

# Factors Affecting Acid Neutralizing Capacity in the Adirondack Region of New York: a Solute Mass Balance Approach

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High rates of acidic deposition in the Adirondack region of New York have accelerated acidification of soils and surface waters. Annual input–output budgets for major solutes and acid-neutralizing capacity (ANC) were estimated for 43 drainage lake–watersheds in the Adirondacks from 1998 to 2000. Sulfate was the predominant anion on an equivalent basis in both precipitation and drainage export. Calcium ion had the largest cation drainage export, followed by  $Mg^{2+}$ . While these watersheds showed net nitrogen (N) retention, the drainage losses of  $SO_4^{2-}$ ,  $Cl^-$ , base cations, and ANC exceeded their respective inputs from precipitation. Land cover (forest type and wetlands) affected the export of  $SO_4^{2-}$ , N solutes, and dissolved organic carbon (DOC). The relationships of solute export with elevation (negative for base cations and  $Cl^-$ , positive for  $NO_3^-$  and  $H^+$ ) suggest the importance of the concomitant changes of biotic and abiotic watershed characteristics associated with elevational gradients. The surface water ANC increased with the sum of base cations and was greatest in the lakes with watersheds characterized by thick deposits of glacial till. The surface water ANC was also higher in the lake–watersheds with lower DOC export. Some variation in lake ANC was associated with variability in acidic deposition. Using a classification system previously developed for Adirondack lakes on the basis primarily of surficial geology, lake–watersheds were grouped into five classes. The calculated ANC fluxes based on the major sinks and sources of ANC were comparable with measured ANC for the thick-till (I) and the medium-till lake–watersheds with low DOC (II). The calculated ANC was overestimated for the medium-till with high DOC (III) and the thin-till with high DOC (V) lake–watersheds, suggesting the importance of naturally occurring organic acids as an ANC sink, which was not included in the calculations. The lower calculated estimates than the measured ANC for the thin-till lake–

watersheds with low DOC (IV) were probably due to the mobilization of Al as an ANC source in these watersheds that were highly sensitive to strong acid inputs. Our analysis of various drainage lakes across the Adirondacks on the basis of solute mass balances, coupled with the use of a lake classification system and GIS data, demonstrates that the lake–watersheds characterized by shallow deposits of glacial till are highly sensitive to acidic deposition not only in the southwestern Adirondack region where previous field-based studies were intensively conducted but also across the entire Adirondack region. Moreover, the supply of organic acids and Al mobilization substantially modify the acid–base status of surface waters.

## Introduction

Acidic deposition has altered the cycling and the interactions of chemical elements, such as S, N,  $H^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and Al, contributing to deleterious impacts to aquatic and terrestrial ecosystems in North America, Europe, and Asia (1). Impacts to sensitive ecosystems have included the acidification of soils through losses of exchangeable nutrient cations, the acidification of surface waters associated with increases in strong acid anions,  $SO_4^{2-}$  and  $NO_3^-$  (1–3), and coastal eutrophication (4).

The Adirondack region of New York receives among the highest rates of atmospheric S and N deposition in the United States. (1). Many surface waters in the Adirondacks are highly sensitive to acidic deposition, being defined as having a baseflow acid-neutralizing capacity (ANC)  $<50 \mu\text{equiv L}^{-1}$  (5). A synoptic survey conducted in the mid 1980s showed that 26% of the 1469 lakes surveyed with the surface area  $>0.5$  ha were chronically acidic, having negative summer ANC values (6). Despite high rates of acidic deposition, the acid–base status varies among surface waters in the Adirondacks. Those variations could arise not only from spatial patterns of acidic deposition but also from variations in soil type and depth, bedrock geology, vegetation type, and other physical and environmental characteristics that affect hydrologic and biogeochemical cycles. Land cover patterns and watershed physical characteristics affect the concentrations and exports of chemical solutes in surface waters (e.g., 7–13). For example, field-based studies reported that surficial geology controlled surface waters in two watersheds within 30 km apart or some watersheds located within a river branch of the southwestern Adirondacks (14, 15). A review of previous studies for the Adirondacks as well as other regions including Europe emphasized the need for consideration of possible effects of land cover and land use changes (16). Further, the interrelationships among slope, vegetation, and surficial geology and their relationships with surface water chemistry in the western United States (7) suggest that a combination of multiple watershed attributes influences surface water chemistry. The input–output budgets for N in the northeastern United States (17) and in the Adirondack region (18) have shown that atmospheric inputs, hydrology, vegetation and other land cover types, and land use history all can affect the N drainage losses.

