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Changes in the chemistry of lakes in the Adirondack region of New York following declines in acidic deposition

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Abstract

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^+ have occurred in wet deposition since the late 1970s. These decreases are consistent with long-term declines in emissions of SO_2 in the eastern US. Changes in wet NO_3^- deposition and NO_x emissions have been minor over the same interval. Virtually all Adirondack lakes have exhibited large decreases in concentrations of SO_4^{2-}, which coincide with decreases in atmospheric S deposition. Since 1992, concentrations of NO_3^- have also decreased in many (27 of 48) Adirondack lakes. As atmospheric N deposition has not changed appreciably over this period (1992–2004), 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; 37 of 48 lakes) and pH (31 of 48 lakes), and decreases in concentrations of inorganic monomeric Al, particularly in acid-sensitive lakes. Concentrations of dissolved organic C (DOC) have also increased in some (15 of 48) lakes coinciding with decreases in acidic deposition. Examination of changes in lake chemistry by hydrologic classes showed that drainage lakes in watersheds with thin deposits of glacial till and mounded seepage lakes have generally been the most responsive to decreases in acidic deposition.

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1. Introduction

There have been marked decreases in emissions of SO_2 and atmospheric deposition of SO_4^{2-} and H^+ in eastern North America and Europe since the early 1970s (Ferrier et al., 2001; USEPA, 2004). Lesser decreases in emissions of NO_x and atmospheric deposition of NO_3^- have also been evident in recent years.Recent decreases in emissions of acidic pollutants have altered the acid-base chemistry of sensitive surface waters. With the exception of the non-glaciated southeastern US, forested regions of eastern North America and Europe which have experienced marked decreases in atmospheric SO_4^{2-} deposition have also shown decreases in concentrations of SO_4^{2-} in surface waters (Evans et al., 2001; Stoddard et al., 2003). There is considerable variability across regions in changes in the acid-base

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status of surface waters in response to decreases in acidic deposition (Evans et al., 2001; Stoddard et al., 2003; Warby et al., 2005).

The Adirondack region of New York, USA experiences elevated acidic deposition (Ito et al., 2002). The Adirondacks is a large forested area (24,000 km^2). The bedrock geology and generally shallow surficial deposits result in soils with low pools of available nutrient cations and lakes that are acidic or sensitive to acidic deposition (Driscoll et al., 1991). There are approximately 2770 lakes in the Adirondacks (>2000 m^2 surface area). A survey of 1469 lakes during 1984–1987 found 27% of these lakes are chronically acidic (ANC < 0 μeq/L), and an additional 21% have summer ANC values between 0 and 50 μeq/L and can experience hydrologic events which decrease ANC values near or below 0 μeq/L (Kretser et al., 1989).

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 (Driscoll et al., 2003). The program was initiated with 17 lakes. It was expanded in 1992 with an additional 35 lakes for a total of 52 sites. One of the original and three of the recent group of ALTM lakes have been previously limed and therefore were not considered in this analysis. The ALTM sites are thought to be representative of classes of lakes across the Adirondacks. In this paper trends in the acid-base status of ALTM lakes and classes of Adirondack lakes relative to changes in acidic deposition are updated and mechanisms responsible for these trends evaluated. Adirondack trends are also compared with other regions in eastern North America and Europe that have been impacted by acidic deposition.

2. Methods

Wet deposition has been monitored at two sites in the Adirondacks (the Huntington Forest, HF, 43° 58′ N, 74° 13′ since 1978 and Whiteface Mountain, WM, 44° 24′ N, 73° 52′ since 1984) as part of the National Atmospheric Deposition Program (NADP). The weekly precipitation collections are measured for major ions using NADP protocols (Bigelow and Dossett, 1993).

