ed.), *The Environmental Chemistry of Aluminum*. Lewis Publishers, Chelsea, MI, pp. 363–418.
- Driscoll, C.T., van Dreason, R., 1993. Seasonal and long-term temporal patterns in the chemistry of Adirondack Lakes. *Water Air Soil Poll.* 67, 319–344.
- Duran, J., Morse, J.L., Groffman, P.M., Campbell, J.L., Christenson, L.M., Driscoll, C.T., Fahey, T.J., Fisk, M.C., Likens, G.E., Melillo, J.M., Mitchell, M.J., Templer, P.H., Vadeboncoeur, M.A., 2016. Climate change decreases nitrogen pools and mineralization rates in northern hardwood forests. *Ecosphere* 7 (3). <http://dx.doi.org/10.1002/ecs2.1251>.
- Effler, S.W., Schafran, G.C., Driscoll, C.T., 1985. Partitioning light attenuation in an acidic lake. *Can. J. Fish. Aquat. Sci.* 42, 1707–1711.
- Evans, C.D., Cullen, J.M., Alewell, C., Kopacek, J., Marchetto, A., Moldan, F., Prechtel, A., Rogora, M., Vesely, J., Wright, R.F., 2001. Recovery from acidification in European surface waters. *Hydrol. Earth Syst. S. C.* 5, 283–298.
- Fakhraei, H., Driscoll, C.T., 2015. Proton and aluminum binding properties of organic acids in surface waters of the Northeastern, USA. *Environ. Sci. Technol.* 49, 2939–2947.
- Fakhraei, H., Driscoll, C.T., Selvendiran, P., DePinto, J.V., Bloomfield, J., Quinn, S., Rowell, C., 2014. Development of a total maximum daily load (TMDL) for acid-impaired lakes in the Adirondack region of New York. *Atmos. Environ.* 95, 277–287.
- Filius, J.D., Lumsdon, D.G., Meeussen, J.C.L., Hiemstra, T., Van Riemsdijk, W.H., 2000. Adsorption of fulvic acid on goethite. *Geochim. Cosmochim. Acta* 64, 51–60.
- Galloway, J.N., Likens, G.E., Keene, W.C., Miller, J.M., 1982. The composition of precipitation in remote areas of the world. *J. Geophys. Res.-Oc. Atm* 87, 8771–8786.
- Galloway, J.N., Norton, S.A., Church, M.R., 1983. Freshwater acidification from atmospheric deposition of sulfuric acid: a conceptual model. *Environ. Sci. Technol.* 17, 541A–545A.
- Gerson, J.R., Driscoll, C.T., Roy, K.M., 2016. Patterns of nutrient dynamics in Adirondack lakes recovering from acid deposition. *Ecol. Appl.* <http://dx.doi.org/10.1890/15-1361.1>.
- Goodale, C.L., Aber, J.D., 2001. The long-term effects of land-use history on nitrogen cycling in northern hardwood forests. *Ecol. Appl.* 11, 253–267.
- Greaver, T.L., Sullivan, T.J., Herrick, J.D., Barber, M.C., Baron, J.S., Cosby, B.J., Deerpake, M.E., Dennis, R.L., Dubois, J.J.B., Goodale, C.L., Herlihy, A.T., Lawrence, G.B., Liu, L.L., Lynch, J.A., Novak, K.J., 2012. Ecological effects of nitrogen and sulfur air pollution in the US: what do we know? *Front. Ecol. Environ.* 10, 365–372.
- Hirsch, R.M., Slack, J.R., 1984. A nonparametric trend test for seasonal data with serial dependence. *Water Resour. Res.* 20, 727–732.
- Johnson, D.W., 1984. Sulfur cycling in forests. *Biogeochemistry* 1, 29–43.
- Johnson, D.W., Todd, D.E., 1983. Relationships among iron, aluminum, carbon, and sulfate in a variety of forest soils. *Soil Sci. Soc. Am. J.* 47, 792–800.
- Josephson, D.C., Robinson, J.M., Chiotti, J., Jirka, K.J., Kraft, C.E., 2014. Chemical and biological recovery from acid deposition within the Honnedaga Lake watershed, New York, USA. *Environ. Monit. Assess.* 186 (7), 4391–4409. <http://dx.doi.org/10.1007/s10661-014-3706-9>.
- Kahl, J.S., Stoddard, J.L., Haeuber, R., Paulsen, S.G., Birnbaum, R., Deviney, F.A., Webb, J.R., DeWalle, D.R., Sharpe, W., Driscoll, C.T., Herlihy, A.T., Kellogg, J.H., Murdoch, P.S., Roy, K., Webster, K.E., Urquhart, N.S., 2004. Have U.S. Surface waters responded to the 1990 clean air act Amendments? *Environ. Sci. Technol.* 38, 484A–490A.
- Kelly, C.A., Rudd, J.W.M., Hesslein, R.H., Schindler, D.W., Dillon, P.J., Driscoll, C.T., Gherini, S.A., Hecky, R.E., 1987. Prediction of biological acid neutralization in acid-sensitive lakes. *Biogeochemistry* 3, 129–140.
