Policy Analysis

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Chemical Response of Lakes in the Adirondack Region of New York to Declines in Acidic Deposition

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Long-term changes in the chemistry of wet deposition and lake water were investigated in the Adirondack Region of New York. Marked decreases in concentrations of SO_4^{2-} and H^+ in wet deposition have occurred at two sites since the late 1970s. These decreases are consistent with long-term declines in emissions of sulfur dioxide (SO_2) in the eastern United States. Changes in wet NO_3^- deposition and nitrogen oxides (NO_x) emissions have been minor over the same interval. Virtually all Adirondack Lakes have shown marked decreases in concentrations of SO_4^{2-}, which coincide with decreases in atmospheric S deposition. Concentrations of NO_3^- have also decreased in several Adirondack lakes. As atmospheric N deposition has not changed over this period, the mechanism contributing to this apparent increase in lake/watershed N retention is not evident. Decreases in concentrations of $SO_4^{2-} + NO_3^-$ have resulted in increases in acid-neutralizing capacity (ANC) and pH and resulted in a shift in the speciation of monomeric Al from toxic inorganic species toward less toxic organic forms in some lakes. Nevertheless, many lakes continue to exhibit pH values and concentrations of inorganic monomeric Al that are critical to aquatic biota. Extrapolation of rates of ANC increase suggests that the time frame of chemical recovery of Adirondack Lakes will be several decades if current decreases in acidic deposition are maintained.

Introduction

The Adirondack Region of New York probably exhibits the most severe ecological impacts from acidic deposition of any region in North America (*1*). This large forested area (24 000 km²) has long been an indicator of the response of forest and aquatic ecosystems to U.S. policy on atmospheric emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) (*2–4*). Because of bedrock geology and generally shallow surficial deposits, the Adirondack Region is characterized by soils with low pools of available nutrient cations and a large number of lakes that are acidic or sensitive to acidic

deposition (*5*). There are approximately 2770 lakes in the Adirondacks (>2000 m² surface area). A survey of 1469 lakes during 1984–1987 found that 27% of these lakes were chronically acidic (acid-neutralizing capacity (ANC) <0 μequiv L^{-1}), and an additional 21% had summer ANC values between 0 and 50 μequiv L^{-1} and could experience hydrologic events, which decrease ANC values near or below 0 μequiv L^{-1} (*6–8*).

There have been marked changes in emissions of SO_2 and atmospheric deposition of sulfate (SO_4^{2-}) and hydrogen ion (H^+) in the United States since the early 1970s. Following the 1970 Amendments of the Clean Air Act (CAAA), emissions of SO_2 in the United States peaked in 1973 at 28.8 Tg/yr and have declined 38% since that time (*9*). In contrast, emissions of NO_x in the United States peaked in 1990 (21.8 Tg/yr), but values have remained relatively constant since 1980. The 1990 CAAA was the first legislation in the United States to specifically address acidic deposition. Through Title IV of the 1990 CAAA, there will be a 13.2 Tg/yr cap in emissions of SO_2 by 2010, in addition to resulting in a 1.8 Tg/yr reduction in emissions of NO_x from utilities than would be expected without the legislation. However, there is no cap on annual emissions of NO_x. Therefore, emissions may increase with future increases in U.S. population and energy consumption. Despite widespread acclaim of the cost-effectiveness of the 1990 CAAA (*2*), there have been several reports of severe acidification of soil due to accelerated losses of calcium (Ca^{2+}) and magnesium (Mg^{2+}) and limited recovery of acidic surface waters (*10–12*).

The Clean Air Act is due for reauthorization (as of 2000). In addition, there is currently considerable debate over U.S. air pollution and energy policies. In this regard, it is a useful time to examine the most recent patterns in the recovery of lakes in the Adirondack Region in response to U.S. emissions control programs. The Adirondack Long-Term Monitoring Program (ALTM) was established in 1982 to assess seasonal and long-term patterns in the chemistry of lakes in the Adirondack Region of New York. The program was initiated with 17 lakes. It was expanded in 1992 with an additional 35 lakes for a total of 52 sites to improve representation of classes of lakes across the Adirondacks (Table 1). Here we report for the first time trends in the acid–base status for the entire group of ALTM lakes and classes of ALTM lakes relative to changes in wet deposition. Moreover, we extrapolated these trends to estimate time to chemical recovery of Adirondack Lakes.

Methods

In the Adirondacks, wet deposition has been monitored at two sites (the Huntington Forest (HF), 43°58′ N, 74°13′ W, and Whiteface Mountain (WM), 44°24′ N, 73°52′ W) as part of the National Atmospheric Deposition Program (NADP) since 1978. The weekly precipitation collections are measured for major ions using NADP protocols (*13*).

The 52 ALTM lakes are sampled monthly, and the collected waters are measured for major solutes (*14, 15*). The watersheds surrounding ALTM lakes are largely forested, with predominantly hardwood or mixed vegetation. One of the original ALTM lakes (Barnes Pond) and three of the recent group of ALTM lakes (Woods Lake, Little Simon Pond, and Little Clear Pond) were limed (i.e., calcium carbonate addition) in the 1980s to mitigate surface water acidification and therefore have been excluded from this analysis.