The Adirondack region exhibits a wide spectrum of surface waters including clearwater and colored, and high ANC and acidic lakes. In the Adirondack Long-Term Monitoring (ALTM) Program, the chemical composition is tracked in lakes that represent a wide range of acid–base chemistry and drain watersheds with different characteristics (19). The water samples from the ALTM lakes enabled us to examine

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**FIGURE 1.** Locations of 43 lake–watersheds in the Adirondack region of New York.

the cycling of strong acids and other elements in various lake–watersheds by applying a solute mass-balance approach over the same study periods, and evaluate the factors affecting surface water chemistry. Spatial data (geographic information system (GIS) data) were used to evaluate influences of land cover and terrestrial factors. A classification system previously developed for Adirondack lakes on the basis primarily of surficial geology was employed to consider the role of groundwater as well as to evaluate the influences of other factors, such as the effect of organic acids on lake chemistry. A previous study by Ito et al. (18) was one of the first studies to evaluate spatial patterns of solute chemistry across the entire Adirondack region, using a solute mass-balance approach over the same study period, but focused only on N solutes and dissolved organic carbon (DOC). In our current study, we estimated annual atmospheric inputs in precipitation and drainage losses of major elements and ANC in 43 drainage lake–watersheds in the Adirondacks from 1998 to 2000, using measured data and empirical and hydrological models, and evaluated components that can influence lake ANC.

## Methods

**Study Sites.** The 43 lake–watersheds are located in the Adirondack region of New York, which is situated between 43°N and 45°N and between 73°W and 76°W over an elevation range from 390 to 880 m (Figure 1). These drainage lakes have been studied under the ALTM Program, which was started in 1982 with the sampling of 17 lakes (5) and increased to 52 lakes in 1992, including 7 groundwater seepage lakes that are not included in this study (19). Among 45 drainage lake–watersheds, two lake–watersheds that had previously been limed (i.e., CaCO<sub>3</sub> addition: Little Simon Pond and Woods Lake) were excluded from our analysis.

The humid continental climate in the Adirondacks is represented by precipitation that varies spatially with its increasing quantity from the northeast to the southwest. The bedrock geology in the Adirondacks is mainly gneisses and metasedimentary rocks with marble and other calcite bearing bedrock in a few scattered locations, mostly to the east (5). Mantled glacial till largely forms the surficial geology of the mountains and uplands, thinner in the upslope and gradually thicker toward the valleys. The surficial geology at lower elevations often includes glacial meltwater deposits of stratified sand and gravel. The soils in the Adirondacks are primarily Spodosols and are generally shallow and acidic, especially in the organic-rich upper horizons (5). The lake–watersheds are predominantly forested. Northern hardwoods compose approximately one-half of the forest vegetation with conifers (10%) and mixed forests (25%). The trees in many stands were 50–70 years old with old-growth forests con-

taining trees of 200–400 years old (5). Wetlands are abundant in the Adirondacks; for example, wetlands constitute about 14% of the land surface of in the Oswegatchie/Black River drainage region of the Adirondacks (20). Most wetlands are forested, while nonforested wetlands include bogs, fens, and open marshes.

**Sampling and Chemical Analyses.** Lake surface water samples were collected monthly at or near the outlets of 43 ALTM drainage lakes from 1998 to 2000 and maintained at 1 °C until analyzed for SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> (by ion chromatography), Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> (by atomic absorption spectrophotometry (AAS)), monomeric Al (PCV colorimetric Technicon), pH (potentiometrically with glass electrode), dissolved Si (colorimetric molybdate), and acid-neutralizing capacity (ANC) (by strong acid titration with Gran plot analysis).

