

Role of within-lake processes and hydrobiogeochemical changes over 16 years in a watershed in the Adirondack Mountains of New York State, USA

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Abstract:

Hydrological and biogeochemical relationships were evaluated for the Arbutus Watershed in the Adirondack Mountains of New York State. Wet-only precipitation inputs (weekly) and discharge losses were evaluated from 1983 to 1998. Precipitation from 1983–98 had significant ($p < 0.05$) decreases in concentrations of Ca^{2+} ($-0.10 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Mg^{2+} ($-0.07 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), K^+ ($-0.01 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Na^+ ($-0.04 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Cl^- ($-0.07 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), SO_4^{2-} ($-0.82 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) and H^+ ($-0.55 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), whereas NH_4^+ and NO_3^- concentrations did not change. For the same period, there were decreases in solute concentrations in the Arbutus Lake outlet for Ca^{2+} ($-1.18 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Mg^{2+} ($-0.32 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), K^+ ($-0.33 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Cl^- ($-0.17 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) and SO_4^{2-} ($-1.90 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) and a significant increase in NH_4^+ concentrations ($+0.07 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$). For the period from 1995 through 1998 the discharge measurements for the outlet and the major inlet of Arbutus Lake were combined with weekly chemical measurements supplemented with storm sampling. At the inlet there were significant relationships ($p < 0.05$) between discharge rates and the concentrations of all solutes except Cl^- , but only for Na^+ , NO_3^- , H^+ and Al did these relationships explain more than 20% of the variation in solute concentrations. April had the greatest rates of discharge and solute flux of any month due to spring snowmelt. The dormant season (October–May) accounted for >80% of the discharge in the inlet and outlet of Arbutus Lake and >78% of the flux of all solutes. For 1995–98 the mass balances of discharge losses from the catchment draining into Arbutus Lake inlet *versus* precipitation inputs suggest that internal watershed processes resulted in net generation of Ca^{2+} ($-1342 \text{ mol}_c \text{ ha}^{-1} \text{ year}^{-1}$), Mg^{2+} ($-313 \text{ mol}_c \text{ ha}^{-1} \text{ year}^{-1}$), K^+ ($-35 \text{ mol}_c \text{ ha}^{-1} \text{ year}^{-1}$), SO_4^{2-} ($-635 \text{ mol}_c \text{ ha}^{-1} \text{ year}^{-1}$) and Cl^- ($-45 \text{ mol}_c \text{ ha}^{-1} \text{ year}^{-1}$) and net retention of inorganic N solutes ($\text{NO}_3^- + \text{NH}_4^+$: $204 \text{ mol}_c \text{ ha}^{-1} \text{ year}^{-1}$) and H^+ ($424 \text{ mol}_c \text{ ha}^{-1} \text{ year}^{-1}$). Concentrations and fluxes of Ca^{2+} , H^+ , NO_3^- , SO_4^{2-} and Al were lower at the lake outlet compared with the inlet. A comparison of mass balances at the Arbutus Lake inlet and outlet suggested that these decreases may have been due to within-lake biotic processes and/or dilution from other water sources to the lake. Copyright © 2001 John Wiley & Sons, Ltd.

KEY WORDS mass balances; discharge; base cations; nitrogen; sulfur

INTRODUCTION

Evaluating hydrological and biogeochemical relationships in small watersheds provides important information on how anthropogenic, as well as natural factors influence forested ecosystems. We have been evaluating hydrobiogeochemical relationships within the Arbutus Watershed at the Huntington Forest (HF) within the central Adirondack Mountains of New York State. A previous study of the Arbutus watershed covering the period from 1983 through 1992 at this site suggested that large drainage losses of SO_4^{2-} contributed to the drainage fluxes of basic cations (C_B : Ca^{2+} , Mg^{2+} , K^+ and Na^+) (Mitchell *et al.*, 1996b). This relationship between the fluxes of SO_4^{2-} and cations was attributed to SO_4^{2-} serving as mobile anion, resulting in

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the mobilization of cations as counter ions to maintain charge balance. During this same period most of the atmospheric input of inorganic N (74% of wet deposition) was retained in the watershed, especially during the growing season, with most losses occurring during the winter period when vegetation was dormant (Mitchell *et al.*, 1996a,b). Specific components of nitrogen biogeochemistry of the terrestrial, wetland and surface water components of the Archer Creek catchment have also recently been evaluated (McHale *et al.*, 2000; Bischoff *et al.*, 2000; Ohrui *et al.*, 1999). A study on the seston of Arbutus Lake has suggested NO_3^- consumption resulted in distinct isotopic ^{15}N values of the lake seston that differed from another Adirondack lake with higher NO_3^- concentrations (Owen *et al.*, 1999).

The current study had three major objectives. (1) extend the analyses of long-term changes in precipitation and outlet chemistry of Arbutus Watershed to 1998 by including new results from 1993 through 1998; (2) evaluate the effect of discharge rates on solute chemistry of surface waters; and (3) for the period from 1996 to 1998 compare solute concentrations and fluxes between the outlet and the major inlet of Arbutus Lake to evaluate the importance of lake processes in affecting elemental mass budgets of the watershed.

SITE DESCRIPTION

Studies at the HF have evaluated a broad range of biogeochemical constituents, including Al (David and Driscoll, 1984), S (David *et al.*, 1987; Mitchell *et al.*, 1992a, 1998), and N (McHale *et al.*, 2000; Mitchell *et al.*, 1992a,b, 1996a,b; Ohrui *et al.*, 1999; Shepard *et al.*, 1990). The Arbutus Lake Watershed at the HF (Figure 1) is located within the Hudson River drainage. The bedrock consists of Precambrian rock of the sienite–granite series (Fisher, 1957). The surficial geology is dominated by glacial till deposited during the recession of the Wisconsin glacial epoch ~14 000 years ago. The ablation till within the watershed was derived of material accumulated on and within the glacier that was deposited as the ice melted. Glacial till in the Adirondacks has a high sand (~75%) and low clay (<10%) content, with cobbles and boulders often being very abundant. The HF is in the centre of the Adirondack Mountains and within the Anorthosite Massif, a large igneous intrusion composed of up to 90% calcium-rich feldspar (Driscoll 1991). This intrusion contributes to the relatively high calcium concentrations in the soils at the HF compared with other forest sites, including other regions in the Adirondacks, especially to southwest (Foster *et al.*, 1992; Mitchell *et al.*, 1994). Groundwater is closest to the surface in deep near-stream peats (1–3 m depth), pockets of glacial till in valley bottoms (0–2 m) and limited zones of glacial outwash deposits. Upland watershed soils are generally <1 m in depth and include Becket–Mundell series sandy loams (coarse-loamy, mixed, frigid typic Haplorthods), whereas Greenwood Mucky peats are found in valley bottom wetlands.