There is considerable variability in the response of lake ecosystems to acidic deposition. As a result, we previously have developed a classification system for the acid–base

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TABLE 1. Lakes of Adirondack Lake Term Monitoring (ALTM) Program, Including the Date Monitoring Was Initiated, Location, Lake/Watershed Class, and Characteristics

lake	location	elev (m)	surficial geology	lake type	DOC	max depth (m)	surf. area (ha)	vol (10^4 m^3)
Windfall Pond[a]	43°48′ N, 74°49′ W	601	carbonate influenced	drainage		6.1	2.4	7.8
Moss Lake[a]	43°46′ N, 74°51′ W	536	medium till	chain drainage	low	15.2	45.7	259.8
Cascade Lake Outlet[a]	43°47′ N, 74°49′ W	552	medium till	chain drainage	low	6.1	40.4	17.5
Heart Lake[a]	44°10′ N, 73°58′ W	661	medium till	drainage	low	16.8	10.7	54.5
Arbutus Lake[a]	43°58′ N, 74°14′ W	513	medium till	drainage	low	7.9	48.2	134.5
Black Pond Outlet[a]	44°26′ N, 74°18′ W	497	thick till	chain drainage	low	13.7	29.0	180.5
Clear Pond[a]	43°59′ N, 73°49′ W	583	thick till	drainage	low	24.4	70.4	651.1
Lake Rondaxe[a]	43°45′ N, 74°54′ W	524	thin till	chain drainage	low	10.1	90.5	273.3
Bubb Lake[a]	43°46′ N, 74°50′ W	553	thin till	chain drainage	low	4.3	18.2	38.5
Dart Lake[a]	43°47′ N, 74°52′ W	536	thin till	chain drainage	low	17.7	51.8	380.7
Big Moose Lake[a]	43°49′ N, 74°51′ W	556	thin till	chain drainage	low	21.3	512.5	3488.2
Squash Pond[a]	43°49′ N, 74°53′ W	648	thin till	chain drainage	high	5.8	3.3	4.5
Constable Pond[a]	43°49′ N, 74°48′ W	582	thin till	chain drainage	low	4.0	20.6	43.5
Otter Lake Outlet[a]	43°10′ N, 74°30′ W	488	thin till	chain drainage	low	4.0	14.8	34.1
West Pond[a]	43°48′ N, 74°53′ W	585	thin till	drainage	low	5.2	10.4	15.2
Little Echo Pond[a]	44°18′ N, 74°21′ W	479		seepage	high	4.6	0.8	2.3
Barnes Lake[a]	43°33′ N, 75°13′ W	396		seepage	high	10.1	2.9	13.1
Middle Pond[b]	44°20′ N, 74°22′ W	484	carbonate influenced	drainage		3.3	24.3	36.9
Little Hope Pond[b]	44°30′ N, 74°07′ W	521	medium till	chain drainage	high	6.2	2.8	10.0
Limekiln Lake[b]	43°42′ N, 74°48′ W	576	medium till	chain drainage	low	21.9	186.9	1147.6
Sagamore Lake[b]	43°45′ N, 74°37′ W	580	medium till	chain drainage	high	22.9	68.0	713.1
Big Hope Pond[b]	44°30′ N, 74°07′ W	522	medium till	drainage	high	11.5	8.9	51.6
Grass Pond[b]	43°41′ N, 75°03′ W	546	medium till	drainage	low	5.2	5.3	7.8
Willis Lake[b]	43°22′ N, 74°14′ W	397	medium till	drainage	low	2.7	14.6	22.9
Nate Pond[b]	43°51′ N, 74°05′ W	614	medium till	drainage	high	6.4	8.3	19.4
Little Simon Pond[b]	44°09′ N, 74°26′ W	545	medium till	drainage	low	32.0	57.5	631.3
Raquette Lake Reservoir[b]	43°47′ N, 74°39′ W	570	medium till	drainage	high	3.0	1.5	2.4
Owen Pond[b]	44°19′ N, 73°54′ W	515	thick till	chain drainage	low	9.4	7.6	28.4
Squaw Lake[b]	43°38′ N, 74°44′ W	645	thin till	chain drainage	low	6.7	36.4	124.9
Indian Lake[b]	43°37′ N, 74°45′ W	654	thin till	chain drainage	low	10.7	33.2	98.1
South Lake[b]	43°30′ N, 74°52′ W	615	thin till	chain drainage	low	18.3	197.4	1630.2
North Lake[b]	43°31′ N, 74°56′ W	555	thin till	chain drainage	low	17.7	176.8	1010.7
Lake Colden[b]	44°07′ N, 73°58′ W	842	thin till	chain drainage	low	7.3	15.4	35.5
Queer Lake[b]	43°48′ N, 74°48′ W	597	thin till	chain drainage	low	21.3	54.5	596.0
East Copperas Pond[b]	44°18′ N, 74°22′ W	479	thin till	drainage	high	6.4	3.6	14.8
Marcy Dam Pond[b]	44°09′ N, 73°57′ W	715	thin till	drainage	low	2.4	1.2	0.8
Loon Hollow Pond[b]	43°57′ N, 75°02′ W	607	thin till	drainage	low	11.6	5.7	19.1
Willys Lake (Horseshoe)[b]	43°58′ N, 74°57′ W	630	thin till	drainage	low	13.7	24.3	118.8
Woods Lake[b]	43°52′ N, 74°58′ W	607	thin till	drainage	low	10.1	24.7	
Middle Settlement Lake[b]	43°41′ N, 75°06′ W	526	thin till	drainage	low	11.0	15.8	54.5
Middle Branch Lake[b]	43°41′ N, 75°06′ W	494	thin till	drainage	low	5.2	17.0	36.3
Brook Trout Lake[b]	43°36′ N, 74°39′ W	722	thin till	drainage	low	23.2	28.7	242.0
Lost Pond[b]	43°38′ N, 74°33′ W	584	thin till	drainage	high	1.2	4.4	3.2
Jockeybush Lake[b]	43°18′ N, 74°35′ W	599	thin till	drainage	low	11.3	17.3	78.6
Long Pond[b]	43°50′ N, 74°28′ W	570	thin till	drainage	high	4.0	1.7	3.3
Avalanche Lake[b]	44°07′ N, 73°58′ W	873	thin till	drainage	low	7.0	4.4	14.6
G Lake[b]	43°25′ N, 74°38′ W	619	thin till	drainage	low	9.8	32.2	143.7
Sunday Pond[b]	44°20′ N, 74°18′ W	485		seepage	low	11.0	4.0	21.9
Sochia Pond[b]	44°21′ N, 74°17′ W	500		seepage	low	5.5	1.6	5.0
Grass Pond[b]	44°39′ N, 74°29′ W	384		seepage	high	7.0	1.6	6.8
Little Clear Pond[b]	44°39′ N, 74°29′ W	384		seepage	low	14.0	1.9	10.2
Carry Pond[b]	43°40′ N, 74°29′ W	649		seepage	low	4.6	2.8	6.2

