

Impacts of changing climate and atmospheric deposition on N and S drainage losses from a forested watershed of the Adirondack Mountains, New York State

Ji-HYUNG PARK*, MYRON J. MITCHELL*, PATRICK J. McHALE*, SHEILA F. CHRISTOPHER* and TILDEN P. MEYERS†

*Faculty of Environmental and Forest Biology, SUNY College of Environmental Science and Forestry, Syracuse, NY 13210, USA,

†Atmospheric Turbulence and Diffusion Division, NOAA/Air Resources Laboratory, 456 South Illinois Ave., Oak Ridge, TN 37830, USA

Abstract

Biogeochemical responses to changing climate and atmospheric deposition were investigated using nitrogen (N) and sulfur (S) mass balances, including dry deposition and organic solutes in the Arbutus Lake watershed in the Adirondack Mountains, New York State. Long-term monitoring of wet-only precipitation (NADP/NTN, 1983–2001) and dry deposition (AIRMoN, 1990–2001) at sites adjacent to the watershed showed that concentrations of SO_4^{2-} in precipitation, SO_4^{2-} in particles, and SO_2 vapor all declined substantially ($P < 0.005$) in contrast to no marked temporal changes observed for most N constituents (NH_4^+ in precipitation, HNO_3 vapor, and particulate NO_3^-), except for NO_3^- in precipitation, which showed a small decrease in the late 1990s. From 1983 to 2001, concentrations of SO_4^{2-} in the lake outlet significantly decreased ($-2.1 \mu\text{eq L}^{-1}\text{yr}^{-1}$, $P < 0.0001$), whereas NO_3^- and dissolved organic N (DON) concentrations showed no consistent temporal trends. With the inclusion of dry deposition and DON fluxes into the mass balance, the retained portion of atmospheric N inputs within the main subcatchment increased from 37% to 60%. Sulfur outputs greatly exceeded inputs even with the inclusion of dry S deposition, while organic S flux represented another source of S output, implying substantial internal S sources. A significant relationship between the annual mean concentrations of SO_4^{2-} in lake discharge and wet deposition over the last two decades ($r = 0.64$, $P < 0.01$) suggested a considerable influence of declining S deposition on surface water SO_4^{2-} concentrations, despite substantial internal S sources. By contrast, interannual variations in both NO_3^- concentrations and fluxes in lake discharge were significantly related to year-to-year changes in air temperature and runoff. Snowmelt responses to winter temperature fluctuations were crucial in explaining large portions of interannual variations in watershed NO_3^- export during the months preceding spring snowmelt (especially, January–March). Distinctive response patterns of monthly mean concentrations of NO_3^- and DON in the major lake inlet to seasonal changes in air temperature also suggested climatic regulation of seasonal patterns in watershed release of both N forms. The sensitive response of N drainage losses to climatic variability might explain the synchronous patterns of decadal variations in watershed NO_3^- export across the northeastern USA.

Keywords: acidic deposition, climate change, DON, DOS, dry deposition, watershed biogeochemistry

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Introduction

Climate change and acidic deposition, along with other drivers of global change, represent multiple environ-

mental stresses to forest ecosystems (Aber & Driscoll, 1997; Aber *et al.*, 2001). Some recent studies have suggested that deviations of the observed long-term stream water chemistry from predicted responses of watershed nitrogen (N) export to atmospheric deposition might be related to interannual climatic variations (Martin *et al.*, 2000; Aber *et al.*, 2002; Driscoll *et al.*, 2003;

Correspondence: Ji-Hyung Park, Arizona State University, School of Life Sciences, PO Box 874501, Tempe, AZ 85287, USA, tel. +1 480 965 8165; fax +1 480 965 6899, e-mail: jhp@asu.edu

Goodale *et al.*, 2003). In response to decreasing sulfur (S) deposition, sulfate concentrations in surface waters have declined over the last two decades across most areas of Europe and North America (Stoddard *et al.*, 1999). In some Canadian watersheds, however, recurrent summer droughts have been suggested to increase the reoxidation and export of stored sulfur from decades of acidic deposition, delaying the recovery of acidified surface waters (Dillon *et al.*, 1997; Eimers & Dillon, 2002). In the northeastern USA, changes in watershed export of nitrate have recently been linked to interannual variations in air temperature (Murdoch *et al.*, 1998) or winter soil freezing (Mitchell *et al.*, 1996a; Fitzhugh *et al.*, 2003).

Although exact quantification of element fluxes in forested watersheds is crucial in predicting the response of watershed element retention to changing climate and atmospheric deposition, some unmeasured fluxes in the traditional monitoring programs have also increased uncertainties in our prediction of the fate of deposited N and S within watersheds (Shepard *et al.*, 1989; Mitchell *et al.*, 1996b; Driscoll *et al.*, 2001). It has recently been suggested that unmeasured fluxes such as dry deposition (Lovett, 1994) or atmospheric organic N (Neff *et al.*, 2002) may represent substantial inputs to forest ecosystems. At several sites in North America, where total deposition to forests has been measured, dry deposition represented a major component of N and S inputs (Ollinger *et al.*, 1993; Lovett, 1994). The total deposition of N and S might be approximately twice as great as the wet deposition for low-elevation forests in the US (Lovett, 1992).