The HF had a mean annual temperature of 4.4°C and mean annual precipitation was 1010 mm from 1950–80 (Shepard *et al.*, 1989). The overstory in the upper slopes is dominated by *Fagus grandifolia* (American beech) and *Acer saccharum* (sugar maple) with *Acer rubrum* (red maple), *Betula alleghaniensis* (yellow birch) and *Pinus strobus* (white pine) also being common. Overstory vegetation at lower elevations is characterized by *Tsuga canadensis* (eastern hemlock), *B. alleghaniensis*, *Alnus rubrum* (alder), *Picea rubens* (red spruce), and scattered individuals of *Abies balsamea* (balsam fir).

Outflow from the Arbutus Lake Watershed (352 ha) has been gauged at the lake outlet since October 1991 with a V-notch weir (Figure 1). Arbutus Lake has a maximum depth of 8.4 m, mean depth of 3 m, surface area of 50 ha and a hydraulic retention time of 0.6 year (Owen *et al.*, 1999). The 135 ha Archer Creek Catchment is the major source of discharge into the lake (McHale *et al.*, 2000). This catchment has been monitored since 1994 using an H-flume equipped with an automated discharge logging and sample collection system. Further details on the Archer Creek Catchment can be found in Bischoff *et al.* (2000), McHale *et al.* (2000) and Ohrui *et al.* (1999).

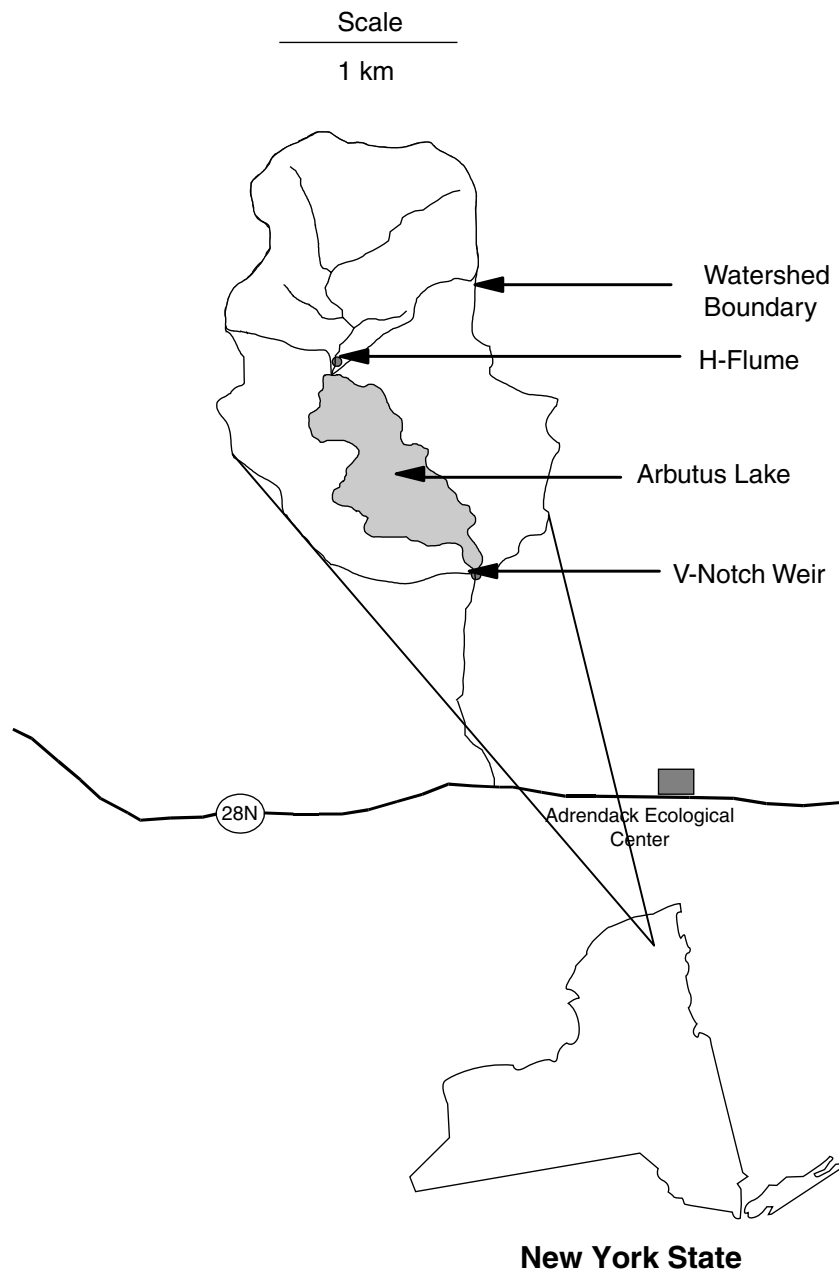


Figure 1. Arbutus Watershed at the HF in the Adirondack Mountains of New York State

METHODS

For the current study we included new data on precipitation and outlet chemistry collected from 1 January 1993 through 31 December 1998. We combined these data with results from 1 January 1983 through 31 December 1992 (Mitchell *et al.*, 1996b) to provide a 16 year record of precipitation and outlet chemistry. For the period from 1 January 1995 through 31 December 1998, we did the most detailed biogeochemical

analyses, since for this period we had complete hydrology and chemistry data, including measurements of storm events, from both the H-flume at the major inlet of Arbutus Lake and the V-notch weir at the lake outlet.

Chemical analyses

Surface water samples from 1983 to 1994 were analysed using the protocols of the Adirondack long-term monitoring (ALTM) program (Driscoll and Van Dreason, 1993). Surface water samples collected from 1995 through 1998 had a similar protocol as that of the ALTM. Following collection of surface water, the samples were stored at $\sim 1^{\circ}\text{C}$ until analysed at the Biogeochemical Laboratory at SUNY–ESF using a glass electrode (pH), ion chromatography (SO_4^{2-} , NO_3^- , and Cl^-) and Wescan Analyzer (NH_4^+) using methods described by Shepard *et al.* (1989). Atomic absorption (AA) spectrometry was used for analysing Na^+ and K^+ . Inductively coupled plasma (ICP) spectrometry was used for analysing Ca^{2+} , Mg^{2+} , and Al. Total dissolved N was determined using persulfate oxidation (Ameel *et al.*, 1993). The Biogeochemical Laboratory at SUNY–ESF follows an extensive QA/QC procedure. Every analytical batch has calibrations QCs, detection limit QCs, an analytical blank, and an analytical replicate. Control charts track variation to ensure a normal distribution around a mean value, to eliminate bias. Performance evaluation (audit) samples are used to estimate intra-laboratory analytical precision and accuracy and to estimate inter-laboratory precision and bias. The Biogeochemical Laboratory participates in the United States Geological Survey (USGS) audit program (Branch of Quality Systems, Standard Reference Sample Project) to ensure data quality.