**Mass Balance and Other Calculations.** Wet deposition as input and drainage loss as output for 43 drainage lake–watersheds were calculated for SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, H<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and ANC from 1998 to 2000. The annual output was also calculated for dissolved Si. The input–output budgets for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> and the annual outputs for dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) were based upon results from Ito et al. (18) for this same study period. Wet deposition was calculated by multiplying the precipitation amount by ion concentration in precipitation. The precipitation amounts and ion concentrations were estimated using the empirical models (21) and the data from the Huntington Wildlife Forest (HWF), a National Atmospheric Deposition Program/National Trends Network (NADP/NTN) site, located in the central Adirondacks. The ANC in precipitation was calculated on the basis of the charge balance approach, assuming [Al<sup>3+</sup>], [F<sup>-</sup>], and [A<sup>-</sup>] (the equivalent concentration of naturally occurring organic anions) were negligible in precipitation (eq 1):

$$\text{ANC} = 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{K}^+] + [\text{Na}^+] + [\text{NH}_4^+] + 3[\text{Al}^{3+}] - [\text{Cl}^-] - [\text{NO}_3^-] - 2[\text{SO}_4^{2-}] - [\text{F}^-] - [\text{A}^-] \quad (1)$$

The drainage loss was calculated by multiplying the discharge by measured solute concentration in lake water. Discharge rates were estimated using a hydrologic simulation model, BROOK90 (22), which was developed for small, forested watersheds. The application of the hydrologic model enabled us to use the mass-balance approach despite limited availability of detailed hydrologic information for most of the watersheds. This model was previously used to estimate the water flux in a gauged lake–watershed in the central Adirondacks (23), for which the model fit was very similar to the results for the Hubbard Brook Experimental Forest, New Hampshire, where the model was originally developed. The estimations of wet deposition and drainage export are explained in more detail elsewhere (18). Our approach using the mass balances facilitated the comparison of multiple sites across the entire Adirondack region. Mass balances for separate terrestrial and lake ecosystems would be of some interest, but detailed hydrologic and biogeochemical information for each stream flowing into a lake or in-lake processes are not currently available for most of the watersheds. The evaluation of drainage losses from the lakes was indeed considered to contribute to meeting immediate management needs and interest for downstream ecosystems. The role of groundwater was taken into consideration by using a classification system previously developed for the Adirondack lakes on the basis primarily of surficial geology (5). With the use of the lake classification system, similarities or differences between calculated and measured ANC based on mass balances could also suggest the influences of other factors, such as the contributions of organic acids and Al mobilization.

The spatial maps of wetlands, land cover (deciduous, mixed, coniferous forests, deciduous forest with open canopy,

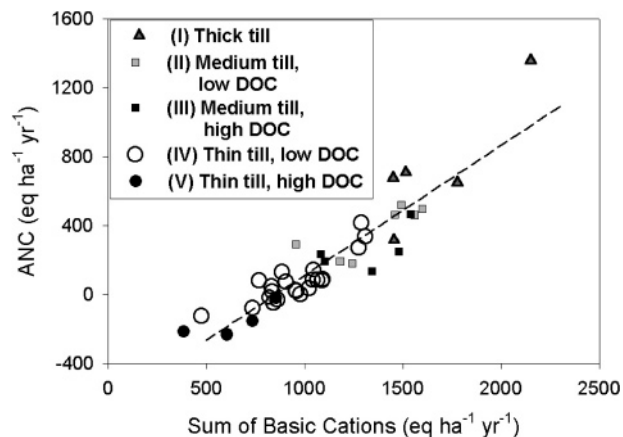
open with vegetation, open), and the boundary of the Adirondack Park were obtained from the Adirondack Park Agency (20, 24). The details on this classification have been previously provided (18). For 20 lake–watersheds for which spatial data of wetland types (1:24 000) were available, watershed boundaries were delineated using the U.S. Geological Survey digital elevation models (a pixel width of 10 m) by external computation (i.e., outside the GIS) on the basis of the flow accumulation values. The flow accumulation values were calculated by TARDEM (25). After the boundaries of watersheds were delineated, the spatial data were processed using ArcInfo Workstation Arc version 8.3, ArcView versions 3.2 and 3.3, and ArcMap 8.3 (Environmental Systems Research Institute, Inc.). The proportion of watershed area occurring as the respective land cover or wetlands was expressed by percentage.

Univariate and stepwise multiple linear regression analyses were applied to examine possible influences on the drainage losses of major elements of acidic wet deposition, land cover (e.g., deciduous, mixed, coniferous forest, wetland area), or elevation. Statistical analyses were performed using SAS version 8.01 (SAS 2002).