Fluxes of organic solutes represent another important, but often unmeasured, component of N and S budgets in watersheds (Williams & Edwards, 1993;

Kaiser *et al.*, 2000). Although intensive research effort has been made to understand the dynamics of dissolved organic matter in forest ecosystems during the last two decades (Sollins & McCorrison, 1981; McDowell & Likens, 1988; Qualls *et al.*, 1991; Michalzik *et al.*, 2001), most studies have focused on dissolved organic carbon (DOC), resulting in limited information about dissolved forms of N, P, and S. Recent studies have shown that dissolved organic nitrogen (DON) comprises the bulk of hydrologic losses of N from forested watersheds located in relatively unpolluted areas (McDowell & Asbury, 1994; Hedin *et al.*, 1995; Perakis & Hedin, 2002). DON may also represent a major source of N losses from forests with elevated N deposition levels (Campbell *et al.*, 2000; McHale *et al.*, 2000). In comparison with DON export from watersheds, relatively little is known about atmospheric inputs of organic N compounds. In a synthesis work using data from 41 measurements of atmospheric organic N deposition, Neff *et al.* (2002) suggested that organic N averages about one-third of the total atmospheric N deposition. A few studies have reported highly variable contributions (ranging from 0% to 50%) of organic S solutes to total S fluxes through forest compartments (Homann *et al.*, 1990; Edwards *et al.*, 1992).

Over the past two decades, the Huntington Wildlife Forest in the Adirondack Mountains of New York State has been the site of a large number of studies on the biogeochemistry of forest ecosystems, including evaluations of atmospheric deposition, elemental cycling, and watershed relationships (Table 1; Mollitor & Raynal, 1982; Shepard *et al.*, 1989; Mitchell *et al.*, 1996b, 2001b; Hicks *et al.*, 2001). The availability of long-term data from this site provides a unique

Table 1 Measured parameters, measurement periods, sampling frequency, and sources of used data sets

	Parameters	Measurement periods	Sampling frequency	Sources
Wet-only precipitation	Volume, NH_4^+ , NO_3^- , SO_4^{2-}	1983–2001	Weekly	NADP/NTN
Dry deposition	Particulate NO_3^- and SO_4^{2-} , HNO_3 vapor, SO_2	1986–1988	Weekly	SUNY-ESF
		1990–2001	Weekly	AIRMoN
Bulk precipitation and throughfall	Volume, NH_4^+ , NO_3^- , DON, SO_4^{2-}	1986–1988; 1995–2001	Biweekly and irregular storm sampling	SUNY-ESF
Lake inlet	Runoff, NH_4^+ , NO_3^- , DON, SO_4^{2-}	1995–2001	Weekly and irregular storm sampling	SUNY-ESF
Lake outlet	Runoff, NH_4^+ , NO_3^- , DON, SO_4^{2-}	1983–1994	Monthly	ALTM
		1995–2001	Weekly and irregular storm sampling	SUNY-ESF

opportunity to evaluate different impacts of changing climate and atmospheric deposition on watershed biogeochemical processes and the importance of dry deposition and organic solute fluxes in N and S budgets within a forested watershed. The objectives of this study were to (1) examine the response of watershed N and S export to changing climate and atmospheric deposition by analyzing long-term trends in surface water chemistry and atmospheric deposition, including wet-only precipitation, dry deposition, bulk precipitation, and throughfall data, and (2) assess the contribution of dry deposition inputs and organic solute fluxes to mass balances of N and S.

Methods

Research site

The Arbutus Lake Watershed is located within the Huntington Wildlife Forest (43°59'N, 74°14'W) in the Adirondack Mountains of New York State, USA. Elevation of the watershed ranges from 513 to 748 m. The watershed is 352 ha and the Archer Creek subcatchment (135 ha) is the major inlet to the Arbutus Lake. The Arbutus Lake is a drainage lake and has a surface area of 50 ha, a maximum depth of 8.4 m, and a retention time of 0.6 years (Driscoll & van Dreason, 1993; Mitchell *et al.*, 2001b). The mean annual temperature and total annual precipitation averaged 4.8 °C and 1080 mm from 1981 to 2000, respectively. The overstory vegetation in the upper slopes is comprised of mixed northern hardwoods, including American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), red maple (*Acer rubrum*), yellow birch (*Betula alleghaniensis*), and white pine (*Pinus strobus*). Lower slopes are often dominated by conifer stands composed of eastern hemlock (*Tsuga canadensis*), red spruce (*Picea rubens*), and balsam fir (*Abies balsamea*), especially along the lake margin or within the wetlands. N-fixing speckled alder (*Alnus incana* ssp. *rugosa*) is also present in the wetlands (Hurd *et al.*, 2001). The surficial geology consists of thin to thick deposits of glacial till with a high sand content, while the bedrock geology is largely composed of igneous rocks with some calcium-rich minerals (Driscoll & van Dreason, 1993). Upland soils are typically <1 m in depth and dominated by coarse, loamy, mixed, frigid, Typic Haplorthods in the Becket-Mundal series, while Greenwood Mucky peats are found in wetlands.