[a] Record start 1982. [b] Record start 1992.

status of Adirondack Lakes, largely based on characteristics of surficial geology and hydrologic flow paths (*15*, *16*). Drainage lakes situated in watersheds with predominantly shallow deposits of glacial till (thin till watersheds; <5% of the watershed containing thick, i.e., >3 m depth, deposits of glacial till) are very sensitive to acidic deposition and are typically chronically acidic (ANC <0 μequiv L^{-1}). Eight of the original and 26 of the entire group of ALTM lakes are in the thin till drainage class. Lakes located in watersheds with intermediate deposits of glacial till (5−25% of watershed area contains thick deposits of glacial till) generally have positive but low ANC values and are susceptible to short-term acidification associated with snowmelt or storm events. Four of the original and 12 of the entire group ALTM lakes are in the medium till drainage class. Drainage lakes with water-

sheds containing calcite or with more than 25% of the watershed with thick deposits of glacial till or stratified drift are insensitive to acidic deposition. Two of the original and three of the entire group of ALTM lakes are in the thick till drainage class, and one of the original and two of the entire group have calcite in the watershed, for a total of five lakes considered insensitive to acidic deposition. Adirondack Lakes also include mounded seepage lakes, which receive most of their water directly from precipitation. One of the original and five of the entire group of ALTM lakes are mounded seepage lakes. In contrast, groundwater flow-through seepage lakes largely receive water from groundwater inflows and are relatively insensitive to acidic deposition. The ALTM program does not have lakes in this class. Wetlands are an important feature of the Adirondack landscape. Wetlands

TABLE 2. Slopes of Significant (at $p < 0.05$) Changes in Concentration of Solutes in Wet Deposition at Huntington Forest and Whiteface Mountain (in μequiv L^{-1} yr^{-1}) from 1978 to 2000[a]

site	SO_4^{2-}	NO_3^-	C_B	NH_4^+	H^+
Huntington Forest	−1.02	−0.29	−0.33	ns	−0.66
Whiteface Mountain	−1.19	ns	−0.13	ns	−0.89

[a] C_B is the sum of basic cations. Nonsignificant trends are indicated as ns.

supply naturally occurring organic acids to surface waters. Each of the Adirondack lake classes is designated as containing high or low concentrations of naturally occurring organic acids on the basis of the concentrations of dissolved organic carbon (DOC; > or < 500 μmol of C/L, respectively; Table 1).

The nonparametric seasonal Kendall Tau (SKT) test was used to detect monotonic trends (generally increasing or decreasing over time) in solute concentrations in precipitation and lake water (17). The tests were run for precipitation chemistry at HF and WM, the original 16 ALTM lakes (1982−2000) that were not limed, and the entire 48 ALTM lakes that were not limed (1992−2000). The SKT test is a robust time−series procedure for data that are nonnormal and characterized by seasonal patterns. This approach corrects data with moderate levels of serial correlation. We used $p < 0.1$ as our criteria for a significant trend.

Results and Discussion

Trends in Atmospheric Deposition. Long-term changes in the chemistry of precipitation have been evident in recent years across the eastern United States (12, 18). NADP sites in the Adirondacks have shown similar changes in the chemical composition of wet deposition (Table 2). Both HF and WM have exhibited declines in concentrations of most major solutes, such that over the last 22 years decreases in the sum of concentrations of strong acid anions (SO_4^{2-} + NO_3^- + Cl$^-$) have greatly exceeded decreases in concentration of the sum of basic cations (C_B = Ca^{2+} + Mg^{2+} + Na$^+$ + K$^+$) plus ammonium (NH$_4^+$), resulting in marked decreases in concentrations of hydrogen ion (H$^+$). For HF, the pH of precipitation has increased from 4.18 in 1979−1981 to 4.5 in 1998−2000. Similarly, the pH of precipitation at WM has increased from 4.1 (1979−1981) to 4.5 (1998−2000).

The most conspicuous change in precipitation chemistry over the last 20 years has been marked decreases in concentrations of SO_4^{2-}. These decreases are clearly driven by reductions in emissions of SO$_2$ that have occurred over the same period. Annual volume-weighted concentration of SO_4^{2-} at HF ($r^2 = 0.38$) and WM ($r^2 = 0.58$) were positively correlated with annual emissions of SO$_2$ from the source area for the northeastern United States (Maine, Vermont, New Hampshire, Massachusetts, Connecticut, Rhode Island, New York, New Jersey, Delaware, Maryland, Virginia, Pennsylvania, Ohio, Indiana, Michigan, North Carolina, West Virginia, Illinois, Kentucky, and Tennessee based on 21-h back-trajectory analysis; 19). Unlike SO$_2$, there was no relationship between emissions of NO$_x$ and precipitation concentrations of NO$_3^-$. This lack of a relationship may reflect the fact that emissions of NO$_x$ have changed little over the study and by the complexities of NO$_3^-$ deposition processes.