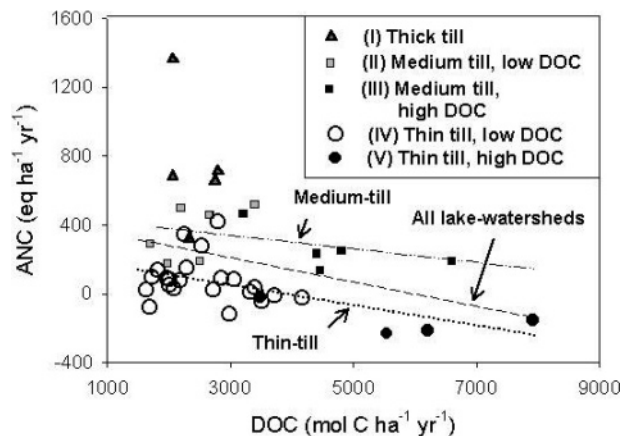
## Results and Discussion

**Major Element Budgets and Acid-Neutralizing Capacity.** The mean annual precipitation estimated for the 43 drainage lake–watersheds ranged from 105 to 125 cm yr<sup>-1</sup> (mean: 116 cm yr<sup>-1</sup>), while the estimated discharge ranged from 65 to 87 cm yr<sup>-1</sup> (mean: 77 cm yr<sup>-1</sup>) from 1998 to 2000. The modeled water yield ranged between 62 and 69% (mean: 66%) of the precipitation input. The variability in water fluxes was not a primary factor controlling spatial variations in solute fluxes in these Adirondack lake–watersheds.

The mean wet deposition rates of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> to the 43 Adirondack lake–watersheds were 316 and 22 eq ha<sup>-1</sup> yr<sup>-1</sup>, respectively, from 1998 to 2000. The mean drainage losses of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> for these same lake–watersheds were 724 and 72 eq ha<sup>-1</sup> yr<sup>-1</sup>, respectively, which were higher than wet deposition by 129 and 229%, respectively. The drainage losses of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> exhibited wider ranges (341–948 and 44–195 eq ha<sup>-1</sup> yr<sup>-1</sup>, respectively) than those for wet deposition (253–354 and 20–24 eq ha<sup>-1</sup> yr<sup>-1</sup>, respectively). These results suggest additional sources of S and Cl<sup>-</sup> to the lake–watershed ecosystems, such as dry deposition or internal watershed sources (e.g., mineral weathering, desorption of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>, net mineralization of organic S compounds). The drainage losses of base cations, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> (mean: 657, 223, 48, and 190 eq ha<sup>-1</sup> yr<sup>-1</sup>, respectively), were also higher than wet deposition (mean: 42, 11, 3, and 14 eq ha<sup>-1</sup> yr<sup>-1</sup>, respectively) by 16, 21, 17, and 14-fold, respectively. The calculated net loss of base cations from lake–watershed ecosystems is due to unmeasured inputs of dry deposition, net desorption from cation exchange sites, net mineralization of soil organic matter, and mineral weathering. The range of drainage export of dissolved Si was from 176 to 1178 mol Si ha<sup>-1</sup> yr<sup>-1</sup> (mean: 626 mol Si ha<sup>-1</sup> yr<sup>-1</sup>) and probably reflects the variability in weathering rates among lake–watersheds. The net watershed losses (drainage losses > wet deposition) of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and base cations contrasted to net watershed retention (wet deposition > drainage losses) of N solutes (i.e., NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) (18). The mean wet deposition and drainage losses were 248 and 149 for NO<sub>3</sub><sup>-</sup> eq ha<sup>-1</sup> yr<sup>-1</sup> and 106 and 28 eq ha<sup>-1</sup> yr<sup>-1</sup> for NH<sub>4</sub><sup>+</sup>, respectively. Net watershed losses of SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> (even with the addition of dry deposition inputs), in contrast with net N watershed retention, have been reported previously for forested watersheds in northeastern United States and Canada (26, 27). Since K<sup>+</sup> tends to be high in throughfall and throughfall is considerably variable, this process likely affects the K<sup>+</sup> drainage losses



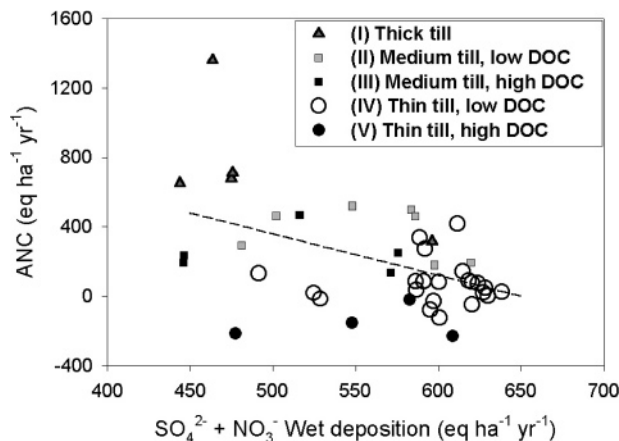
**FIGURE 2.** The relationship between ANC and the sum of basic cations for the Adirondack lake–watersheds. The fluxes for various lake–watershed classes are shown.