Sampling and chemical analysis

Wet deposition in precipitation has been monitored since November 1978 as part of the National Atmo-

spheric Deposition Program/National Trends Network (NADP/NTN; monitoring location NY20) at a clearing 1.3 km from the Arbutus watershed outlet (elevation: 500 m) (Table 1). The monitoring program of NADP/NTN is based on a weekly sampling using an AeroChem-Metrics wet-dry deposition sampler and a Belfort 5-780 universal recording precipitation gage and controlled by extensive quality control procedures (Lynch *et al.*, 1995; Nilles & Conley, 2001). Weekly composite samples collected each Tuesday were analyzed by the NADP central analytic laboratory for pH, specific conductance, and major anions (NO_3^- , SO_4^{2-} , and Cl^-) and cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and NH_4^+). More details about the monitoring site (NY20) and sample handling and analysis can be found on an NADP/NTN website (<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?id=NY20&net=NADP>). The Huntington Forest has also been a site of the Atmospheric Integrated Research and Monitoring Network (AIR-MoN) of NOAA since July 1990 (Table 1). A 38 m walk-up tower adjacent to the watershed is equipped with meteorological instrumentation and filter packs for air sampling. Atmospheric concentrations of HNO_3 vapor, SO_2 , and particulate NO_3^- and SO_4^{2-} have been monitored on a weekly basis using the filter pack sampling system that is composed of a heated inlet tube followed by a Teflon filter to collect particles, a nylon filter to collect nitric acid vapor, and a cellulose filter treated with potassium carbonate to collect SO_2 (Hicks *et al.*, 2001).

The chemistry of bulk precipitation and throughfall has been monitored at irregular intervals by various studies at the Huntington Forest (Table 1; Shepard *et al.*, 1989; McHale *et al.*, 2000; Mitchell *et al.*, 2001a). From 1995 to 2001, bulk precipitation and throughfall were usually collected on a regular basis (biweekly) in the Archer Creek subcatchment using replicated collectors (elevation range: 520–540 m). The collectors were composed of a plastic funnel (16 cm diameter) attached to a 1.9 L plastic bottle. For bulk precipitation sampling, two or three collectors were located in a clearance adjacent to the watershed, while three transects of up to 12 collectors each were located along the slope gradient within the Archer Creek subcatchment. For some periods, bulk precipitation and throughfall were also sampled immediately after major storm events.

The surface water chemistry of the Arbutus Lake was monitored on a monthly basis by the Adirondack Long-Term Monitoring (ALTM) program from February 1983 to the early 1990s (Driscoll & van Dreason, 1993). Discharge from the lake has been measured with a V-notch weir at the lake outlet since October 1991. The Archer Creek subcatchment has also been gaged using an H-flume since October 1994. Water chemistry

samples have been taken weekly from both the lake inlet and outlet since October 1994, with more intensive sampling being carried out for some storm events during 1995–1996 (McHale *et al.*, 2000) and 2000–2001 (Table 1).

Following collection, water samples (bulk precipitation, throughfall, and surface water) in opaque, brown polyethylene bottles (soaked for 24 h following a three-time rinse in deionized distilled water) were refrigerated in the field and during the transport until analysis following storage at 1 °C at the Biogeochemical Laboratory at SUNY-ESF. We made every effort to minimize sample-holding time, which can influence the accuracy of measurement results. Samples were analyzed generally within 2 weeks following collection. Chemical analyses at our laboratory have been evaluated by protocols provided by the US Geological Survey Standard Reference Sample Project (<http://bqs.usgs.gov/srs/FactSheet.htm>). NH_4^+ was analyzed with an ammonia analyzer (Wescan, Model 360) up to March 2000 and subsequently by an autoanalyzer. Major anions including NO_3^- , SO_4^{2-} , and Cl were analyzed using ion chromatography (Dionex, DX-120 IC). The total dissolved N (TDN) was determined by persulfate oxidation (Ameel *et al.*, 1993). A $50 \mu\text{mol L}^{-1} \text{NO}_3^-$ standard, $59 \mu\text{mol L}^{-1} \text{NH}_4^+$ standard, and $50 \mu\text{mol L}^{-1}$ L-cysteine were used for the analyses of N species, including TDN digestion. DON was calculated by subtracting $\text{NO}_3^- + \text{NH}_4^+$ from TDN. The analytical uncertainty for DON analysis was estimated to be ± 5 –10% (McHale *et al.*, 2000). Inductively coupled plasma (ICP) spectrometry (Spectro Analytical, FMA-03 ICP Spectrometer) was used for analyzing Ca^{2+} , Mg^{2+} , and Al. For all analytes, except for DON, concentrations below the detection limits were replaced by the half of each detection limit value. For DON, however, values below a determination limit ($2 \mu\text{mol L}^{-1}$), including negative ones (6.3% of all measurements), were discarded from all the data sets, because those values were assessed to result from analytical uncertainties, given the accuracy and general range of our measurements of TDN, NH_4^+ , and NO_3^- .

Data compilation and budget calculations

Wet-only precipitation chemistry data at various time scales were obtained from the homepage of NADP/NTN (<http://nadp.sws.uiuc.edu>). We used the weekly data set to calculate total precipitation volumes and precipitation-weighted mean solute concentrations either on a monthly basis or annual basis. Although the total precipitation amounts were calculated with all measured and estimated values irrespective of data validation criteria, volume-weighted means of solute

concentrations were calculated using only the values that were assessed to be valid according to NADP/NTN data validation rules. Monthly or annual solute fluxes were obtained by multiplying the total precipitation amount for a period by the volume-weighted monthly or annual mean concentrations, respectively. The calculation methods used for NADP/NTN data sets were also applied for calculating volume-weighted mean concentrations and fluxes of N and S solutes in bulk precipitation, throughfall, and discharge water into and from the lake.