Data compilation and determination of solute fluxes

From 1983 to 1994, monthly solute concentrations were available as part of the Adirondack long-term monitoring project (Driscoll and Van Dreason, 1993; W. Kretser, personal communication). Wet-only precipitation chemistry data were obtained for the NADP/NTN (NADP, 1999) site located 1–3 km from the watershed. Nutrient fluxes for precipitation were computed by multiplying precipitation inputs by concentrations. Discharge rates at the outlet were recorded hourly from 1 October 1991 and inlet discharge rates were measured at 15 min intervals from 1 January 1994 (McHale *et al.*, 2000). Water chemistry data were available as a combination of weekly sampling and automatic event sampling using an ISCO sampler. Although weekly sampling data were available for the 1995–98 period, automated event sampling data were available only in 1995 and 1996.

For 1995 through 1998 the daily discharge rates for the inlet and outlets were computed by summing hourly and 15 min discharge rates respectively. For days on which discharge-event chemical concentrations were collected, flow-weighted chemical concentrations were calculated. For a day when chemical concentrations were unavailable, concentrations were computed by linear interpolation using the two measured concentrations closest to that day. Daily nutrient fluxes were then determined as a product of the discharge rate and the nutrient concentration for each day. Monthly or annual fluxes were then determined by summing daily solute fluxes.

Weighted mean precipitation and surface water concentrations were calculated using either precipitation or discharge values respectively (SAS, 1994). The seasonal Kendall Test (Gilbert, 1987) was used for evaluating long-term trends in solute concentrations for wet-only precipitation and the water discharged from the outlet of Arbutus Lake. Tests were made using monthly concentration values for precipitation and drainage water from the outlet. Monthly precipitation values were calculated from volume-weighted weekly samples.

RESULTS AND DISCUSSION

Long-term changes in solute concentrations

Precipitation. The mean annual precipitation input of 1149 mm from 1983 to 1998 was greater (139 mm) than the average reported from 1930 to 1980 (Shepard *et al.*, 1989). During the current study

Table I. Mean solute concentrations of wet-only precipitation at HF and drainage water from Arbutus Lake from 1983 through 1998 (means weighted by annual precipitation or discharge rates (mm); (SE) = square root (weighted sample variance/sum of weights) SAS (1994)

Component	Solute (μmol_c)								
	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	H ⁺	NH ₄ ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
Wet-only precipitation	4.5 (0.28)	1.4 (0.09)	0.3 (0.03)	2.2 (0.15)	41.9 (1.51)	11.8 (0.66)	25.3 (1.13)	2.9 (0.15)	37.4 (1.6)
Discharge from outlet	154.0 (1.57)	44.5 (0.45)	9.2 (0.18)	34.1 (0.54)	0.58 (0.03)	1.9 (0.12)	13.2 (0.73)	11.0 (0.14)	128.8 (1.39)

(1983–98) the average pH of precipitation was an acidic 4.4 ($[\text{H}^+] = 41.9 \mu\text{mol}_c \text{ l}^{-1}$) (Table I), as is characteristic for most of this region (Driscoll, 1991). For the period of 1978–81, Mollitor and Raynal (1983) reported an average pH value of 4.10, thus suggesting that pH values have increased from this early period. As has been found previously at the HF (Driscoll *et al.*, 1995), the sum of strong acid anion ($\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-$) concentrations ($65.6 \mu\text{mol}_c \text{ l}^{-1}$) greatly exceeded the sum of basic cation (C_B : $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) concentrations ($8.4 \mu\text{mol}_c \text{ l}^{-1}$) in precipitation (Table I). There were highly significant ($p < 0.01$) decreases in Ca^{2+} ($-0.10 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Mg^{2+} ($-0.07 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), K^+ ($-0.01 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Cl^- ($-0.07 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), SO_4^{2-} ($-0.82 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) and H^+ ($-0.55 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) (Figure 2). A significant ($p = 0.04$) decrease was detected for Na^+ ($-0.04 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) and no decreases ($p > 0.05$) were found for NO_3^- , NH_4^+ and H^+ . Decreasing concentrations of Ca^{2+} ($-0.32 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Mg^{2+} ($-0.14 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), NH_4^+ ($-0.57 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), H^+ ($-0.80 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Cl^- ($-1.45 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), NO_3^- ($-0.13 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), and SO_4^{2-} ($-1.83 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) in wet deposition were reported for the period from 1978 to 1994 for the HF (Driscoll *et al.*, 1995). These results indicate that the annual rates of decrease of solute concentrations were greater during 1978–94 than for 1983–96 reported in the current study. The greater change in annual rates for the former period can be attributed to the substantially higher atmospheric inputs of these solutes from 1978 through 1992. Although a more substantial decrease in H^+ concentrations might be expected due to the marked decreases in SO_4^{2-} concentrations due to the contribution of H_2SO_4 to precipitation acidity, as was found from 1978 to 1994 by Driscoll *et al.* (1995), the concomitant changes in Ca^{2+} , Mg^{2+} and K^+ suggest that there were also concomitant decreases in chemical sources that would consume acidity. It has been suggested that these decreases in these base cation atmospheric inputs have had a marked effect on the biogeochemistry of forested watersheds in the northeastern USA (Likens *et al.*, 1996; DeHayes *et al.*, 1999).

Arbutus Lake discharge. For 1983 to 1998, there were highly significant decreases ($p < 0.01$) in solute concentrations in the Arbutus Lake outlet for Ca^{2+} ($-1.18 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Mg^{2+} ($-0.32 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), K^+ ($-0.33 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$), Cl^- ($-0.17 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) and SO_4^{2-} ($-1.90 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) (Figure 3). There was a significant increase in NH_4^+ concentrations ($+0.07 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$). The decrease in the concentrations of three of the base cations (Ca^{2+} , Mg^{2+} and K^+) was likely attributed to both a change in atmospheric inputs of these elements and to a decrease in the concentration of SO_4^{2-} , which is the dominant mobile anion. A decrease in the flux of a mobile anion such as SO_4^{2-} will result in a concomitant decrease in the major counter cations (Reuss and Johnson, 1986) that are dominated by base cations (C_B) for the Arbutus Watershed surface waters. The reason for the small increase in NH_4^+ concentrations is not known. Driscoll *et al.* (1995) reported changes in solute concentrations in 16 ALTM lakes, including Arbutus Lake, from 1982 to 1993 for which significant changes ($p < 0.05$) were found for H^+ ($-0.02 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$) and SO_4^{2-} ($-1.02 \mu\text{mol}_c \text{ l}^{-1} \text{ year}^{-1}$).