The ALTM lakes are sampled monthly and the collected waters are measured for major solutes (Driscoll et al., 2003). All seepage lakes ($n = 5$) and remote drainage lakes accessed by helicopter ($n = 15$) are sampled at 0.5 m below the surface over the deepest portion of the lake using a plastic Kemmerer sampler. Samples are obtained at lake outlets or the shoreline for seepage lakes to permit collection when the surface is not accessible (i.e., during ice development and break-up). The drainage lakes accessed on foot ($n = 28$) are routinely sampled at the outlet. Water samples are directly collected or transferred into 1-L acid-washed, distilled water rinsed high-density polyethylene bottles. All samples are kept cold until transferred to the Adirondack Lakes Survey Corporation (ALSC) laboratory in Ray Brook, NY. A description of field and analytical methods are summarized by Driscoll and van Dreason (1993). Lake and watershed characteristics are summarized by Driscoll et al. (2003).

The watersheds surrounding ALTM lakes are largely forested, with predominantly hardwood or mixed conifer vegetation. The authors previously developed a classification system for the acid-base status of Adirondack lakes, largely based on characteristics of surficial geology and hydrologic flowpaths (Baker et al., 1990). 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 μeq/L). 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 snow melt or storm events. Four of the original and 12 of the entire group of ALTM lakes are in the medium till drainage class. Drainage lakes with watersheds which either have calcite containing bedrock or with more than 25% of the area 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. Adirondack lakes also include mounded seepage lakes, which receive most of their water directly from precipitation and shallow hydrologic flow paths. One of the original and five of the entire group of ALTM lakes are mounded seepage lakes. In contrast, ground water flow-through seepage lakes largely receive water from ground water inflows and are relatively insensitive to acidic deposition. The ALTM program does not have lakes in this class.

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 (Hirsch and Slack, 1984). The tests were run for precipitation chemistry at HF and WM, the original 16 ALTM lakes (1982–2004) that were not limed and the entire 48 ALTM lakes that were not limed (1992–2004). 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.

3. Results and discussion

3.1. Trends in atmospheric deposition

Long-term changes in the chemistry of precipitation have been evident in recent years across the eastern US (Lynch et al., 2000). The NADP sites in the Adirondacks have shown similar changes in the chemical composition of wet deposition (Table 1). Both HF and WM have exhibited declines in concentrations of most major solutes. For HF, the pH of precipitation has increased from 4.18 in 1979–1981 to 4.6 in 2001–2004. Similarly the pH of precipitation at WM has increased from 4.1 (1984–1987) to 4.6 (2001–2004).

Large decreases in concentrations of SO_4^{2-} in Adirondack precipitation have occurred over the last two decades due to reductions in emissions of SO_2. Annual volume-weighted concentration of SO_4^{2-} at HF ($r^2 = 0.53$) and WM ($r^2 = 0.38$) were positively correlated with annual emissions of SO_2 from the source area for the northeastern US (states of Maine, Vermont, New Hampshire, Massachusetts, Connecticut, Rhode Island, New York, New Jersey, Delaware, Maryland, Virginia, Pennsylvania, Ohio, Michigan, West Virginia, and provinces of Quebec and Ontario) based on 24-h back trajectory analysis (Butler et al., 2003). 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 period and by the complexities of NO_3^- deposition processes (Butler et al., 2003).

Table 1
Slopes of significant (at $p < 0.05$) changes in the concentration of solutes in wet deposition at Huntington Forest (1978–2004) and Whiteface Mountain (1984–2004; in μeq/L-a)

Site	SO_4^{2-}	NO_3^-	C_B	NH_4^+	H^+
Huntington Forest	−0.84	−0.23	−0.26	NS	−0.72
Whiteface Mountain	−0.97	−0.28	−0.11	NS	−0.99

C_B is the sum of basic cations. Non-significant trends are indicated as NS.

Unfortunately, measurements of dry deposition are not available for the entire study period. Chen and Driscoll (2004) investigated dry S deposition for the Adirondacks and found it to be a substantial and changing component of total atmospheric S deposition. These authors also observed that since the 1990s, when dry S deposition monitoring was initiated at the HF, the rates of decrease of dry S deposition has been greater than the decrease of wet SO_4^{2-} deposition.