For calculating the monthly average air concentrations of HNO_3 vapor, SO_2 , and particulate NO_3^- and SO_4^{2-} , concentration values from each measurement were weighted with the number of hours of each sampling period to reflect different sampling length and subsequently different air volumes sampled each period. Following the recommendation of Hicks *et al.* (2001), we applied a correction of +25% to all measurements of HNO_3 vapor to account for the HNO_3 vapor being collected on the surface of the gas inlet tubing. Dry deposition was estimated for each weekly sampling period by multiplying air concentrations by deposition velocities that were calculated from meteorological and land surface measurements using a multi-layer model in which the quasi-laminar boundary layer is treated explicitly at each layer in the canopy after the computation of the within-canopy wind profile (Meyers *et al.*, 1998). Monthly or annual total dry deposition fluxes were obtained by summing these weekly fluxes for each commensurate period.

For time-series analyses, volume-weighted monthly mean concentrations were generally used. The observation period of NADP/NTN data presented spans from February 1983 to December 2001 in order to compare solute concentrations in precipitation with surface water data available for this period, while AIRMoN data were presented for a shorter period from September 1990 to July 2001. Since NADP/NTN and AIRMoN measurement programs do not include organic N components, our measurements of DON in bulk precipitation (August 1995–December 1996; June 1999–December 2001) were used as an approximate estimate of the atmospheric organic N input at this site. Atmospheric organic N includes a variety of organic N compounds that can be deposited in both wet and dry forms (Neff *et al.*, 2002). It should be noted that DON fluxes in bulk precipitation only cover the dissolved organic N forms in precipitation, and thus they might overestimate or underestimate the actual total organic N input depending on the contribution of dry deposition. Long-term trends in surface water chemistry were analyzed using chemistry data from the outlet of the Arbutus Lake (February 1983–December 2001).

Input–output budgets of N and S were calculated for the Archer Creek subcatchment (the major inlet to the Arbutus Lake) using 6-year annual flux data from 1995 to 2000. During this period, the most comprehensive and intensive measurements were made for all input and output parameters. Dissolved organic S (DOS) has never been measured for precipitation and surface water samples from the Arbutus watershed. However, at a hardwood stand adjacent to the Arbutus Lake inlet, DOS concentrations and fluxes in precipitation and soil water were measured at various times during 1987 and 1988 (Homann *et al.*, 1990). During this study period, the annual average air temperature (4.4 °C for 1987; 3.9 °C for 1988) and total precipitation (914 mm for 1987; 929 mm for 1988) were somewhat lower than long-term averages of temperature (4.9 °C) and precipitation (1080 mm) from 1983 to 2001. However, summer (June–August) precipitation (273 mm for 1987; 304 mm for 1988) was not less than the long-term average (270 mm), indicating no drought effect on S turnover in soils as reported for some Canadian watersheds (Dillon *et al.*, 1997; Eimers & Dillon, 2002). Homann *et al.* (1990) found that organic S represented 0% and 8% of total S in bulk precipitation and soil solution sampled from the lower B horizon (Bs2, 58 cm), respectively. We used these proportions to estimate organic S fluxes in bulk precipitation and drainage from the Archer Creek. The composition of S solutes in drainage water from the watershed was assumed to be similar to soil solution from the lower B horizon because S constituents in solution at this depth may reflect major changes in solution chemistry by adsorption of both sulfate and organic S in the above soil horizons.

Air temperature data were obtained from a National Weather Service station close to the watershed (Newcomb, Essex county; elevation: 506 m). The mean daily temperature was computed as the average of the maximum and minimum daily values. The annual means of these average daily temperatures were used to investigate the effects of temperature variability on hydrological losses of N and S from the watershed. Depths of ground snow cover at the Huntington Wildlife Forest site have been monitored on a daily basis by Adirondack Ecological Center staff for several decades. We used snowpack data from 1983 to 2001 (especially 1995/1996 winter) to relate snow pack dynamics with NO_3^- concentrations in the lake outlet.

Statistical analysis

Temporal trends in the monthly concentrations of all monitored N and S compounds were analyzed using the nonparametric seasonal Kendall test (here, season defined as month), which was developed to test data

sets with seasonality for monotonic trends (Hirsch *et al.*, 1982). We used a modified seasonal Kendall test that includes the estimate of covariance between the seasonal Kendall statistics rather than setting it to zero to account for serial correlations (Hirsch & Slack, 1984). Slopes for long-term trends were estimated using the seasonal Kendall slope estimator (Hirsch *et al.*, 1982). Pearson's correlation coefficients were used to evaluate significant relationships between surface water chemistry data and climatic variables such as air temperature and precipitation.