Trends in Lake Sulfate and Nitrate. As observed for patterns of wet deposition, there have been marked changes in the chemical composition of Adirondack Lakes in recent years. All of the original ALTM lakes have shown significant ($p < 0.05$) decreases in concentrations of SO_4^{2-} since 1982, with a mean rate of decline of 2.06 μequiv L^{-1} yr^{-1} (e.g., Figures 1 and 2). The range of this decline was remarkably uniform

(−1.53 to −2.50 μequiv L^{-1} yr^{-1}) across the region and strongly suggests that decreases in SO$_2$ emissions and atmospheric SO_4^{2-} deposition are responsible for this change. The rate of SO_4^{2-} decrease was more rapid in lakes in the thin till drainage class (mean value −2.27 μequiv L^{-1} yr^{-1}) as compared to the medium and thick till drainage classes (mean value −1.77 μequiv L^{-1} yr^{-1}). This difference may reflect less attenuation of atmospheric S deposition in shallow surficial materials. This pattern suggests that lakes in the most sensitive and impacted drainage class (i.e., thin till) are the most responsive to controls in SO$_2$ emissions. Similar decreases in concentrations of SO_4^{2-} were evident for the entire 48 ALTM lakes sampled since 1992. Forty-four of the 48 lakes studied showed a significant decrease in concentrations of SO_4^{2-} ($p < 0.1$). (One lake showed a significant increase in SO_4^{2-} concentrations.) Although the rate of SO_4^{2-} decline for the more recent interval (1992−2000) was more variable (−4.93 to −0.80 μequiv L^{-1} yr^{-1}) than observed for the lakes with the longer record, the mean rate of decline for those lakes with significant decreasing trends was greater (−2.57 μequiv L^{-1} yr^{-1}) than that observed for the longer period (−2.06 μequiv L^{-1} yr^{-1}). Similarly, the original 16 ALTM show a greater rate of SO_4^{2-} decline since 1992 (−2.67 μequiv L^{-1} yr^{-1}) than observed for the longer interval.

The rate of decline in lake SO_4^{2-} concentrations we observed for the Adirondacks spans the range of values reported previously for eastern North America. Mattson et al. (20) observed that the average rate of SO_4^{2-} decrease for 300 streams in Massachusetts (−1.8 μequiv L^{-1} yr^{-1}) was similar to our observed values for the Adirondacks. Stoddard et al. (11) conducted a regional analysis of trends in surface water chemistry with respect to changes in atmospheric deposition from the early 1980s to 1995. For the Adirondack and Catskill Regions of New York, they reported lower rates of decreases in SO_4^{2-} concentrations than we observed, particularly for the 1990s (−0.9 μequiv L^{-1} yr^{-1}). Moreover, they reported a faster rate of SO_4^{2-} decline in the 1980s as compared to the early 1990s. They observed decreases in surface water concentrations of SO_4^{2-} in the 1980s and 1990s throughout eastern North America, including Maine/Atlantic Canada, Vermont/Quebec, South/Central Ontario, and Midwestern North America, with these regions all showing greater rates of decline in the 1990s than the 1980s.