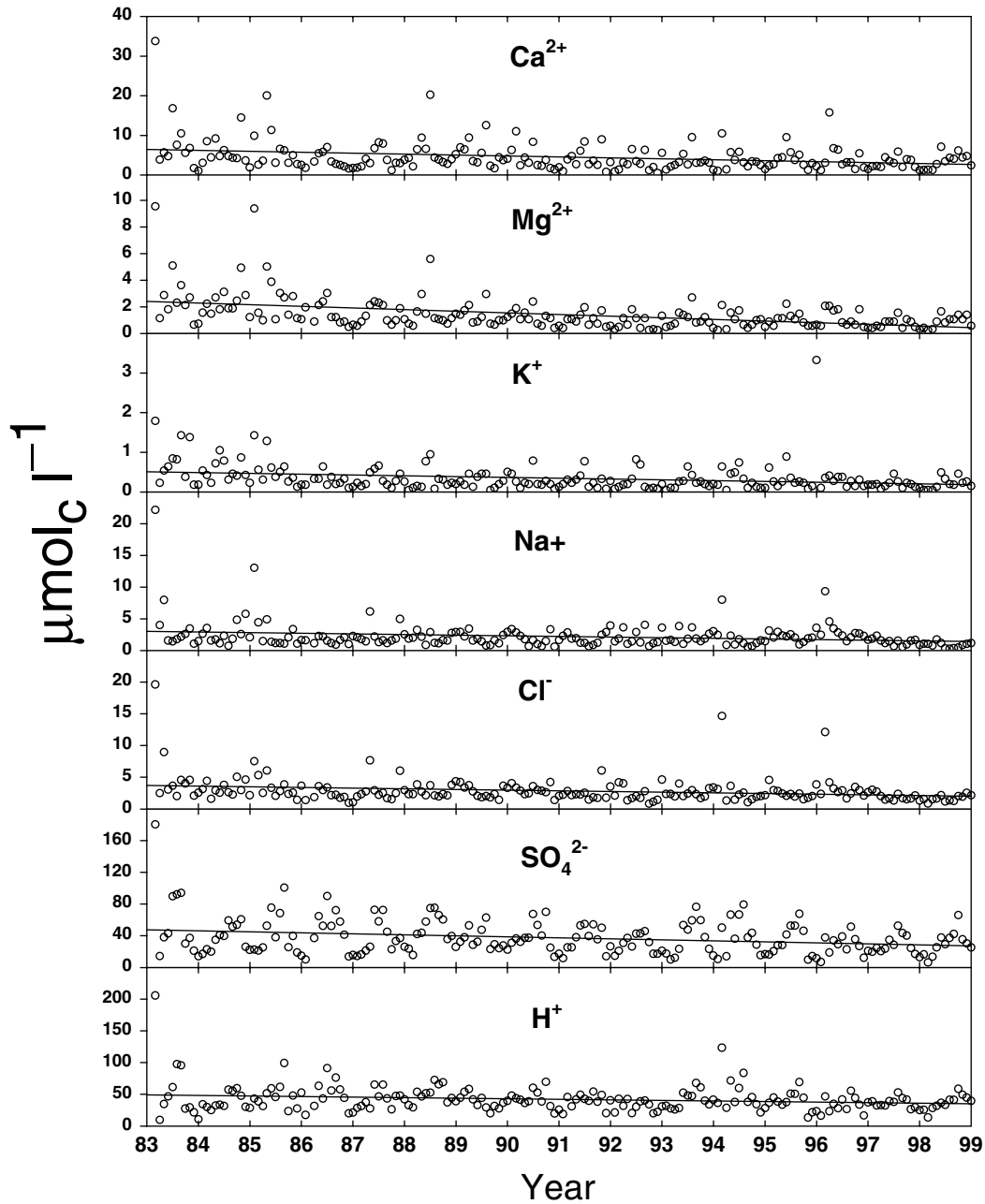


Figure 2. Significant ($p < 0.05$) temporal changes detected by the seasonal Kendall test in monthly solute concentrations in wet-only precipitation at the HF

Effects of discharge rates on solute concentrations

The concentrations of the major solutes were regressed against daily discharge rates for the period from 1995 through 1998 that had the most complete information on hydrology and solution chemistry (Table II). For the H-flume at the inlet there was significant effect (slope greater than or less than zero; $p < 0.05$)