Results and discussion

Long-term changes in N and S concentrations in precipitation, air, and surface waters

Different long-term temporal patterns were observed for the concentrations of N and S compounds in wet-only precipitation and filter-pack air samples (Table 2). The concentrations of all monitored S compounds declined significantly ($P < 0.005$) over the monitoring periods. The declining trend in S constituents was consistent with other studies that have reported concomitant decreases in S emission and both wet and dry deposition in the northeastern US over the last two decades (Butler *et al.*, 2001; Hicks *et al.*, 2001; Nilles & Conley, 2001). In general, monitored N parameters (NH_4^+ in precipitation, particulate NO_3^- , and HNO_3 vapor) showed substantial variations and little overall change (Table 2). Concentrations of NO_3^- in wet-only precipitation exhibited a slightly decreasing trend ($-0.32 \mu\text{eq L}^{-1} \text{yr}^{-1}$; $P < 0.05$), with somewhat lower concentrations in the 1990s (data not shown). Although the implementation of Phase I of the Clean Air Act Amendments of 1990 has not resulted in the reduction of NO_x emissions in most of the US, the states of New York and Pennsylvania have shown significant reductions since 1991 (Butler *et al.*, 2001). Whether this regional trend in N emissions was reflected in the observed decline in NO_3^- concentrations in precipitation during the late 1990s is not clear, because other N constituents did not exhibit any significant changes.

The concentrations of SO_4^{2-} in drainage water from the lake outlet displayed a clear declining trend (Table 2; Fig. 1), in accordance with general long-term declines in surface water SO_4^{2-} concentrations in the northeastern US during the past 25 years (Likens *et al.*, 1996; Stoddard *et al.*, 1999). This decrease has become more evident since the 1990s, as observed for many surface waters across most of Europe and North America (Stoddard *et al.*, 1999; Lawrence *et al.*, 2000b). As earlier studies reported (Driscoll & van Dreason, 1993), NO_3^- concentrations in the lake outlet increased substantially

Table 2 Results of the seasonal Kendall test for significant temporal trends in the concentrations of N and S species in wet-only precipitation (1983–2001), atmosphere (1990–2001), and drainage water at the Arbutus Lake outlet (1983–2001)

Species	Wet-only or dry deposition		Drainage	
	<i>P</i>	Slope ($\mu\text{eq L}^{-1}\text{yr}^{-1}$ or $\mu\text{g m}^{-3}\text{yr}^{-1}$ for particulates and vapors)	<i>P</i>	Slope ($\mu\text{eq L}^{-1}\text{yr}^{-1}$)
N	NH_4^+	0.481	0.000	0.075
	NO_3^-	0.016	-0.319	0.810
	NO_3^- (particulate)	0.649		
	HNO_3 (vapor)	0.131		
S	SO_4^{2-}	0.000	0.000	-2.123
	SO_4^{2-} (particulate)	0.003	-0.053	
	SO_2 (vapor)	0.001	-0.087	

In the case of significant trends ($P < 0.05$), the slope indicates mean annual changes in concentrations.

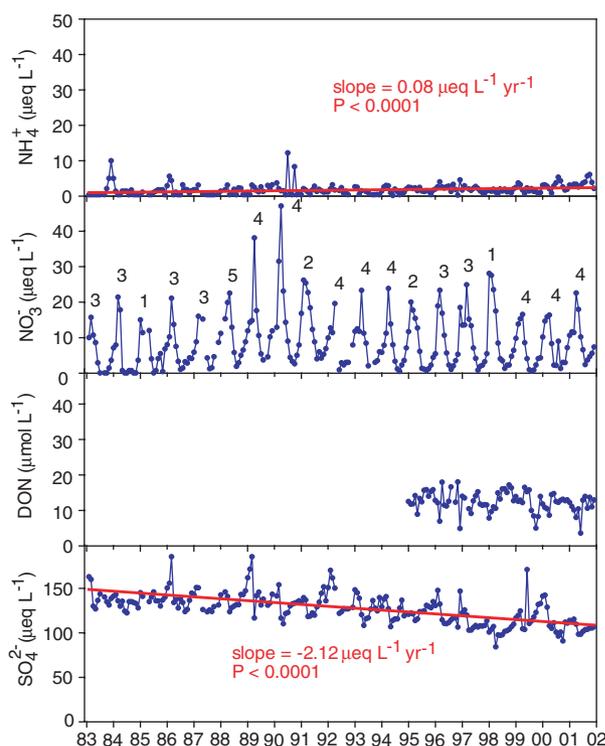


Fig. 1 Temporal variations in the volume-weighted monthly mean concentrations of N and S solutes in drainage water from the Arbutus Lake outlet (1995–2001 for DON; 1983–2001 for all other solutes). A significant trend was indicated as a line through the plot. Peak NO_3^- concentrations of each year were marked with corresponding month names as numbers to indicate interannual variability in peak concentrations.

in the late 1980s (Fig. 1). However, over the whole monitoring period spanning up to 2001, no trend was found (Table 2). The reversal of NO_3^- trends in the 1990s was a common phenomenon for the northeastern

region, including the Adirondacks (Mitchell *et al.*, 1996a; Stoddard *et al.*, 1999; Lawrence *et al.*, 2000b). The only temporal pattern that emerged from the monitored N compounds was a slightly increasing trend in NH_4^+ concentrations in the late 1990s for unknown reasons. The concentrations of DON were generally within the range of NO_3^- concentrations, with no significant trends over time (Fig. 1).