3.2. 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 (±standard deviation) of 2.09 ± 0.38 μeq/L-a (Fig. 1). The uniform range of decline across the region (−1.58 to −2.61 μeq/L-a) suggests that decreases in SO_2 emissions and atmospheric SO_4^{2-} deposition are largely contributing to this change. Similar decreases in concentrations of SO_4^{2-} were evident for the entire 48 ALTM lakes sampled since 1992. Forty-seven of the 48 lakes studied showed a significant decrease in concentrations of SO_4^{2-} ($p < 0.1$). Although the rate of SO_4^{2-} decline for the more recent interval (1992–2004) was more variable (−0.55 to −4.16 μeq/L-a) than observed for the lakes with the longer record, the mean rate of decline for those lakes with significant decreasing trends was similar (−2.16 ± 0.81 μeq/L-a) to that for the longer period (−2.09 ± 0.38 μeq/L-a).

The rate of decline in lake SO_4^{2-} concentrations observed for the Adirondacks is similar to values reported previously for eastern North America. Stoddard et al. (2003) conducted a regional analysis of trends in surface water chemistry with respect to changes in atmospheric deposition through the 1990s. Rates of SO_4^{2-} decrease were greatest in lakes of the Upper Midwest (−3.36 μeq/L-a) and

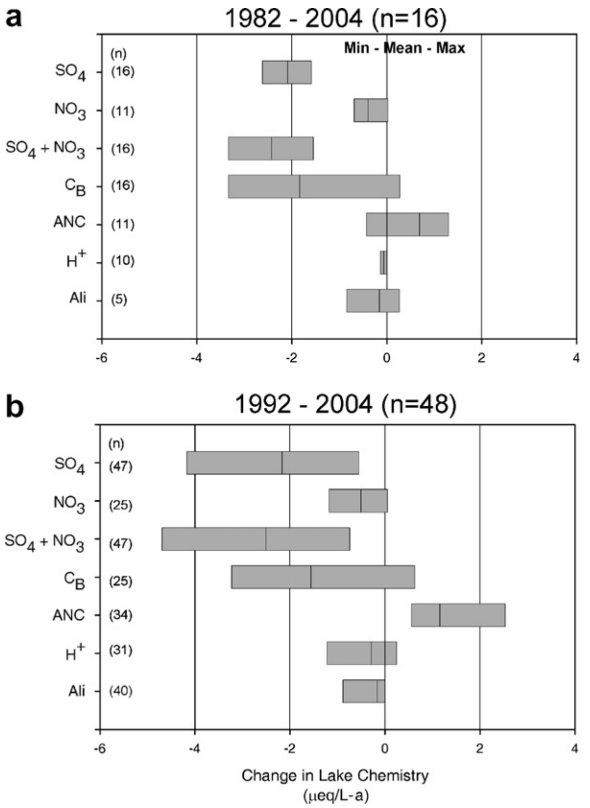

Fig. 1. Mean rates of change in solute concentrations in 16 lakes from 1982–2004 (a) and 48 lakes from 1992–2004 (b) of the Adirondack Long-Term Monitoring (ALTM) program. Minimum, mean and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in μeq/L-a, except for concentrations of inorganic monomeric Al (Ali) which is expressed in μmol/L-a.

decreased eastward in Appalachian streams (−2.27 μeq/L-a) and New England lakes (−1.77 μeq/L-a). Streams in the Ridge and Blue Ridge Provinces of the southeastern US exhibited increasing concentrations of stream SO_4^{2-} due to retention of SO_4^{2-} by highly weathered unglaciated soils. Their observed decreases in SO_4^{2-} for Adirondack lakes (−2.26 μeq/L-a) were slightly lower than the present values, reflecting a somewhat different period over which time-series analyses were conducted. Rates of SO_4^{2-} decline observed for the Adirondacks were similar to median estimates for Europe (−1.92 μeq/L-a), with greater decreases observed in the Czech Republic (−3.47 μeq/L-a) and Slovakia (−4.17 μeq/L-a) and lower declines in the United Kingdom (−1.10 μeq/L-a) and Italy (−1.00 μeq/L-a; Evans et al., 2001). These variations in decreases in surface water SO_4^{2-} are likely due to differences in changes in atmospheric SO_4^{2-} deposition, and soils and surficial geology and hydrologic flowpaths within watersheds.