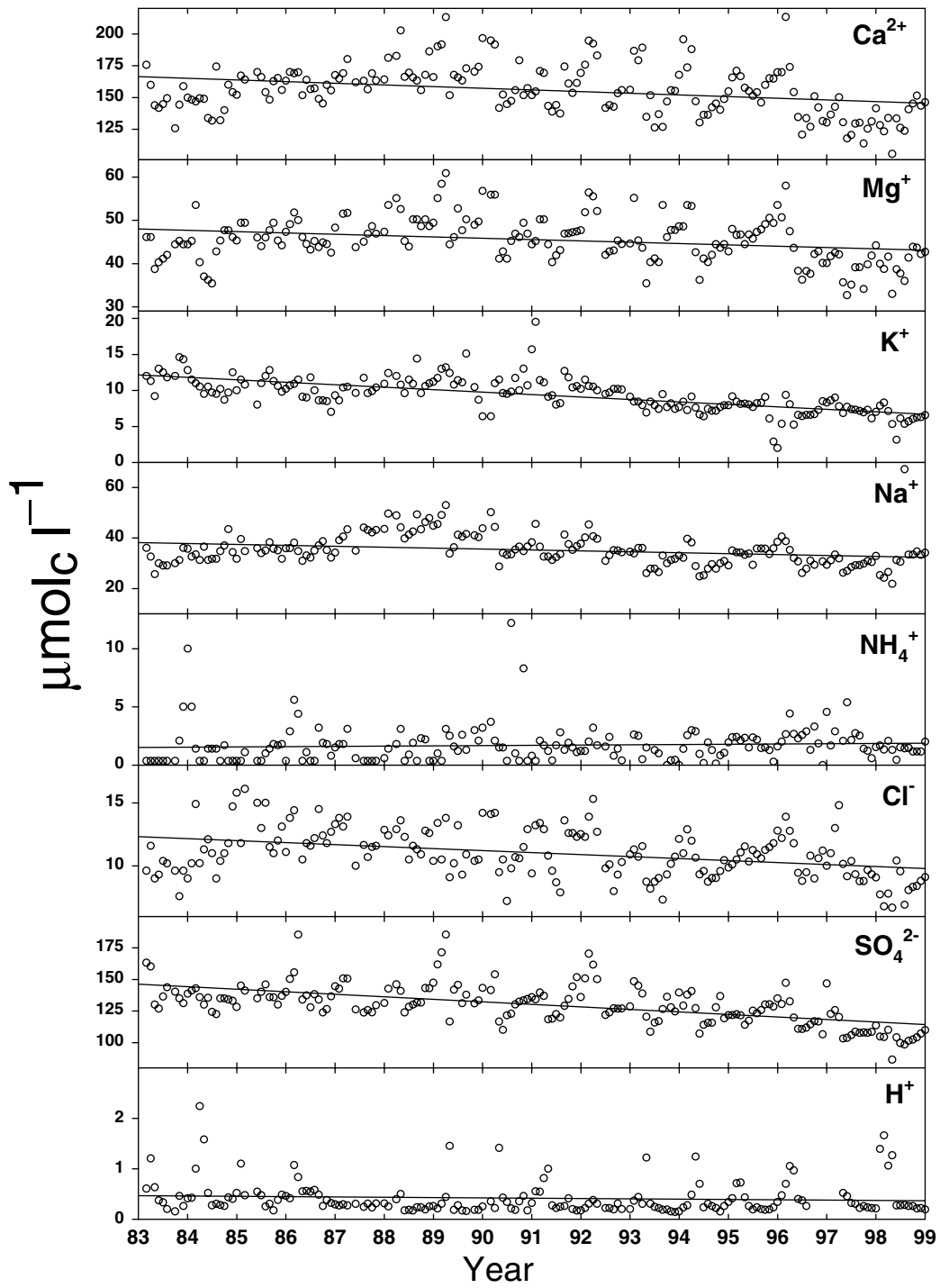


Figure 3. Significant ($p < 0.05$) temporal changes detected by the seasonal Kendall test in monthly solute concentrations at the outlet of the Arbutus Watershed at the HF. Line is the calculated regression line

Table II. Results of regression of solute concentrations [$\mu\text{mol}_c \text{ l}^{-1}$ or $\mu\text{mol l}^{-1}$ (DON, Al) against mm day^{-1}] against discharge rate for the inlet H-flume and outlet V-notch flume in the Arbutus Watershed (1995–98). Results presented when slope of regression was significantly different from zero ($p \leq 0.05$)

Solute	Regression analyses		
	Slope	p of slope	R^2
Inlet			
NH_4^+	0.06	0.0026	0.063
K^+	0.17	0.0002	0.094
Na^+	-1.55	0.0001	0.217
Ca^{2+}	-2.95	0.0001	0.110
Mg^{2+}	-0.91	0.0001	0.137
Al	0.53	0.0001	0.206
NO_3^-	1.55	0.0001	0.238
SO_4^{2-}	-0.78	0.0460	0.028
DON	0.30	0.0028	0.062
H^+	0.17	0.0001	0.464
Outlet			
Al	0.23	0.0028	0.065
NO_3^-	1.54	0.0001	0.108
SO_4^{2-}	-1.32	0.0310	0.035
H^+	0.83	0.0001	0.106

with discharge rates on the concentrations of all solutes except Cl^- , but only for Na^+ , NO_3^- , H^+ and Al did the regression equations explain more than 20% of the variation (i.e. $R^2 > 0.20$) (Figure 4). At the outlet only NO_3^- , SO_4^{2-} , H^+ and Al concentrations were affected by discharge rates. Substantially less of the variation was explained by the discharge rates at the outlet ($R^2 < 0.11$) compared with the inlet. If the discharge rates of the inlet are transformed to \log_{10} then the regression equation for Na^+ improves to $R^2 = 0.563$ (slope: -19.5 ; $p < 0.0001$), suggesting exponential dilution of this solute. McHale *et al.* (2000) found in their 1 year study that NO_3^- concentrations also were positively related to discharge rates when the full year data were analysed as done in the current study. However, when the year was divided between growing (June–September) and dormant (October–May) seasons the relationship was not significant during the dormant season and a significant but negative relationship was found during the growing season (McHale *et al.*, 2000).

Seasonal patterns in solute fluxes

These relationships between solute concentration and flux were reflected in seasonal patterns of solute flux (Figure 5). Owing to the melting of the snow pack, April had the greatest discharge at both the inlet and outlet. January showed the second greatest discharge losses, which were due to rain on snow events that occurred during this period. For all solutes there was a direct correspondence between discharge water losses and solute fluxes, with lowest fluxes occurring during the later summer and early fall (August–September). In April and January the solute fluxes were high not only due to the high discharge rates, but also because of higher solute concentrations, especially for NO_3^- and H^+ in the inlet. Snow-melt episodes with high NO_3^- concentrations and low pH occur in surface waters of the northeastern USA, including the Adirondacks (Wigington *et al.*, 1996). In the Arbutus Watershed the pH of the surface waters may be depressed during storm events during the dormant season. For example, a precipitation event (72 mm day^{-1}) on 21 October 1995 increased daily