Unlike SO_4^{2-}, trends in lake NO_3^- concentrations have not been consistent over the record. For the first time since monitoring was initiated in 1982, many of the ALTM lakes showed significant decreases in concentrations of NO_3^-. Of the original ALTM lakes, 8 of the 16 sites exhibited a significant decrease in NO_3^- ($p < 0.1$; mean value −0.44 μequiv L^{-1} yr^{-1}, range −0.21 to −0.66 μequiv L^{-1} yr^{-1}). Only the mounded seepage lake (Little Echo Pond) had a small but significant increase in concentrations of NO_3^- (0.01 μequiv L^{-1} yr^{-1}; $p < 0.06$). These trends of decreases in concentrations of NO_3^- in the Adirondack Lakes are different than patterns reported previously for the same lakes. Driscoll and Van Dreason (14) conducted time−series for the original 16 ALTM lakes from 1982 to 1991 and reported that many (9 of 16) had a pattern of increasing NO_3^- concentration. This trend of increasing NO_3^- generally offset a pattern of decreasing SO_4^{2-} concentrations, resulting in no change or in some cases decreases in surface water ANC (5 of 16 lakes) at that time. There was some speculation in this and other papers (4, 21, 22) that long-term increases in NO_3^- indicate that forest watersheds are approaching a condition of N saturation with respect to atmospheric inputs of N. This condition is thought to occur under elevated atmospheric N deposition and decreasing watershed retention of N associated with relatively mature forest ecosystems with a history of limited land disturbance (e.g., not previously in agriculture or severely burned). More recently, Driscoll et al. (15) conducted a time−series analysis
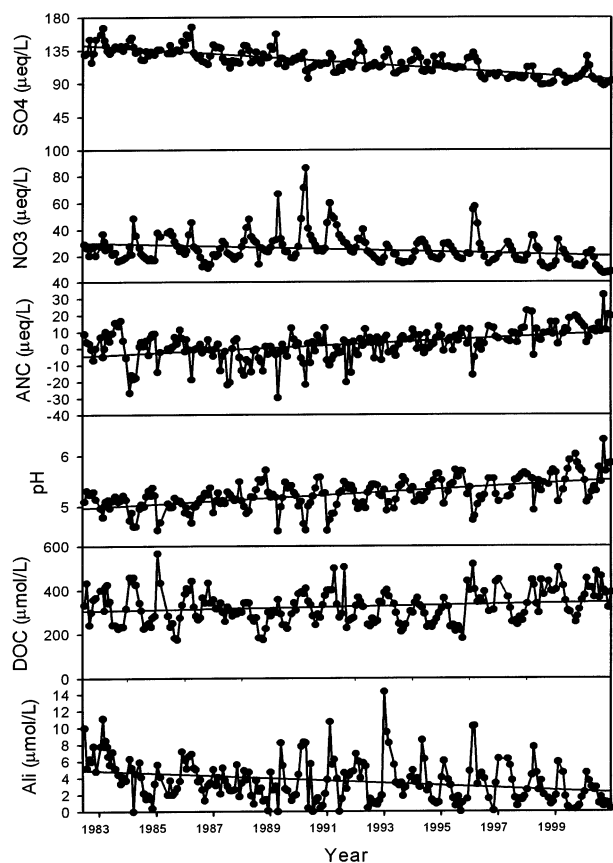
FIGURE 1. Concentrations of SO_4^{2-} (a), NO_3^- (b), acid-neutralizing capacity (ANC; c), pH (d), dissolved organic carbon (DOC; e), and monomeric Al (f) in Big Moose Lake. A significant trend is indicated by a line.
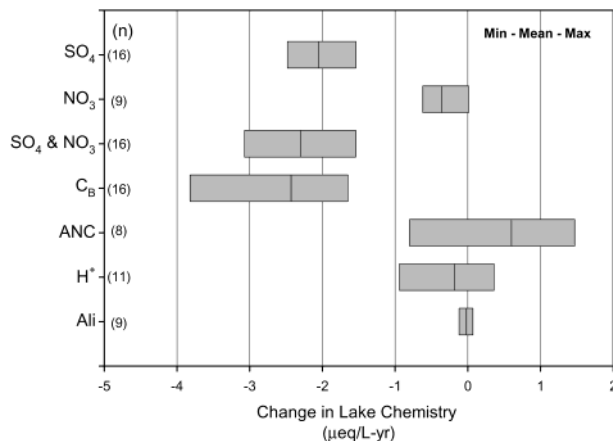

FIGURE 2. Mean rates of change in solute concentration in 16 lakes of the Adirondack Long-Term Monitoring (ALTM) program from 1982 to 2000. Minimum, mean, and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in μequiv L^{-1} yr^{-1}, except for concentrations of inorganic monomeric aluminum (Ali), which is expressed in μmol L^{-1} yr^{-1}.

of the original 16 ALTM lakes over the period 1982−1997, finding essentially no long-term trends in lake NO_3^-. For the 15-yr interval, the increases in lake NO_3^- observed in the 1980s had changed such that trends were no longer significant. Our most recent analysis shows this pattern of NO_3^- concentrations has essentially completely reversed from previous analyses (e.g., Figure 1). This trend is confirmed from time−series analysis for the complete group of ALTM lakes for the interval 1992−2000. Sixteen of the 48 lakes showed significant changes in concentrations of NO_3^- ($p <$ 0.1), with 15 showing decreasing trends. Although 8 yr is a relatively short period to conduct time−series analysis, particularly for a solute that is so inherently variable and susceptible to disturbance like NO_3^-, these data suggest that the 1990s was generally a period of decreasing concentrations of NO_3^- for a portion of Adirondack Lakes.

It is not clear why some Adirondack watersheds are retaining N to a greater extent than was observed in the 1980s. This pattern of decreasing NO_3^- loss runs counter to what would be expected if the Adirondacks were approaching a condition of N saturation. As discussed above, there has not been any appreciable change in emissions of NO_x or atmospheric NO_3^- deposition since the ALTM program began in 1982. Using the model PnET-CN to gain insight, Aber and co-workers (23, 24) observed that long-term (~30 yr; from 1963 to the early 1990s) patterns in stream NO_3^- loss at the Hubbard Brook Experimental Forest in New Hampshire were largely explained by long-term climatic patterns and minor disturbance events (e.g., insect defoliation). However, the pattern of decreasing stream NO_3^- concentrations through the 1990s could not be explained by climate. Using the model, these investigators speculated that the long-term decreased NO_3^- was associated with increased retention of N due a

fertilization effect from increases in atmospheric CO_2. Recent experiments have shown that increases in atmospheric CO_2 cause increases in plant growth and N accumulation (25, 26), possibly resulting in decreases in losses of NO_3^- in drainage waters. It seems likely that climate could be a strong driver controlling N retention and loss in Adirondack watersheds (e.g., ref 27). Note that long-term declines in lake concentrations of NO_3^- were observed across all Adirondack drainage lakes, which may be suggestive of climatic controls. Lawrence et al. (28) evaluated long-term patterns in the hydrology of the Adirondack Region, showing generally high discharge during the early 1990s and conditions of low discharge in the late 1990s. This trend in hydrologic conditions may be partially responsible for the observed declines in lake concentrations of NO_3^- through the 1990s.

As concentrations of both SO_4^{2-} and NO_3^- were decreasing in ALTM lakes, the sum of $SO_4^{2-} + NO_3^-$ exhibited marked decreases as well. For the original 16 ALTM lakes, all sites showed significant decreases in $SO_4^{2-} + NO_3^-$ ($p < 0.05$), with a mean value of -2.31 μequiv L^{-1} yr^{-1}. For the entire set of ALTM lakes, 41 of the 48 sites showed significant decreases in $SO_4^{2-} + NO_3^-$ ($p < 0.1$) with a mean value of -3.26 μequiv L^{-1} yr^{-1}. One lake (East Copperas Pond) exhibited a significant increase in $SO_4^{2-} + NO_3^-$.