The declines in Adirondack lake SO_4^{2-} have not been uniform over the monitoring period. The rates of SO_4^{2-} declines were moderate in the 1980s (Driscoll and van Dreason, 1993) and increased in the 1990s (Driscoll et al., 2003) presumably in response to the marked decreases in atmospheric SO_4^{2-} associated with SO_2 emission controls from the 1990 Amendments of the Clean Air Act. Over the last 5 a, emissions of SO_2 and wet SO_4^{2-} deposition have leveled off. This appears to have coincided with reduced rates of lake SO_4^{2-} decline.

Many of the ALTM lakes showed significant decreases in concentrations of NO_3^-. Of the original ALTM lakes, 10 of the 16 sites showed a significant decrease in NO_3^- ($p < 0.12$; mean value −0.45 μeq/L-a, range −0.17 to −0.68 μeq/L-a). Two sites, a mounded seepage (Little Echo Pond; 0.02 μeq/L-a) and a lake draining a watershed of deep stratified drift (Black Pond; 0.03 μeq/L-a), had small but significant increases in concentrations of NO_3^- ($p < 0.05$). Twenty-seven of the 48 ALTM lakes (1992–2004) showed significant ($p < 0.14$) decreases in NO_3^-, with only 3 exhibiting increases ($p < 0.13$).

Decreases in surface water NO_3^- concentrations have been reported elsewhere in forested watersheds of the northeastern US (Goodale and Aber, 2001; Stoddard et al., 2003). This pattern of decreasing NO_3^- concentrations runs counter to what would be expected if the Adirondacks were approaching a condition of N saturation. There has not been any appreciable change in emissions of NO_x or atmospheric NO_3^- deposition since the ALTM program was initiated in 1982. Investigators have speculated that the long-term pattern of decreasing NO_3^- loss is associated with increased retention of N due to a fertilization effect from increases in atmospheric CO_2 (Aber et al., 2002; Oren et al., 2001). It seems likely that climate or hydrologic change could also be a strong driver controlling N retention and loss in Adirondack watersheds. Finally, decreases in NO_3^- in surface waters could also reflect a shift in forest tree species, with decreases in species where mineralization and nitrification of litter readily occurs (i.e., *Acer saccharum*) being replaced by species that do not (e.g., *Fagus grandifolia;* Lovett and Mitchell, 2004). Note that long-term declines in lake concentrations of NO_3^- across the entire region of Adirondack drainage lakes, may be suggestive of a driver (or combination of drivers) that occurs across the region (e.g., CO_2 fertilization, climatic controls, shifts in tree species).

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 ± 0.74 μeq/L-a. For the entire set of ALTM lakes, 47 of the 48 sites showed significant decreases in $SO_4^{2-} + NO_3^-$ ($p < 0.09$) with a mean value of -2.50 ± 1.05 μeq/L-a. One lake (E. Copperas) exhibited a significant increase in $SO_4^{2-} + NO_3^-$.

3.3. Trends in lake basic cations

A near stoichiometric correspondence between declines in $SO_4^{2-} + NO_3^-$ and decreases in C_B has been observed in most ALTM lakes (Figs. 1 and 2a). The original 16 ALTM lakes, all exhibited significant declines in the sum of basic cation (C_B; $p < 0.05$; mean rate -1.97 ± 0.51 μeq/L-a), 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 -2.06 ± 0.42 μeq/L-a) compared to the acidic lakes in the thin till drainage class (mean value -1.90 ± 0.60 μeq/L-a). This difference can be attributed to high rates of decline in concentrations of inorganic monomeric Al and H^+ that have occurred in these 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^+, K^+) had highly significant decreasing trends, except for Na^+ in several of the lakes ($n = 8$). 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 -1.32 ± 0.36 μeq/L-a). Since 1992, 27 of the 48 ALTM lakes have also shown significant decreases in C_B ($p < 0.14$) coinciding with decreases in $SO_4^{2-} + NO_3^-$, again with the medium and thick till drainage lakes (mean value -2.15 ± 0.76 μeq/L-a) showing a greater rate of decline than the thin till drainage lakes (mean value -1.38 ± 0.58 μeq/L-a).