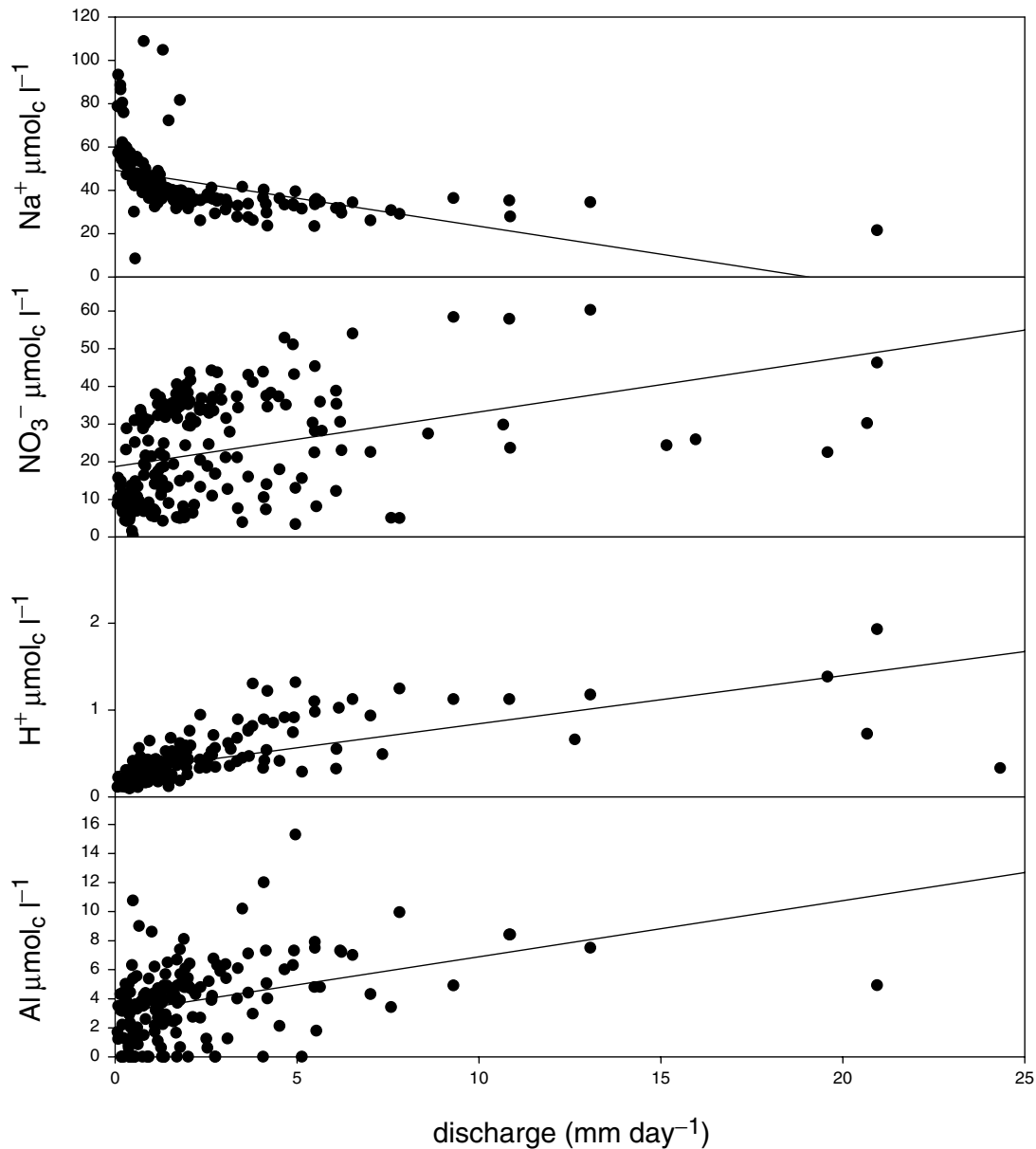


Figure 4. Relationship of solute concentrations *versus* daily discharge rates at the inlet to Arbutus Lake. Relationships shown with $R^2 > 0.200$. (See also Table III). Line is the calculated regression line

discharge rates to 21 mm day^{-1} at the inlet for 2 days and pH values decreased to 5.14 compared with an average pH at the inlet of 5.85. At the outlet, the lowest pH value was 5.76 on 10 February 1998 compared with an average 6.21. Values of pH < 6 may be lethal to certain sensitive species of the aquatic biota (Baker and Christensen, 1991).

From 1995 through 1998, the dormant season accounted for 84% and 80% of the discharge in the inlet and outlet of Arbutus Lake respectively, and $> 78\%$ of the flux of all solutes. For those solutes that have important biotic reactions, the relative losses during the dormant season were even greater. For example, 94% and 95%

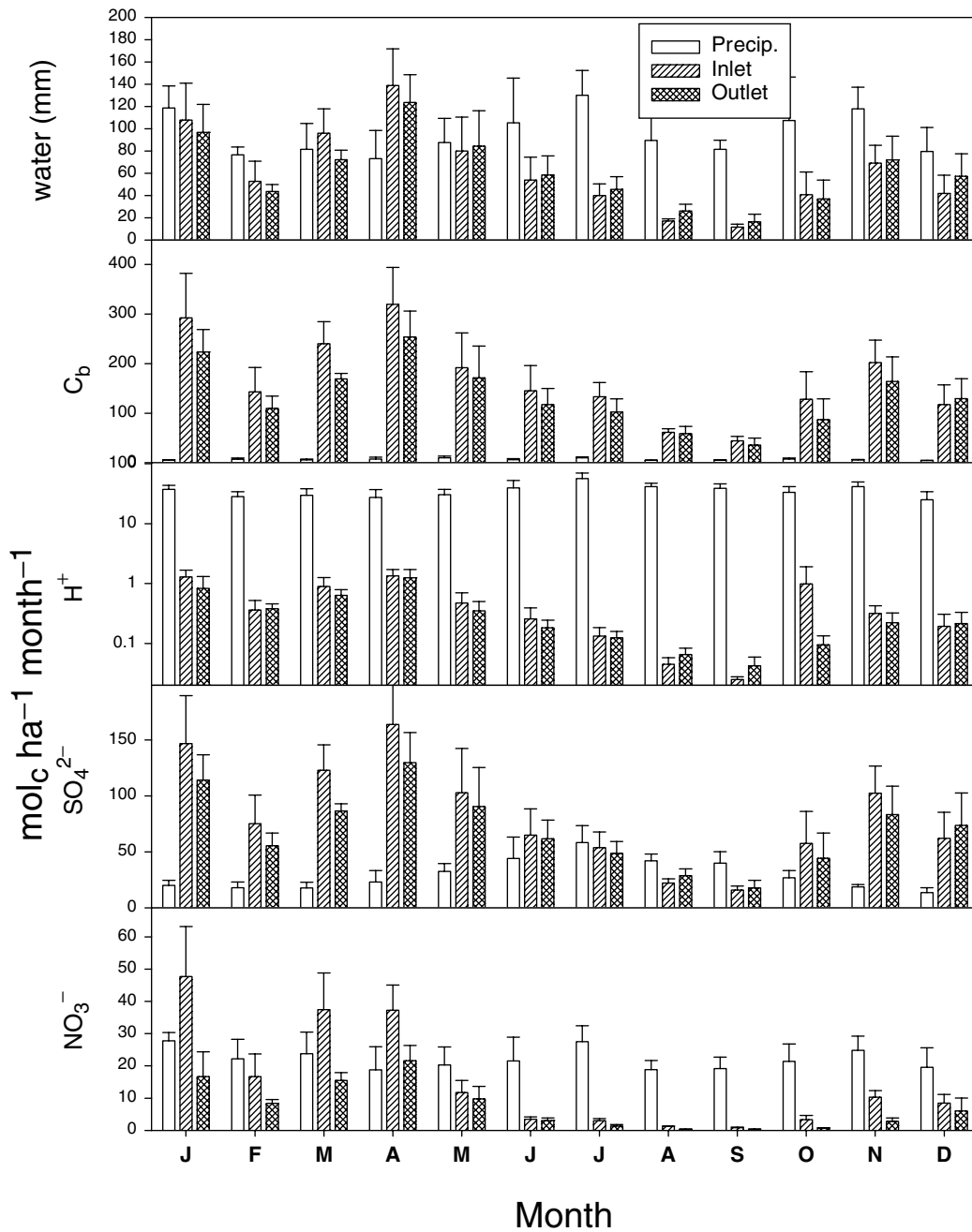


Figure 5. Monthly fluxes of selected solutes in wet-only precipitation and at the inlet and outlet of Arbutus Lake from 1 January 1995–31 December 1998. $C_B = (Ca^{2+} + Mg^{2+} + K^+ + Na^+)$. Concentration of H^+ plotted on logarithmic scale. Vertical error bars are standard errors

of NO_3^- loss occurred during the dormant season at the inlet and outlet respectively. The high loss rates of NO_3^- during the dormant season at the outlet of Arbutus Lake, as well as for three other forested watersheds in the northeast USA, was reported previously for the period from 1982–94 (Mitchell *et al.*, 1996a).