**FIGURE 3.** The relationship between ANC and DOC fluxes in the Adirondack lake–watersheds. The fluxes for various lake–watershed classes are shown.

(26), and thus K<sup>+</sup> budgets can vary substantially. The ANC of wet deposition was very low, ranging from -477 to -304 eq ha<sup>-1</sup> yr<sup>-1</sup> (mean: -411 eq ha<sup>-1</sup> yr<sup>-1</sup>). In contrast, the mean volume-weighted lake ANC based on each site ranged from -32 to 206  $\mu$ equiv L<sup>-1</sup> (mean: 28  $\mu$ equiv L<sup>-1</sup>) and the ANC fluxes from these surface waters ranged from -232 to 1360 eq ha<sup>-1</sup> yr<sup>-1</sup> (mean: 202 eq ha<sup>-1</sup> yr<sup>-1</sup>).

**Controls of Acid-Neutralizing Capacity.** There was a close correspondence between ANC fluxes from the lakes and the sum of base cations (C<sub>B</sub>) fluxes ( $R^2 = 0.84$ ,  $p < 0.0001$ ) (Figure 2). The drainage loss of C<sub>B</sub> was positively related to dissolved Si ( $R^2 = 0.32$ ,  $p < 0.0001$ ), suggesting a linkage between base cation supply and the weathering of silicate minerals (28). In many terrestrial environments, dissolved Si is relatively conservative and is not strongly retained in soils (29, 30). Thus, dissolved Si has been used as an indicator of chemical weathering rates with high Si concentrations often associated with large groundwater supply (31–33). The relationships between ANC and C<sub>B</sub> and between C<sub>B</sub> and dissolved Si suggest that the contribution of groundwater inputs likely influenced the drainage losses of base cations and therefore ANC fluxes. The ANC fluxes were also influenced by DOC drainage fluxes for the lake–watersheds, decreasing as DOC increased ( $R^2 = 0.11$ ,  $p = 0.03$ ) (Figure 3). Some influence of wet deposition of strong acids, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, on the spatial pattern in ANC fluxes was also evident in an inverse relationship between lake ANC fluxes and wet deposition of SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup> ( $R^2 = 0.24$ ,  $p = 0.0009$ ; Figure 4). The drainage losses of both SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> increased with SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>



**FIGURE 4.** The relationship between lake-watershed ANC flux and  $\text{SO}_4^{2-} + \text{NO}_3^-$  wet deposition.

deposition rates ( $R^2 = 0.23$ ,  $p = 0.001$  and  $R^2 = 0.13$ ,  $p = 0.016$ , respectively).

**Land Cover and Terrestrial Factors.** We also evaluated the influences of land cover (forest type and wetlands) and elevation on drainage losses of chemical species in the Adirondack region. Wetlands are abundant in the Adirondacks (20), and we anticipated relationships with solute fluxes. Stepwise multiple regression analyses with land cover types (forest type and wetlands) showed that the  $\text{SO}_4^{2-}$  drainage loss increased with increasing proportion of coniferous forest and decreasing proportion of wetland area in the lake-watershed (adj.  $R^2 = 0.58$ ,  $p = 0.0002$ ). Drainage losses of other solutes were not related to land cover type, except for N solutes and DOC (18). Simple linear regression analyses showed similar results; the proportion of wetland area in lake-watersheds was inversely related with  $\text{SO}_4^{2-}$  ( $R^2 = 0.22$ ,  $p = 0.03$ ) and positively with DON and DOC drainage losses ( $R^2 = 0.28$ ,  $p = 0.017$  and  $R^2 = 0.44$ ,  $p = 0.001$ , respectively). The proportion of coniferous forest area in the lake-watersheds was related to the  $\text{SO}_4^{2-}$  drainage loss ( $R^2 = 0.37$ ,  $p = 0.005$ ) as well as the  $\text{NO}_3^-$  drainage loss (18). The relationship between the  $\text{SO}_4^{2-}$  loss and forest type reflects higher atmospheric S inputs in coniferous stands than deciduous stands because of higher efficiency of the coniferous canopy for capturing atmospheric S or higher S leaching from the coniferous foliage (34). The decrease in  $\text{SO}_4^{2-}$  with increasing wetland area was presumably due to the loss of  $\text{SO}_4^{2-}$  from dissimilatory  $\text{SO}_4^{2-}$  reduction under anaerobic conditions (35), where the production of dissolved organic matter (DOM) increases (36–37).