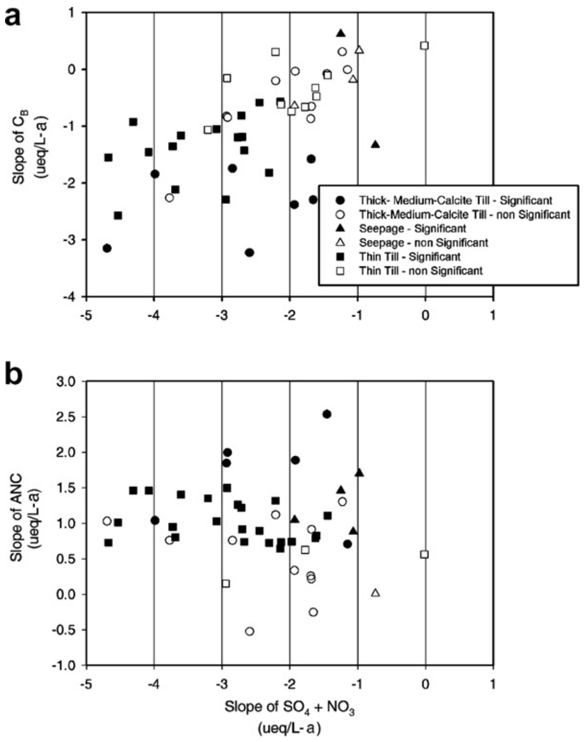

Fig. 2. Change in lake water concentrations of the sum of base cations (C_B; a) and acid neutralizing capacity (ANC; b) with changes in $SO_4^{2-} + NO_3^-$ over 1992–2004. Shown are values for different lake classes. Significant relationships ($p < 0.1$) are shown with filled symbols and non-significant relationships are indicated by open symbols.

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

The analyses indicate that 11 of the 16 original ALTM lakes had a significant trend of increasing ANC ($p < 0.1$; Fig. 1) from 1982–2004. The mean rate of ANC increase for those lakes showing a significant increasing trend was 0.76 ± 0.28 μeq/L-a, with a range from 0.35 to 1.30 μeq/L-a. Most of the lakes (i.e., 7) showing significant increases in ANC were in the thin till drainage class. Note the mounded seepage lake, Little Echo Pond, that receives water largely from direct precipitation inputs, had by far the greatest rate of ANC increase (1.30 μeq/L-a) of all the sites studied for the 1982–2004 period. Thirty-seven of the 48 ALTM lakes had significant trends of increasing ANC ($p < 0.13$) for the period 1992–2004. Twenty-four of the 26 thin till drainage lakes exhibited increases in ANC ($p < 0.07$). The mean rate of ANC increase for lakes showing a significant trend over the 1992–2004 interval was 1.13 ± 0.44 μeq/L-a. This recent increase in ANC can be largely 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. Note that while the relatively large numbers of lakes exhibiting increases in ANC is indicative of the success of emission control strategies to curtail surface water acidification, rates of ANC increase are relatively slow. At current rates of ANC increase it will be several decades before chemical recovery is adequate to support a diverse biological community in acid impacted lakes (Driscoll et al., 2001, 2003; Chen and Driscoll, 2005).