Inclusion of dry deposition and organic solutes into N and S mass balances

Atmospheric deposition

Total atmospheric deposition was estimated for each major N and S species (Table 3). Among three N species, NO_3^- made the largest contribution to the total input of N both in precipitation and dry deposition. The estimated total input of NO_3^- (sum of the wet and dry deposition) was comparable to the previous estimates either from the Integrated Forest Study (IFS; Shepard *et al.*, 1989) in the late 1980s or from the Adirondack Manipulation and Modeling Project (AMMP; Mitchell *et al.*, 2001a) in the early 1990s conducted at this site, reflecting no clear temporal trends in N deposition over the last two decades. Since the AIRMoN measurement program did not include particulate NH_4^+ , the IFS estimate for NH_4^+ deposition in fine and coarse particles was used as a surrogate of NH_4^+ dry deposition during the years from 1996 to 2000. Although organic solute fluxes have often not been considered to be an important pathway of atmospheric N input, recent studies have shown that the contribution of organic N to total atmospheric N loading can range between 10% and 90% in various types of ecosystems (Cornell *et al.*, 1995; Scudlark *et al.*, 1998; Neff *et al.*, 2002). In our study, DON flux in bulk precipitation was used as an approximate estimate of

Table 3 Annual input–output budgets of N and S in the Archer Creek subcatchment

	NH ₄ ⁺ -N	NO ₃ ⁻ -N	DON	SO ₄ ²⁻ -S	DOS
	(kg N ha ⁻¹ yr ⁻¹)			(kg S ha ⁻¹ yr ⁻¹)	
Input					
Wet-only precipitation	1.6 (1.9)	3.3 (2.6)	NA	5.0 (5.7)	NA
Dry deposition	NA (0.2)	2.6 (3.2)	NA	1.3 (2.1)	NA
Bulk precipitation	3.0 (2.5)	4.4 (3.4)	2.4 (1.7)	8.1	NA (0.0)
Throughfall	1.6 (1.2)*	4.3 (3.9)*	2.8 (1.8)*	9.1	NA (0.8)
Estimated total input	1.8 (2.1)	5.9 (5.8)	2.4	6.3 (7.8)	0.0
Output					
Runoff to lake inlet	0.1	2.9	1.2	15.2	NA (1.3)
Balance	1.7	3.0	1.2	-8.9	-1.3

Fluxes in wet-only precipitation, dry deposition, and runoff to the lake inlet are 6-year means (1995–2000), while those of bulk precipitation and throughfall data are averages for the years 1996, 2000, and 2001. Values in parentheses are from the data of the Integrated Forest Study (IFS) (May 1986 to April 1988), with the exception of DOS values, which were estimated from the relationship between DOS and total S measured at the IFS site by Homann *et al.* (1990). NA and asterisks indicate parameters not measured and the sum of throughfall and stemflow fluxes, respectively. Values with boldface represent those involved in the actual input–output mass balance.

total organic N deposition and this estimate (2.4 kg N ha⁻¹ yr⁻¹) amounted to approximately 24% of the total N input (wet + dry + organic solute deposition).

The deposition of SO₄²⁻ decreased both in precipitation and dry deposition compared with the measurement period (1986–1988) of the IFS (Table 3), reflecting the declining trend in S concentrations in precipitation and air through the 1990s. Organic S inputs were difficult to estimate, because this form of S has been measured at this site for only a short period (Homann *et al.*, 1990). Homann *et al.* (1990) found that concentrations of organic S (as the difference between total S and SO₄²⁻-S) were near zero in bulk precipitation samples from the IFS site at the Huntington Forest. Total S in precipitation has generally been assumed to be composed almost entirely of SO₄²⁻-S (David *et al.*, 1987; Homann *et al.*, 1990), although significant amounts of organic S have also been detected in precipitation samples in Scotland (Edwards *et al.*, 1992; Williams & Edwards, 1993).

Nitrogen export

In comparison to input estimates, hydrologic losses of solutes from the Archer Creek subcatchment were estimated with a greater confidence because of intensive measurements, especially since 1995. Although NO₃⁻ comprised the largest fraction of N export from the watershed, DON also represented a substantial portion of N losses (about 30% of the total N flux). For all N species, inputs exceeded outputs, with positive balances as a consequence (Table 3). The inclusion of

dry deposition and organic N fluxes both led to large increases in the positive mass balance (Fig. 2). In both cases, the increases in the input greatly exceeded those of the output, elevating the N retention efficiency (the proportion of retained N in the input) from 37% to ~60%.

Different estimates for N retention capacity of the Arbutus watershed and nearby hardwood stands have been made previously. Including dry deposition as part of N input substantially increased N retention in the IFS site and Arbutus watershed up to 85% (Shepard *et al.*, 1989; Mitchell *et al.*, 1996b). When DON was included as part of N export from the Archer Creek watershed N retention decreased from 45% to 13% (McHale *et al.*, 2000). Based on this N budget, considering only the output of organic N fluxes, McHale *et al.* (2000) suggested that the Archer Creek subcatchment might be approaching a stage with considerable N loss in drainage waters. In the current study, however, including organic N input as well as DON loss resulted in a much higher N retention estimate, suggesting that the watershed is quite retentive for all N species, including DON. Hydrologic losses of DON have been suggested to constrain the accumulation of N in forested watersheds under a wide range of N deposition levels through biologically uncontrollable leaching, contributing to a persistent N limitation in late-successional forests (Hedin *et al.*, 1995; Campbell *et al.*, 2000; Perakis & Hedin, 2002). However, the positive balance between DON input and output observed in our study suggests that the inclusion of organic N deposition as an input parameter along with DON loss might significantly