Although drainage losses of most solutes did not show significant relationships with land cover, the export of base cations,  $\text{Cl}^-$ , and ANC all increased with decreasing elevation,

while  $\text{NO}_3^-$  and  $\text{H}^+$  increased with increasing elevation. There was no relationship between elevation and drainage losses of  $\text{SO}_4^{2-}$  or  $\text{NH}_4^+$ . The increases in base cations and ANC with decreasing elevation or catchment slope have been observed in previous studies (e.g., 8, 38). Such increases have been attributed to longer hydraulic residence time and hence longer contact time of water with thicker deposits of surficial materials at lower elevations, thereby increasing the release of weathering products, such as base cations and dissolved Si (7), and increasing production of ANC. The relationships with elevation are complicated by various interactions among physical, chemical, and biotic watershed attributes that can be caused at least in part by changes in temperature and precipitation along elevation. Productivity, aboveground biomass, and soil depth and development, which affect chemical cycling and losses, are closely related to precipitation and temperature (39) with greater aboveground biomass and soil depth at lower elevations.

**Lake Classes and the Sinks and Sources of ANC.** The depth of unconsolidated surficial sediments influences water flowpaths. In an Adirondack lake-watershed with thick deposits of glacial till (Panther Lake), precipitation infiltrated glacial till during most hydrologic events, resulting in drainage water enriched in solutes because of long hydraulic residence time within till deposits (40). Using a classification system based on hydrologic flow paths and associated with surficial geology (5), the 43 Adirondack lake-watersheds were grouped into five classes: (I) lake-watersheds covered by thick glacial till (>25% of the watershed area is covered by thick (>3 m) till and stratified drift) (5 lakes); (II) medium till watersheds (5–25% of the watershed area is underlain by thick till and stratified drift) with low DOC (<417  $\text{mmol L}^{-1}$  or 5  $\text{mg C L}^{-1}$ ) (7 lakes); (III) medium till watersheds with high DOC (>417  $\text{mmol L}^{-1}$  or 5  $\text{mg C L}^{-1}$ ) (5 lakes); (IV) thin till watersheds (<5% of the watershed area is underlain by thick till and stratified drift) with low DOC (22 lakes); and (V) thin till watersheds with high DOC (4 lakes). The distinction of lake DOC helps characterize the importance of wetlands and the associated supply of naturally occurring organic acids. The exports of  $C_B$  from the lakes were higher in the lake-watersheds covered by thick glacial till (I) (mean: 1670  $\text{eq ha}^{-1} \text{yr}^{-1}$ ) and successively decreased in the lake-watersheds underlain by medium till with low DOC drainage export (II), medium till with high DOC (III), thin till with low DOC (IV), and thin till with high DOC (V) (mean: 1358, 1309, 972, and 645  $\text{eq ha}^{-1} \text{yr}^{-1}$ , respectively). Similar to  $C_B$ , ANC flux decreased with decreasing glacial till depth of the lake-watersheds and was higher for the lake-watersheds exporting low DOC (Table 1).