- Kretzer, W.J., Gallagher, J., Nicolette, J., 1989. An Evaluation of Fish Communities and Water Chemistry. Adirondack Lakes Survey Corporation. Ray Brook, NY.
- Lehmann, C.M.B., Bowersox, V.C., Larson, S.M., 2005. Spatial and temporal trends of precipitation chemistry in the United States, 1985–2002. *Environ. Pollut.* 135, 347–361.
- Likens, G.E., Driscoll, C.T., Buso, D.C., 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272, 244–246.
- Lovett, G.M., Likens, G.E., Buso, D.C., Driscoll, C.T., Bailey, S.W., 2005. The biogeochemistry of chlorine at Hubbard Brook, New Hampshire, USA. *Biogeochemistry* 72, 191–232.
- Melillo, J.M., Richmond, T.C., Yohe, G.W. (Eds.), 2014. *Climate Change Impacts in the United States: the Third National Climate Assessment*. U.S. Global Change Research Program. <http://dx.doi.org/10.7930/J0231WJ2>, 841 pp.
- Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopáček, J., Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450, 537–540.
- Oren, R., Ellsworth, D.S., Johnsen, K.H., Phillips, N., Ewers, B.E., Maier, C., Schafer, K.V.R., McCerthy, H., Hendry, G., McNulty, S.G., Katul, G.G., 2001. Soil fertility limits carbon sequestration by forest ecosystems in a CO<sub>2</sub>-enriched atmosphere. *Nature* 411, 469–472.
- Pourmokhtarian, A., Driscoll, C.T., Campbell, J.L., Hayhoe, K., 2012. Modeling potential hydrochemical responses to climate change and rising CO<sub>2</sub> at the Hubbard Brook Experimental Forest using a dynamic biogeochemical model (PnET-BGC). *Water Resour. Res.* 48, 13. W07514.
- Rice, K.C., Scanlon, T.M., Lynch, J.A., Cosby, B.J., 2014. Decreased atmospheric sulfur deposition across the Southeastern US: when will watersheds release stored sulfate? *Environ. Sci. Technol.* 48, 10071–10078.
- Rochelle, B.P., Church, M.R., 1987. Regional patterns of sulfur retention in watersheds of the eastern US. *Water Air Soil Pollut.* 36, 61–73.
- Schaefer, S.C., Alber, M., 2007. Temperature controls latitudinal gradient in the proportion of watershed nitrogen exported to coastal ecosystems. *Biogeochemistry* 85, 333–346.
- Schaefer, S.D., Hollibaugh, J.T., Alber, M., 2009. Watershed nitrogen input and riverine export on the west coast of the US. *Biogeochemistry* 93, 219–233.
- Schwede, D., Lear, G., 2014. A novel hybrid approach for estimating total deposition in the United States. *Atmos. Environ.* 92, 207–220.
- Schwede, D., Zhang, L., Vet, R., Lear, G., 2011. An intercomparison of the deposition models used in the CASTNET and CAPMoN networks. *Atmos. Environ.* 45, 1337–1346.
- Strock, K.E., Nelson, S.J., Kahl, J.S., Saros, J.E., McDowell, W.H., 2014. Decadal trends reveal recent acceleration in the rate of recovery from acidification in the Northeastern US. *Environ. Sci. Technol.* 48, 4681–4689.
- Tipping, E., Hurley, M.A., 1988. A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances. *J. Soil Sci.* 39, 505–519.
- USEPA, 2015. [U.S. Environmental Protection Agency]. *Clean Power Plan for Existing Power Plants. Policies and Guidance*. <http://www2.epa.gov/cleanpowerplan/clean-power-plan-existing-power-plants>.
- Ussiri, D.A.N., Johnson, C.E., 2004. Sorption of organic carbon fractions by spodosol mineral horizons. *Soil Sci. Soc. Am. J.* 68, 253–262.
- Waller, K., Driscoll, C.T., Lynch, J., Newcomb, D., Roy, K., 2012. Long-term recovery of lakes in the Adirondack region of New York to decreases in acidic deposition. *Atmos. Environ.* 46, 56–64.
- Warby, R.A.F., Johnson, C.E., Driscoll, C.T., 2005. Chemical recovery of surface waters across the northeastern United States from reduced inputs of acidic deposition: 1984–2001. *Environ. Sci. Technol.* 39, 6548–6554.
- Warby, R.A.F., Johnson, C.E., Driscoll, C.T., 2009. Continuing acidification of organic soils across the northeastern USA: 1984–2001. *Soil Sci. Soc. Am. J.* 73, 274–284.
- Yanai, R.D., Vadeboncoeur, M.A., Hamburg, S.P., Arthur, M.A., Fuss, C., Groffman, P.M., Siccama, T.G., Driscoll, C.T., 2013. From missing source to missing sink: long-term changes in the nitrogen budget of a northern hardwood forest. *Environ. Sci. Technol.* 47, 11440–11448.