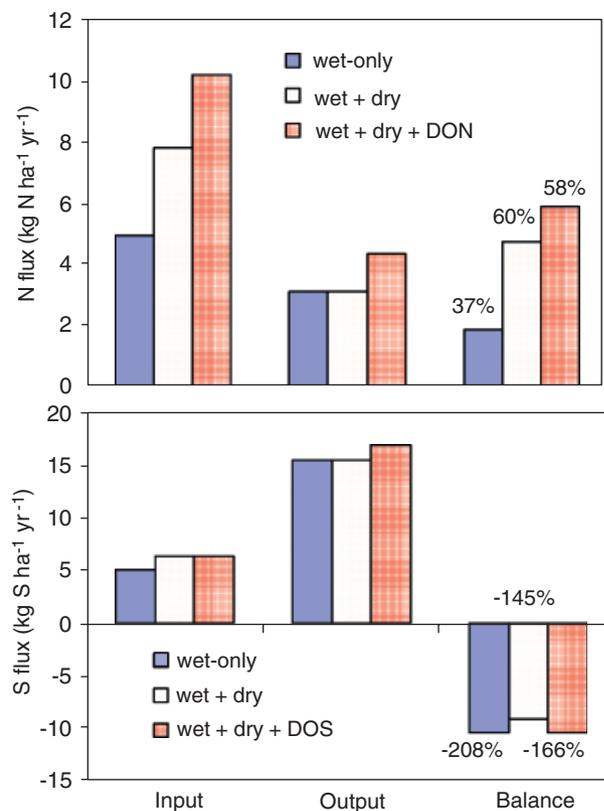


Fig. 2 Changes in input–output mass balances of N and S depending on the inclusion of dry deposition and organic solutes (DON or DOS). The symbols ‘wet-only’ and ‘dry’ represent only inorganic components of element fluxes. Values are 6-year means (1995–2000). Positive or negative values of balance indicate a retention or loss of elements, respectively. Values above the balance bars indicate the proportion of retained or lost element in the input.

change the watershed mass balance of N in terms of net flux, warranting further study of organic N inputs either in precipitation or dry deposition.

Sulfur export

Watershed S loss greatly exceeded total S input, including dry deposition (Table 3; Fig. 2), in accordance with previous studies conducted at this site that found negative balances of S even if dry deposition was added to the total S input (Shepard *et al.*, 1989; Mitchell *et al.*, 1996b). Some studies have suggested dry deposition as a significant source of net watershed loss of SO_4^{2-} (Likens *et al.*, 1990; Driscoll *et al.*, 1998), while others have stressed the importance of internal soil sources, including mineral weathering, SO_4^{2-} desorption, and mineralization of organic S as possible sources that would account for discrepancies in watershed S mass balances (Alewell *et al.*, 1999; Likens *et al.*, 2002). Based on lower $\delta^{34}\text{S}$ values of SO_4^{2-} in stream water than

those for bulk precipitation at the Hubbard Brook Experimental Forest, Alewell *et al.* (1999) suggested that most of the deposited SO_4^{2-} could be incorporated into soil organic pools prior to leaching and the mineralization of soil organic S might be a major contributor to stream water SO_4^{2-} . The importance of the cycling of SO_4^{2-} through soil organic pools has also been documented for some Central European forests with high atmospheric S deposition (Novak *et al.*, 1996). The importance of mineral weathering as S sources for some watersheds in the northeast US has also been recently established (Bailey *et al.*, in press).

Our results indicated that organic S export could represent another important pathway of S loss from the internal S cycling through soil organic pools (Table 3). Although uncertainties remain unresolved regarding the actual proportion of organic S in the total S in drainage water from the Archer Creek subcatchment, our estimate of DOS (using 8% as the proportion of DOS in the total S) does not seem to overestimate the actual flux. This estimate can be evaluated using the stoichiometric relationship between C and S of dissolved organic matter in discharge water. The C/S ratio of dissolved organic matter in drainage water was approximately 38 when calculated with the estimated average concentration of DOS (0.18 mg L^{-1}) and the measured average concentration of DOC (6.8 mg L^{-1} ; unpublished data). This estimated C/S ratio was slightly higher than those measured for Scottish surface waters (14–30; Edwards *et al.*, 1992) and lower than those for some high-DOC Canadian surface waters (53–120; Eimers & Dillon, 2002). The average proportion of DOS in total S was 18% for Scottish surface waters (Edwards *et al.*, 1992). Eimers & Dillon (2002) found at watersheds in Ontario, Canada, that organic S accounts for from almost zero up to 23% of total S export in stream waters, with high-DOC streams (annual average concentrations ranging from 14 to 26 mg L^{-1}) having relatively high organic S proportions.