Fluxes of ANC fluxes decreased with increasing DOC drainage fluxes for the 43 lake-watersheds ( $R^2 = 0.11$ ,  $p = 0.03$ ). When we examined only the thin till lake-watersheds

**TABLE 1.** Major ANC Sinks and Sources and the Calculated and Measured ANC for Lake-Watershed Classes<sup>a</sup>

lake-watershed class	ANC sinks (A)			ANC sources (B)		ANC sources minus sinks (C) = (B) - (A)		measured ANC (D)	difference (C)-(D)	monomeric Al
	n	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{Cl}^-$	base cations	$\text{NH}_4^+$	(C)			
(I) thick till	5	746 (42)	148 (59)	69 (5)	1670 (134)	33 (9)	740 (179)	744 (170)	-4 (27)	21 (6)
(II) medium till low DOC	7	741 (37)	130 (28)	100 (22)	1357 (89)	20 (1)	406 (73)	373 (55)	33 (20)	27 (6)
(III) medium till high DOC	15	741 (98)	114 (27)	79 (12)	1309 (94)	25 (5)	401 (71)	257 (57)	144 (49)	42 (11)
(IV) thin till low DOC	22	736 (16)	172 (15)	64 (2)	959 (42)	27 (3)	14 (43)	76 (27)	-62 (20)	58 (6)
(V) thin till high DOC	4	584 (86)	97 (41)	57 (5)	645 (100)	47 (16)	-45 (91)	-154 (48)	109 (89)	79 (24)

<sup>a</sup> Mean values are listed with standard errors in parentheses. The units are  $\text{equiv ha}^{-1} \text{yr}^{-1}$ , except that for Al, which is  $\text{mol ha}^{-1} \text{yr}^{-1}$ .

(IV, V), which helped exclude the influence of the till depth on ANC production, the inverse relationship between ANC and DOC fluxes was stronger ( $R^2 = 0.34$ ,  $p = 0.0018$ ; Figure 3). The ANC flux also appeared to decrease with increasing DOC flux for the medium-till lake-watersheds (II, III), although this pattern was not statistically significant ( $p > 0.05$ ). The inverse relationships between ANC and DOC and the stronger relationship for the thin-till lake-watersheds (IV, V) appear to be indicative of elevated fluxes of naturally occurring organic acids as an ANC sink for the lake-watersheds with high DOC export and an abundance of wetlands. In an Adirondack lake with high DOC (i.e., West Pond), organic anions were the second most abundant anion after  $\text{SO}_4^{2-}$  (5). While glacial till depth, and thus the contribution of groundwater inputs with high  $\text{C}_D$  levels, may primarily regulate spatial patterns in ANC, the supply of DOC and associated organic acids are an important regulator of ANC in the lake-watersheds with shallow hydrologic flow-paths (i.e., thin-till watersheds).

We calculated the ANC fluxes on the basis of the fluxes of major solutes that contribute to ANC (i.e., base cations,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ; eq 1) and compared these values with measured ANC fluxes for the five lake classes (Table 1). The calculated ANC flux (on the basis of the fluxes of major ionic solutes) for the thick-till (I) and the medium-till with low DOC lake-watersheds (II) were similar to the measured values. However, the calculated ANC flux was greater than the measured ANC flux for the medium-till with high DOC (III) and the thin-till with high DOC lake-watersheds (V), while the calculated ANC flux was smaller than the measured value for the thin-till with low DOC lake-watersheds (IV). The major ANC sinks (i.e.,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ) did not show distinctive patterns among the lake classes, in contrast to that exhibited by base cations, as discussed above. The marked overestimation of the calculated ANC for the medium-till watersheds with high DOC (III) and the thin-till watersheds with high DOC lake-watersheds (V) is presumably due to the elevated supply of naturally occurring organic acids, which was not included in the ANC calculation. For the thin-till watersheds with low DOC (IV), the mobilization of monomeric Al from soil, which generates ANC, was substantial, resulting in the underestimation of the calculated ANC (Table 1). Since the lakes in the watersheds with shallow deposits of glacial till are less influenced by groundwater, higher fluxes of Al are expected in those lakes. Indeed, the fluxes of monomeric Al were higher in the thin-till lake-watersheds, compared with medium-till and thick-till lake-watersheds (Table 1), suggesting the importance of the role of Al mobilized from soil for ANC production at these sites.

The evaluation of the sinks and sources of ANC emphasizes the importance of the combination of surficial geology (i.e., depth of surficial deposits), wetlands, and associated supply of base cations, Al, and DOC in the regulation of ANC in surface waters. While land cover (e.g., forest types) influenced drainage losses of some solutes as well, its limited effects on ANC also suggest a need for the consideration of the role of lakes in the watershed ecosystem, including lake hydrology and in-lake processes in future studies. Understanding the influence of watershed characteristics in the generation and control of ANC is important for evaluating spatial patterns of the recovery of surface waters from the elevated inputs of acidic deposition in the Adirondacks.

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