Role of watershed in affecting solute concentrations and mass balances

The analyses of changes in solute concentrations and mass balances focused on the period from 1995 through 1998, since this period had the most complete information. Evapotranspiration losses (399 mm) were estimated by subtracting the average annual discharge from the lake inlet (750 mm) from precipitation inputs (1149 mm). Evapotranspiration resulted in a 35% loss of precipitation, which is similar to the 38% loss at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire. The water fluxes at the Archer Creek catchment were lower, however, than those at the HBEF, where evapotranspiration, stream discharge and precipitation were 494 mm, 801 mm, and 1295 mm respectively (Likens and Bormann, 1995).

There were marked changes in solute chemistry as precipitation inputs passed through the terrestrial portion of the Arbutus Watershed and drained into the lake inlet (Table III). Although there were increases in SO₄²⁻ and Cl⁻ concentrations in the inlet compared with precipitation (*ca* threefold), the relative increases in the concentrations of base cations (12–32-fold) and decreases in H⁺ (72-fold) were even greater. The mean pH at the inlet was 5.85 ([H⁺] = 1.41 μmol_c l⁻¹). As the water passed through the lake, Ca²⁺, NO₃⁻ and SO₄²⁻ concentrations decreased and pH increased further to 6.21 ([H⁺] = 0.61 μmol_c l⁻¹).

For most solutes (Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻ and SO₄²⁻) there was a net loss to drainage compared with precipitation inputs (precipitation inputs – discharge losses) (Table IV). Although the precipitation inputs do not include estimates of dry deposition, previous studies at this watershed that included dry deposition estimates (Mitchell *et al.*, 1996b; Shepard *et al.*, 1989) found that, even with dry deposition added to the mass balances, these solutes exhibited net losses from the watershed. The loss of SO₄²⁻ is especially important since these loss rates (990 mol_c ha⁻¹ year⁻¹) greatly exceed estimates of the sum (585 mol_c ha⁻¹ year⁻¹) of wet

Table III. Mean solute concentrations of wet-only precipitation, drainage water near Arbutus Lake inlet and drainage water from Arbutus Lake from 1995 through 1998 (means weighted by precipitation or discharge rates (mm); (SE) = square root (weighted sample variance/sum of weights) SAS (1994)

Component	Solute (μmol _c l ⁻¹)									Solute (μmol _c l ⁻¹)	
	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	H ⁺	NH ₄ ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Al	DON
Wet-only precipitation	2.5 (0.19)	0.7 (0.04)	0.2 (0.04)	1.7 (0.08)	35.5 (1.32)	9.8 (0.67)	19.6 (1.00)	2.1 (0.09)	26.3 (1.5)	NA ^a	NA
Discharge to inlet	186.2 (2.12)	43.0 (0.52)	6.2 (0.20)	33.4 (0.61)	1.41 (0.12)	1.5 (0.11)	31.0 (1.15)	10.5 (0.19)	130.1 (1.11)	7.6 (0.44)	13.5 (0.54)
Discharge from outlet	144.9 (1.57)	42.2 (0.40)	7.0 (0.12)	32.1 (0.66)	0.61 (0.04)	2.3 (0.14)	13.4 (0.49)	10.3 (0.13)	114.4 (0.80)	1.9 (0.11)	12.7 (0.43)

^a Not available.

Table IV. Annual hydrological and biogeochemical solute fluxes at Arbutus watershed from January 1985 through December 1998

Flux	Water (mm year ⁻¹)	Solute (mol _c ha ⁻¹ year ⁻¹)									Solute (mol _c ha ⁻¹ year ⁻¹)	
		Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	H ⁺	NH ₄ ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Al	DON
Wet Only Precipitation	1149	42	11	3	22	430	128	266	28	355	na	na
Discharge to inlet	750	1384	324	38	271	6	9	181	78	990	35	85
Discharge from outlet	734	1033	307	51	232	4	15	87	73	834	24	91
Precipitation—discharge to inlet	399	-1342	-313	-35	-249	424	119	85	-50	-635	na	na
Precipitation—discharge from outlet	415	-991	-296	-48	-210	426	113	179	-45	-479	na	na

(355 mol_c ha⁻¹ year⁻¹; current study) and dry (129 mol_c ha⁻¹ year⁻¹; Shepard *et al.*, 1989) deposition at this site. Analyses using stable isotopes of sulfur at the HBEF (Alewell *et al.*, 1999) and model results for the northeastern USA (Driscoll *et al.*, 1998a) suggest that, within this region, these high losses are likely attributable to internal S sources that could include sulfate desorption, S mineral weathering or net mineralization of organic S pools. The amount of SO₄²⁻ entering surface waters will slow the recovery of these waters from acidification (Johnson and Mitchell, 1998; Driscoll *et al.*, 1998a). The high loss rates of the base cations, especially Ca²⁺ and Mg²⁺, are due to their role as positively charged counter ions that maintain charge neutrality as the mobile SO₄²⁻ and NO₃⁻ anions move through the watershed (Reuss and Johnson, 1986). Charge balances for the measured ions in precipitation, inlet and outlet waters were +2.4, +99.7 and +91.0 respectively. Much of the charge imbalance for the inlet and outlet waters is likely attributable to negatively charged dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) that may be important solutes in surface waters in the Adirondacks (Driscoll *et al.*, 1998b). For Arbutus Lake, using data from the Adirondack Lake Survey Corporation from 1983 through 1992, the mean DOC and DIC values were 397 ± 6 μmol l⁻¹ (SE) and 116 ± 4 μmol l⁻¹ respectively. Estimates of contribution of organic acids to solution charge can be estimated using the following two equations:

$$[\text{RCOO}^-] = \frac{pK_a m [\text{DOC}]}{pK_a + [\text{H}^+]}$$

and

$$pK_a = a + (b\text{pH}) - (c\text{pH}^2)$$

where [RCOO⁻] is the (μmol_c l⁻¹) organic anion concentration, pK_a is the dissociation constant of humic acid, *m* is the concentration of acidic functional groups per mole C of DOC, [DOC] is the (μmol_c l⁻¹) and dissolved organic carbon concentration, *a*, *b* and *c* are operationally defined by model calibration.

Using the parameter values provided by Driscoll *et al.* (1989) for Adirondack lakes (*a* = 0, *b* = 1.45, *c* = 0.08, *m* = 0.17), the charge contribution by RCOO⁻ would be 65 μmol_c l⁻¹. The HCO₃⁻ fraction of DIC, which would provide additional negative charge, together with organic acids, could account for the difference in the charge balance between measured anions and cations in water discharged from Arbutus Lake.