An important consideration is the increase in ANC in response to unit decreases in strong acid anions. For the ALTM sites, the stoichiometric response of decreases in C_B (ΔC_B) and increases in ANC (ΔANC) for a unit decrease in $SO_4^{2-} + NO_3^-$ were calculated for different lake classes using all the ALTM sites (1992–2004; Fig. 2; Table 2). In general there has been an overall decrease in C_B with decreases in $SO_4^{2-} + NO_3^-$, although there are interesting patterns across the lake classes (Fig. 2). In general, those lakes showing the greatest decreases in $SO_4^{2-} + NO_3^-$ have also tended to have significant decreases in C_B. The thin till drainage lakes exhibit a strong relationship of decreasing C_B with decreasing $SO_4^{2-} + NO_3^-$, with 16 of the 26 sites showing a significant relationship ($p < 0.1$) (for all thin till sites the change in $C_B = 0.48 *$ the change in $SO_4^{2-}+ NO_3^- + 0.35$; in μeq/L-a; $r^2 = 0.49$). In contrast the more insensitive classes (i.e., medium till, thick till and calcite lake watershed classes lumped together) generally showed greater decreases in C_B per unit decrease in $SO_4^{2-} + NO_3^-$ and greater variability in the response, than the thin till drainage lakes (Fig. 2a, Table 2). Seven of the 17 medium and thick till and calcite influenced sites showed a significant relationship between decreasing C_B and decreasing $SO_4^{2-} + NO_3^-$. This pattern is consistent with the greater rate of base cation supply at sites with thicker surficial deposits or calcite in the watershed than thin till watersheds. Only two of the five mounded seepage lakes showed a significant relationship between decreases in C_B with decreasing $SO_4^{2-} + NO_3^-$.

The response of ANC to changes in $SO_4^{2-} + NO_3^-$ (ΔANC) for most sites mirrors the patterns for ΔC_B for the different lake classes (Fig. 2b). The mounded seepage lakes exhibited a nearly equivalent increase in ANC for every unit decrease in $SO_4^{2-} + NO_3^-$ (ΔANC = −0.86). This response is due to hydrologic inputs in these ecosystems largely occurring from direct precipitation and shallow flowpaths resulting in little contact with surficial materials. These lakes are very sensitive and 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 $SO_4^{2-} + NO_3^-$ ($p < 0.1$). Twenty-three of the thin till drainage lakes have significant increases in ANC with decreases in $SO_4^{2-} + NO_3^-$. The thin till drainage lakes exhibited a 0.38 equivalent increase in ANC for every equivalent unit decrease in $SO_4^{2-} + NO_3^-$ (ΔANC = −0.38).

The stoichiometric results for medium and thick till and calcite impacted drainage lakes were somewhat unexpected. These calculations indicate that a unit decrease in $SO_4^{2-} + NO_3^-$ resulted in approximately an equivalent decrease in C_B leaching ($\Delta C_B = 0.94$). This response is what might be expected for watersheds with moderate to thick surficial deposits. Surprisingly these sites also exhibited moderate increases in ANC per unit decrease in $SO_4^{2-} + NO_3^-$. This result may reflect a small number of medium and thick till and calcite impacted drainage lakes with significant increases in ANC ($n = 6$) and that few sites have both significant decreases in C_B and increases in ANC ($n = 1$). Four medium till sites had the greatest rates of ANC increase from 1992–2004 of all the ALTM sites (i.e., Limekiln, Little Hope, Big Hope, Owen). It is not clear why these sites showed large increases in ANC. However, three of the four sites were heavily impacted by an ice storm in January 1998, resulting in loss of canopy and downed trees in a large portion of the watersheds. Values of ANC increased markedly after the ice storm at these sites. These lakes were also characterized by short-term increases in NO_3^- (~2 a) and longer-term increases in concentrations of nutrient cations (Ca^{2+}, Mg^{2+},

Table 2
Stoichiometric decreases in C_B (ΔC_B) and increases in ANC (ΔANC) for an equivalent decrease in $SO_4^{2-} + NO_3^-$ in surface waters for the Adirondacks for the period 1992–2004 and other regions

Site	ΔC_B	ΔANC	Reference
Adirondacks			This study
Perched Seepage	0.65 (2)	−0.86 (4)	
Thin Till	0.43 (16)	−0.38 (23)	
Medium/Thick Till/ Calcite	0.94 (7)	−0.82 (6)	
New England	0.84	−0.06	Stoddard et al. (2003)
Appalachian	0.94	−0.22	Stoddard et al. (2003)
Upper Midwest	0.42	−0.32	Stoddard et al. (2003)
Europe	0.5	−0.5	Evans et al. (2001)

The number of significant relationships ($p < 01$) the value is based on is shown in parenthesis for Adirondack lake classes.