Trends in Lake Basic Cations. In soil−water systems, concentrations of basic cations generally respond to changes in concentrations of strong acid anions (e.g., $SO_4^{2-} + NO_3^-$) through the displacement of cations from cation-exchange sites (29). We have observed a near stoichiometric correspondence between declines in $SO_4^{2-} + NO_3^-$ and decreases in C_B (Figure 2). For the original 16 ALTM lakes, all exhibited significant declines in C_B ($p < 0.05$; mean rate -2.32 μequiv L^{-1} yr^{-1}) except the mounded seepage lake Little Echo Pond. The rate of C_B decline was somewhat greater for lakes in the medium and thick till drainage classes (mean value -2.52 μequiv L^{-1} yr^{-1}) as compared to the acidic lakes in the thin till drainage class (mean value -2.22 μequiv L^{-1} yr^{-1}). This difference can be attributed to high rates of decline in concentrations of inorganic monomeric Al and H^+ that have occurred in the low ANC lakes, which help balance the decline in $SO_4^{2-} + NO_3^-$ (see below). Note that all of the individual basic cations (i.e., Ca^{2+}, Mg^{2+}, Na^+, and K^+) had highly significant decreasing trends, except for Na^+ concentrations in Little Echo Pond. Although all individual basic cations have shown decreasing concentrations, the overall decrease

in C_B was largely due to decreases in Ca^{2+} (mean rate of decline $-1.30\ \mu$equiv L^{-1} yr^{-1}). Since 1992, 26 of the 48 ALTM lakes have also shown significant decreases in C_B ($p < 0.1$) coinciding with decreases in $SO_4^{2-} + NO_3^-$, again with the medium and thick till lakes (mean value $-4.64\ \mu$equiv L^{-1} yr^{-1}) showing a greater rate of decline than the thin till drainage lakes (mean value $-2.96\ \mu$equiv L^{-1} yr^{-1}).

Inputs of C_B to forest watersheds is largely derived from weathering supply and atmospheric deposition, with weathering generally dominating (30). In addition to these inputs, surface waters losses of C_B may originate from changes in ecosystem pools, such as net mineralization of soil organic matter or the net displacement from the soil exchange complex. It has generally been assumed that the declines in concentrations of C_B observed in low ANC waters are due to decreases in the leaching of exchangeable cations corresponding to declines in $SO_4^{2-} + NO_3^-$. Indeed the close stoichiometry of declines in C_B with decreases in $SO_4^{2-} + NO_3$ are consistent with this process being the major mechanism responsible for declines in lake concentrations of C_B (29, 31). However, patterns in the original 16 ALTM lakes may suggest that there also may be a long-term decline in weathering inputs to these watersheds. Because of limited interactions with vegetation and soil exchange surfaces, investigators have used concentrations of Na^+ and H_4SiO_4 as indicators of weathering inputs (10, 31, 32). We observed small but significant decreases in lake concentrations of both Na^+ (15 of 16 lakes ($p < 0.1$), with a mean rate of decline of 0.36 μmol L^{-1} yr^{-1}) and H_4SiO_4 (7 of 16 lakes exhibited decreases ($p < 0.1$) with a mean rate of decline of $-0.96\ \mu$mol L^{-1} yr^{-1}).

Trends in Lake ANC and pH. Of particular interest is the long-term change in ANC of Adirondack Lakes. Previous studies, including those involving ALTM lakes, have shown little response of ANC to decreases in acidic deposition or decreases in $SO_4^{2-} + NO_3^-$ concentrations in surface waters (4, 10–12, 14, 15). Our analyses indicate that 7 of the 16 original ALTM lakes have had significant increases in ANC ($p < 0.1$; Figure 2) from 1982 to 2000. One lake, West Pond, significantly decreased in ANC. Note that 23% of the watershed area of West Pond is wetlands and that lake water is characterized by elevated concentrations of dissolved organic carbon (DOC; mean value 667 μmol of C /L). The mean rate of ANC increase for those lakes showing a significant increasing trend was 0.78 μequiv L^{-1} yr^{-1}, with a range from 0.42 to 1.54 μequiv L^{-1} yr^{-1}. Most of the lakes (i.e., 5) showing significant increases in ANC were in the thin till drainage class. Note that the mounded seepage lake, Little Echo Pond, which receives water largely from direct precipitation inputs, had by far the greatest rate of ANC increase (1.54 μequiv L^{-1} yr^{-1}) of all the sites studied. For the entire group, 29 of the 48 ALTM lakes had significant trends of increasing ANC ($p < 0.1$) for the period 1992–2000. Twenty-one of the 26 thin till drainage lakes exhibited increases in ANC. This pattern of increasing ANC has never been previously reported for large numbers of Adirondack Lakes. The mean rate of ANC increase for lakes showing a significant trend over the 1992–2000 interval was 1.60 μequiv L^{-1} yr^{-1}. This recent increase in ANC can be attributed to the fact that both SO_4^{2-} and NO_3^- concentrations have been decreasing, resulting in a marked rate of decline in the sum of strong acid anions. If watershed retention of N should decrease in the future, as observed in the 1980s, then NO_3^- concentrations could increase and limit increases in ANC. Despite recent improvements, ANC values remain at levels of concern for aquatic biota in the majority of lakes in the study. An ANC value of 50 μequiv L^{-1} has been used as a threshold to indicate chemical conditions under which aquatic organisms are largely protected from the effects of surface water acidification from atmospheric deposition (12). In 2000, 34 of the 48 lakes
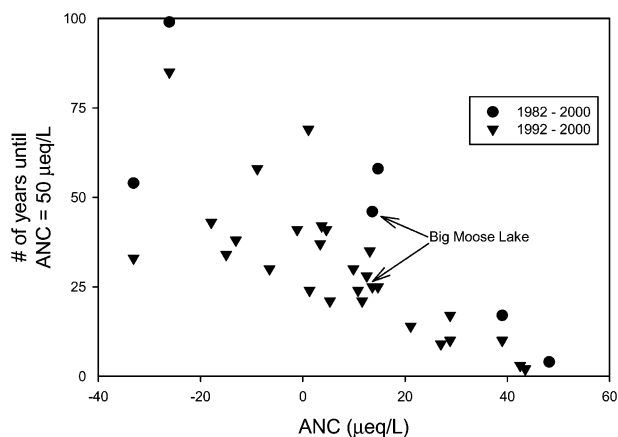
FIGURE 3. Time for lakes to reach acid-neutralizing capacity (ANC) values of 50 μequiv L^{-1} as a function of ANC value in the year 2000. These values are extrapolated assuming a linear rate of change based in slope of ANC change from time–series analysis. The extrapolation was done for two intervals, 1982–2000 and 1992–2000. Six lakes were evaluated for the longer record, and 28 lakes were evaluated for the shorter record. Note that rates of ANC increase were generally greater when calculated over the later interval, so the time to reach 50 μequiv L^{-1} is shorter. Lakes with $\geq$50 μequiv L^{-1} in 2000 or not showing a positive trend in ANC are not represented here.