The Arbutus Watershed retained H⁺, NH₄⁺ and NO₃⁻ (Table IV). Owing to the relatively high base status of the soils at this site (Foster *et al.*, 1992; Johnson and Lindberg, 1992), base cations dominate the soil exchange complex and by exchanging with H⁺ contributed to H⁺ retention and the higher pH of drainage waters (Mitchell *et al.*, 1992a). The relatively high base status of the soils within the watershed contributes to its low Al solute concentrations at the inlet and outlet of Arbutus Lake. The net retention of NH₄⁺ and NO₃⁻ is due to the high demand of the biota for N, especially during the growing season (Mitchell *et al.*, 1996a, Vitousek *et al.*, 1997). Dissolved organic nitrogen (DON) contributed a substantial portion of total solute N losses in this watershed, especially at the lake outlet, where it constituted 47% of the total N solute fluxes. McHale *et al.* (2000) previously reported for the period from June 1995 to May 1996 that DON in the Arbutus Lake outlet contributed 61% of total N solute fluxes. Campbell *et al.* (2000) found that DON was the major form of dissolved N in the drainage waters of nine forested watersheds in New England. The analysis of Driscoll *et al.* (1995) classified the Arbutus Watershed as an intermediate till, low DOC system and, based upon this classification, the watershed should be somewhat more responsive to changes in atmospheric inputs than thick till watersheds. The results of the current study indicate that there is considerable alteration of solute chemistry as water passes through the watershed, and thus its surface waters may be less responsive than in other areas of the Adirondacks with shallower soils and lower amounts of base cations (Newton *et al.*, 1987).

Within-lake processes

Internal lake processes can have marked effects on solute chemistry, especially in shallow lakes with relatively long retention times (Kelly *et al.*, 1987). At the inlet and outlet of Arbutus Lake the conservative

solutes Na^+ ($33.4 \mu\text{mol l}^{-1}$ and $32.1 \mu\text{mol}_c \text{l}^{-1}$ respectively) and Cl^- ($10.5 \mu\text{mol l}^{-1}$ and $10.3 \mu\text{mol}_c \text{l}^{-1}$ respectively) had almost identical concentrations (Table III). Concentrations of Mg^{2+} , K^+ and DON were also similar. There were reductions in the concentrations of Ca^{2+} , H^+ , NO_3^- , SO_4^{2-} and Al. The decrease in NO_3^- and SO_4^{2-} may have been due to both assimilatory and dissimilatory biotic processes that would remove these solutes. For example, the Baker *et al.* (1986) model on SO_4^{2-} retention predicts that dissimilatory sulfate reduction is a function of lake morphometry and water residence time:

$$R = \frac{0.46 \times 100}{0.46 + \frac{z}{t_w}}$$

where R is the retention of SO_4^{2-} , as percentage input, z is the mean depth (3 m) and t_w is the water residence time (0.6 year). Using this model, 8% SO_4^{2-} retention would be predicted, which is considerably less than the mass balance calculation of 16% retention. This result suggests that the model is either under-predicting dissimilatory sulfate reduction in Arbutus Lake or that other water sources to the lake have lower SO_4^{2-} concentrations, resulting in a dilution of SO_4^{2-} discharged from the lake. Owen *et al.* (1999) compared Arbutus Lake NO_3^- concentrations and $\delta^{15}\text{N}$ values in the seston to the more acidic Dart Lake with higher NO_3^- and suggested that the biota consumed a substantial fraction of the NO_3^- in Arbutus Lake. McHale *et al.* (2000) also found in a 1 year study (June 1995–May 1996) that, as water passed from the inlet to the outlet of Arbutus Lake, there was substantial consumption of NO_3^- , especially during the summer. Chemical reduction of SO_4^{2-} and NO_3^- processes would contribute to the consumption of H^+ (Kelly *et al.*, 1987) and the higher pH at the outlet.

The lower concentrations of Ca^{2+} in the outlet *versus* the inlet could be due to various factors, including groundwater inputs to the lake, other water sources (Peters and Driscoll, 1987; Schafran and Driscoll, 1993), or alteration by within-lake biotic processes (Kelly *et al.*, 1987). Analyses of variation in the solute chemistry of the surface and groundwaters of the Archer Creek Catchment (McHale, 1999; Mitchell *et al.*, unpublished data) indicate that there is considerable spatial variation in Ca^{2+} , SO_4^{2-} and NO_3^- concentrations in the Archer Creek Catchment. Groundwater and/or drainage from that portion of the watershed not represented by Archer Creek (167 ha) may have lowered Ca^{2+} , SO_4^{2-} and NO_3^- concentrations, and thus could also have contributed to the lower concentrations of these solutes being discharged from the Arbutus Lake outlet. The similarities in Na^+ and Cl^- fluxes between the inlet and outlet, however, do not directly support groundwater, but marked spatial variability of these solutes in the surface and groundwaters of Archer Creek catchment has not been found. Thus, owing to the possible contribution of other water sources to the lake besides Archer Creek that could have lowered concentrations of SO_4^{2-} and NO_3^- , it cannot be assumed that decreases in SO_4^{2-} and NO_3^- concentrations at the outlet compared with the inlet can be attributed entirely to biotic reduction processes. Further studies on the various sources of water to the Arbutus Watershed, including other inputs to Arbutus Lake, are needed to evaluate the relative importance of within-lake processes *versus* variation in water sources in affecting solute chemistry.

CONCLUSIONS

There is considerable interest in the response of surface waters in the Adirondacks to changes in atmospheric deposition. Although SO_4^{2-} inputs have decreased and precipitation inputs have increased, there has been little recovery of surface waters from acidification (Driscoll *et al.*, 1998b). The results of this study show that, despite these changes in precipitation inputs, discharge water losses of SO_4^{2-} and base cations (especially Ca^{2+}) have remained as high as in early periods. These results suggest that within the Arbutus Watershed there is an additional supply of S that may include the mineralization of organic S and/or the weathering of S minerals. Owing to the relatively high availability of Ca in this watershed, these high rates of SO_4^{2-} loss have not caused any marked depletion of this base cation. Average annual discharge water losses of NO_3^- ,

NH₄⁺ and DON from the lake outlet indicate that most atmospherically deposited N is either retained or lost within the watershed, although considerable variability of NO₃⁻ losses occurs among individual years (Mitchell *et al.*, 1996a). Within-lake processes consume significant amounts of NO₃⁻, especially during the growing season, and attenuate acidic episodes throughout the year. The importance of these lake processes needs to be considered when evaluating the biogeochemical changes and spatial patterns of surface waters in the Adirondacks. The portion of the watershed above the inlet has a complex topography that includes both wetland and upland systems. To understand the hydrobiogeochemistry of this watershed, attention needs to be focused on evaluating how various landscape components influence the temporal and spatial patterns of solute chemistry.

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