K^+; ~5 a) following the disturbance, likely contributing to high rates of ANC increase.

This stoichiometic approach can be used to compare recovery results following decreases in acidic deposition for the Adirondacks with other regions (Table 2). Lakes in New England and Appalachian streams largely respond to a unit decrease in $SO_4^{2-} + NO_3^-$ by reduced leaching of C_B, with little increase in ANC (Stoddard et al., 2003). Lakes in the Upper Midwest exhibit a mixture of decreased C_B leaching and ANC increase per unit decrease $SO_4^{2-} + NO_3^-$. This pattern may reflect the relatively large number of seepage lakes monitored in this region. For European surface waters a unit decrease $SO_4^{2-} + NO_3^-$ contributes to both decreased C_B leaching and increases in ANC (Evans et al., 2001).

The analysis also showed significant ($p < 0.1$) decreases in concentrations of H^+ in 12 of the 16 original ALTM lakes. Not surprisingly, rates of H^+ decrease were highly variable. Lakes in the thin till drainage class (mean value 0.18 ± 0.18 μeq/L-a; except West Pond) and the mounded seepage lake Little Echo Pond (−0.84 μeq/L-a) had the highest rates of H^+ decrease. One lake, West Pond, exhibited a significant increase in H^+. Over the shorter record, 31 of 48 ALTM lakes had significant decreases in H^+ ($p < 0.14$). These decreases in H^+ concentration were most prominent in the mounded seepage and thin till drainage classes. Two lakes, West Pond and Sunday Pond, showed a significant increase in H^+.

Changes in Al concentrations were largely restricted to thin till drainage lakes. In the original 16 lakes, 5 of the 8 lakes in the thin till drainage class showed significant ($p < 0.05$) decreases in concentrations of inorganic monomeric Al. These rates of decline were highly variable ranging from −0.13 to −0.02 μmol/L-a. For the entire group of ALTM lakes (1992–2004), 24 out of the 26 thin till seepage lakes had significant decreasing concentrations of inorganic monomeric Al.

Some Adirondack lakes exhibited increases in DOC. Ten of the original 16 ALTM lakes had significant increases in DOC at a mean rate of 4.5 ± 3.8 μmol C/L-a. Two of the lakes showed decreases in DOC. Trends were less distinct for the entire group of 48 lakes from 1992–2004; 15 exhibited significant increases in DOC while 4 showed decreasing trends ($p < 0.14$).

The mechanism responsible for increases in DOC is not evident. Several processes could contribute to increases in lake DOC. Long-term temperature and precipitation change could change DOC concentrations. In particular, increased discharge should increase DOC due to increases in flow along shallow hydrologic flowpaths. However, Lawrence et al. (2004) evaluated hydrologic conditions in the Adirondack streams and observed variable flow patterns over the period of the ALTM program. It appears unlikely that changes in hydrology can explain this long-term DOC pattern. Decreases in inputs of acidic deposition could also increase DOC concentrations in surface waters either by decreases in DOC sorption to soil with increases in soil pH (Ussiri and Johnson, 2004) and or decreases in coagulation and subsequent deposition of DOC associated with decreases in Al concentrations (Effler et al., 1985). The data may be consistent with these latter mechanisms.

Regardless of the mechanism, the phenomenon of increases in DOC has important implications for lake ecosystems. Variation in DOC is an important controller of the attenuation of light and the thermal stratification of Adirondack lakes (Effler et al., 1985). An increase in DOC in response to decreases in acidic deposition will limit increases in the pH and ANC due to the role of DOC in controlling the acid-base status of lakes (Driscoll et al., 1994). However, increases in DOC may serve as a complexing ligand and diminish the toxicity of Al in acid-sensitive surface water.

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