had mean ANC values <50 μequiv L^{-1}; including 10 lakes with ANC values <0 μequiv L^{-1}.

There is considerable policy interest in rates of ANC increase in response to decreases in acidic deposition to quantify the time scale of recovery of surface water acidification. To date, acidification models have been used to estimate changes in surface waters chemistry in response to anticipated future emissions and atmospheric deposition and rates of chemical recovery (e.g., refs 12 and 33). However, estimates of the rate and extent of recovery are tenuous because of uncertainty in (i) future atmospheric emissions of SO_2, NO_x, NH_3, and other materials (e.g., C_B) and relationships between changes in emissions and deposition; (ii) the response of watershed processes to changes in atmospheric deposition (e.g., cation exchange, weathering, mineralization of soil S and N pools); and (iii) climatic and land disturbances that may occur in the future and alter the acid–base status of soil and surface waters. To try to provide bounds on the time scale of chemical recovery of Adirondack Lakes, we used linear rates of ANC increase obtained from time–series analysis to extrapolate the time it would take for lakes with ANC <50 μequiv L^{-1} to reach a value of 50 μequiv L^{-1}. The results of this extrapolation suggest that lakes with low ANC values that are susceptible to episodic acidification (0–50 μequiv L^{-1}) will reach the 50 μequiv L^{-1} values over the period ranging from a few years to approximately 50 yr (Figure 3). For lakes that are chronically acidic (ANC <0 μequiv L^{-1}), the time period to reach an ANC of 50 μequiv L^{-1} was estimated between 25 and 100 yr. Note that of the original ALTM lakes, 10 had ANC values <50 μequiv L^{-1} and that 6 of these exhibited a significant trend of increasing ANC. Of the entire group of ALTM lakes, 39 had ANC values <50 μequiv L^{-1}, and of these, 28 showed a significant increase in ANC. Hence, a large fraction ($\sim$30–40%) of ALTM lakes with ANC values <50 μequiv L^{-1} have shown no change in ANC in recent years or were decreasing in ANC. This coarse calculation must be considered with caution. It assumes the ANC increases are maintained at a constant linear rate for a period that extends to recovery (i.e., 50 μequiv L^{-1}). Indeed data from the original ALTM sites show that changes in ANC values have been variable over the measurement period (see Figure 1). For example, Big Moose Lake is chronically acidic. The

rate of ANC increase over the monitoring period (1982–2000) was 0.79 μequiv L^{-1} yr^{-1}. Assuming a linear extrapolation of this rate, Big Moose Lake is expected to reach ANC = 50 μequiv L^{-1} in 46 yr. In contrast, the rate of ANC increase for Big Moose Lake over the more recent 1992–2000 period was 1.44 μequiv L^{-1} yr^{-1}, resulting in a time to reach ANC = 50 μequiv L^{-1} of 25 yr. Despite problems and uncertainty associated with these estimates, it appears that at current rates of change in acidic deposition it will be several decades before chronically acidic lakes in the Adirondacks will approach chemical conditions to alleviate acidification stress to aquatic biota. This length of time to reach chemical recovery is comparable to estimates based on model calculations for chronically acidic surface waters in the Northeast (*12, 33*). Note that, once chemical stress is mitigated, there will be additional delays in the recovery of aquatic biota (*12, 34*).

Our analysis showed significant ($p < 0.1$) decreases in concentrations of H$^+$ in 9 of the 16 original ALTM lakes. One lake, West Pond, exhibited a significant increase in H$^+$. Not surprising, rates of H$^+$ decrease were highly variable. Lakes that are chronically acidic or have low ANC values in the thin till drainage class such as Big Moose Lake (-0.33 μequiv L^{-1} yr^{-1}), Constable Pond (-0.20 μequiv L^{-1} yr^{-1}), and Squash Pond (-0.58 μequiv L^{-1} yr^{-1}); the perched seepage lake Little Echo Pond (-0.94 μequiv L^{-1} yr^{-1}) had the highest rates of H$^+$ decrease. Over the shorter record, 18 of 48 lakes had significant decreases in H$^+$, while two lakes (West Pond and Sunday Pond) showed a significant increase in H$^+$. Similarly, pH was shown to be increasing in small (mean 0.01 pH unit/yr) but significant increments in 8 of the 16 original lakes, with West Pond pH decreasing at 0.02 pH unit/yr. Since 1992, a significant increase has been evident in 20 of 48 ALTM lakes ($p < 0.1$), with two lakes decreasing. Note, however, in 2000, 23 lakes still had mean pH values <5.5, including 13 with pH <5.0.

Trends in Lake Dissolved Organic Carbon and Aluminum Speciation. One of the more intriguing patterns observed in this time–series investigation was changes in concentrations of DOC. Eight of the original ALTM lakes exhibited changes in DOC, with concentrations increasing in seven lakes. The mean rate of DOC increase in those lakes showing significant increases was 6.6 μmol of C L^{-1} yr^{-1}. In general, the rate of DOC increase was more rapid at higher lake DOC concentrations (increase in DOC (in μmol of C L^{-1} yr^{-1}) = 0.015 $\times$ DOC (in μmol of C/L) $-$ 1.7; $r^2 = 0.97$). Seven of the 48 lakes showed increases in DOC concentrations over the shorter interval. Although our observed pattern of increases in DOC in some Adirondack Lakes in response to decreases in acidic deposition is tentative, if real, it may have important ecological implications. Krug and Frink (*35*) hypothesized that acidic deposition resulted in a shift in the nature of the acidity of surface waters, from acidity derived from naturally occurring organic acids to largely strong inorganic acids. Since that time, there has been considerable debate and discussion over the role of naturally occurring organic acids in the acidification of surface waters and how organic solutes change in response to changes in acidic deposition (*36–39*). If DOC is a surrogate for naturally occurring organic acids, increases in DOC should offset, to some extent, increases in pH and ANC in surface waters that result from decreases in acidic deposition. Increases in DOC should also increase the concentration of organic ligands that are available to complex potentially toxic inorganic species of aluminum (Al; see below). To bound the extent of this process, we applied a triprotic organic acid analogue model (*39*) developed for Adirondack Lakes to times–series data for the 16 original ALTM lakes. These results show that increases in pH and DOC in some lakes resulted in significant increases in calculated organic anion concentrations in 9 of

the 16 lakes. One lake had a significant decrease in estimated concentrations of organic anions. The mean increase in organic anion concentration for lakes with significant increasing trends was 0.56 μequiv L^{-1}, with values ranging from 0.37 to 1.03 μequiv L^{-1}. Note, this rate of increase in estimated concentrations of organic anions is considerably lower than the observed declines in SO$_4^{2-}$ + NO$_3^-$ (Figure 2). The organic acid model also suggests that some of the functional groups associated with naturally occurring organic solutes are strongly acidic. The mean increase in DOC concentration would result in a 0.36 μequiv L^{-1} yr^{-1} loss in ANC because of the dissociation of strongly acidic organic functional groups. This rate of ANC loss for those lakes exhibiting DOC increases is clearly significant in comparison to observed rates of ANC increase for the region.

An important consequence of acidic deposition is the mobilization of Al from soil resulting in elevated concentrations of inorganic species in surface waters that may be toxic to aquatic biota (*40, 41*). Paradoxically, 9 of the 16 original ALTM lakes had increases in concentrations of monomeric Al (Alm), despite decreases in concentrations of SO$_4^{2-}$ + NO$_3^-$, with one lake (Big Moose Lake) exhibiting decreasing concentrations. This unexpected result was due to increases in concentrations of the organic fraction of monomeric Al (Alo) in 13 of the 16 lakes (mean rate of increase 0.07 μmol L^{-1} yr^{-1}). Eight of the 16 lakes showed significant trends in concentrations of inorganic monomeric Al (Ali). Three lakes in the thin till drainage class with low values of ANC (Big Moose Lake, Darts' Lake, and Otter Lake) showed the highest rates of Ali decrease (-0.14, -0.09, and -0.04 μmol L^{-1} yr^{-1}, respectively). West Pond had significant increases in Ali (0.07 μmol L^{-1} yr^{-1}), consistent with observed decreases in pH and ANC. The other four lakes showed low rates of change in concentrations of Ali (i.e., <0.02 μmol L^{-1} yr^{-1}). Over the more recent period, the entire group of ALTM lakes exhibited a somewhat different pattern. Twenty of the 48 lakes showed a significant change in concentrations of Alm; one lake with increasing concentrations and 19 with decreasing concentrations. As with the longer record of original ALTM lakes, six sites exhibited increases in Alo. Twenty-eight lakes had decreases in Ali, with a mean rate of decline of -0.31 μmol L^{-1} yr^{-1}. As observed for the longer record, the thin till drainage class of lakes with chronically acidic conditions exhibited the highest rates of decreases in Ali. The marked extent and rate of decreases in concentrations of Ali in Adirondack Lakes in the 1990s is consistent with the high rates of SO$_4^{2-}$ + NO$_3^-$ decrease. These trends in Al chemistry in ALTM lakes clearly show a shift in speciation from toxic inorganic form toward less toxic organic forms with decreases in atmospheric deposition and increases in DOC concentrations. However in 2000, 16 out of 48 lakes showed mean Ali concentrations above 2 μmol/L, a value identified as toxic to aquatic organisms, including juvenile forms of Adirondack fish (*42*).

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