Biogeochemical responses to temporal variations in climate and atmospheric deposition

Long-term variations

The solutes of N and S discharged from the Arbutus Lake exhibited different long-term temporal patterns (Fig. 1). Concentrations of SO_4^{2-} in lake discharge correlated significantly with precipitation concentrations ($r = 0.63$, $P < 0.01$; Table 4), indicating a direct influence of the declining S deposition on the watershed S export. Although NO_3^- and DON played an almost equal role as the dominant N solutes in surface waters, NO_3^- concentrations generally showed larger variations among years compared with NH_4^+ or DON

Table 4 Correlations between volume-weighted annual mean concentrations of inorganic N and S solutes in the lake outlet and major climatic and water chemistry variables from 1984 to 2001 ($n = 18$)

	Correlations with				
	Annual mean temperature	Annual total precipitation	Concentrations in precipitation	Ca ²⁺ in lake discharge	Mg ²⁺ in lake discharge
NH ₄ ⁺	-0.05	0.35	0.19	-0.14	-0.14
NO ₃ ⁻	0.51*	0.53*	-0.03	0.15	0.23
SO ₄ ²⁻	-0.40	-0.20	0.64**	0.86**	0.85**

Values are Pearson's correlation coefficients and statistical significance is indicated by asterisks (* $P < 0.05$, ** $P < 0.01$).

concentrations (Fig. 1). The differences among years in NO₃⁻ concentrations were not related to NO₃⁻ concentrations in precipitation ($r = -0.03$; Table 4). Moreover, dry deposition of N also showed little change over the monitoring period (Table 2), thus indicating that the temporal pattern of N deposition could not explain the changes in surface water NO₃⁻ concentrations among years. Significant correlations between NO₃⁻ concentrations in lake outlet and annual average air temperature ($r = 0.51$, $P < 0.05$; Table 4) and total precipitation ($r = 0.53$, $P < 0.05$; Table 4) suggested possible climatic controls on long-term variations in surface water NO₃⁻ concentrations. In a forested watershed within the Catskill Mountains of New York State, Murdoch *et al.* (1998) also found a positive correlation between stream NO₃⁻ concentrations and mean annual air temperature during the period from 1983 to 1995. They suggested that temperature-dependent N turnover processes play a more important role in controlling N export than N deposition. A similar relationship between air temperature and interannual variability in stream NO₃⁻ concentrations was found for the Hubbard Brook Experimental Forest in New Hampshire between 1990 and 1997 (Fitzhugh *et al.*, 2003).

Because most of the interannual variations in NO₃⁻ concentrations in the Arbutus Lake outlet were evident immediately before or during spring snowmelt (Fig. 1), the relationship between climatic variability and NO₃⁻ export during this winter/spring period was explored further. Frequent event samplings of drainage water in the lake inlet (December 1995 to May 1996; McHale *et al.*, 2002) made it possible to investigate the response of watershed N and S export to temperature variations during the months before spring snowmelt (Fig. 3). During this observation period, daily average air temperatures went above 0 °C for several consecutive days once per month from January to March, with immediate reductions in snowpack depth as a consequence (Fig. 3a). Runoff increases in response to these snowmelt events resulted in increases in the drainage water concentrations of both NO₃⁻ (Fig. 3c) and DON

(Fig. 3d) and decreases in SO₄²⁻ concentrations (Fig. 3b), possibly reflecting different source areas and transport paths of N and S solutes within the watershed.

Schaefer *et al.* (1990) also observed diluted SO₄²⁻ concentrations and increased NO₃⁻ concentrations in some Adirondack lakes during snowmelt events from January to May, and attributed these different export patterns to changes in hydrologic flow paths and the increasing contribution of shallow soil water during snowmelt. The forest floor was suggested as a primary source of NO₃⁻ and DOC during the snowmelt period (Rascher *et al.*, 1987). Increased NO₃⁻ and DON concentrations in response to increasing snowmelt flow are consistent with the flushing hypothesis (Hornberger *et al.*, 1994; Creed *et al.*, 1996), which links increased solute export during storm or snowmelt events to the hydrologic flushing of accumulated solutes in surface soil horizons by the rising water table. However, results from hydrograph separations and chemical end-member mixing analysis conducted for the Archer Creek subcatchment (McHale *et al.*, 2002) indicated that snowmelt, in a mixture with high N soil water, first recharges till groundwater rather than being directly flushed to the stream.

The sensitive response of N release mechanisms to changes in temperature and runoff seems to explain a large portion of the interannual variations in NO₃⁻ concentrations in lake discharge from January to March or April (Table 5). The average daily air temperature during the months before spring snowmelt (especially January–March) significantly correlated with both runoff and NO₃⁻ concentrations, consistent with the results from the 1996 event samplings (Fig. 3). The number of days with average air temperature over 1 °C (as a critical temperature for snowmelt; Aber & Federer, 1992) was assumed to reflect the frequency of snowmelt and also significantly correlated with interannual changes in NO₃⁻ concentrations from January to March. The average daily air temperatures also had a significantly positive relationship with NO₃⁻ export either for the entire year or for the months preceding major

Table 5 Correlations between winter (either January–April or January–March) average concentrations of NO_3^- and SO_4^{2-} in the lake outlet and climatic variables for the corresponding periods from 1984 to 2001 ($n = 18$)

	Correlations with					
	NO_3^-		SO_4^{2-}		Runoff	
	Jan–Mar	Jan–Apr	Jan–Mar	Jan–Apr	Jan–Mar	Jan–Apr
Average daily air temperature	0.84**	0.74**	-0.23	-0.27	0.80**	0.62**
Number of days with average temperature >1 °C	0.59*	0.45	-0.05	-0.17	0.74**	0.58*
Runoff	0.75**	0.50*	-0.15	-0.09		

Values are Pearson’s correlation coefficients and statistical significance is indicated by asterisks (* $P < 0.05$, ** $P < 0.01$).

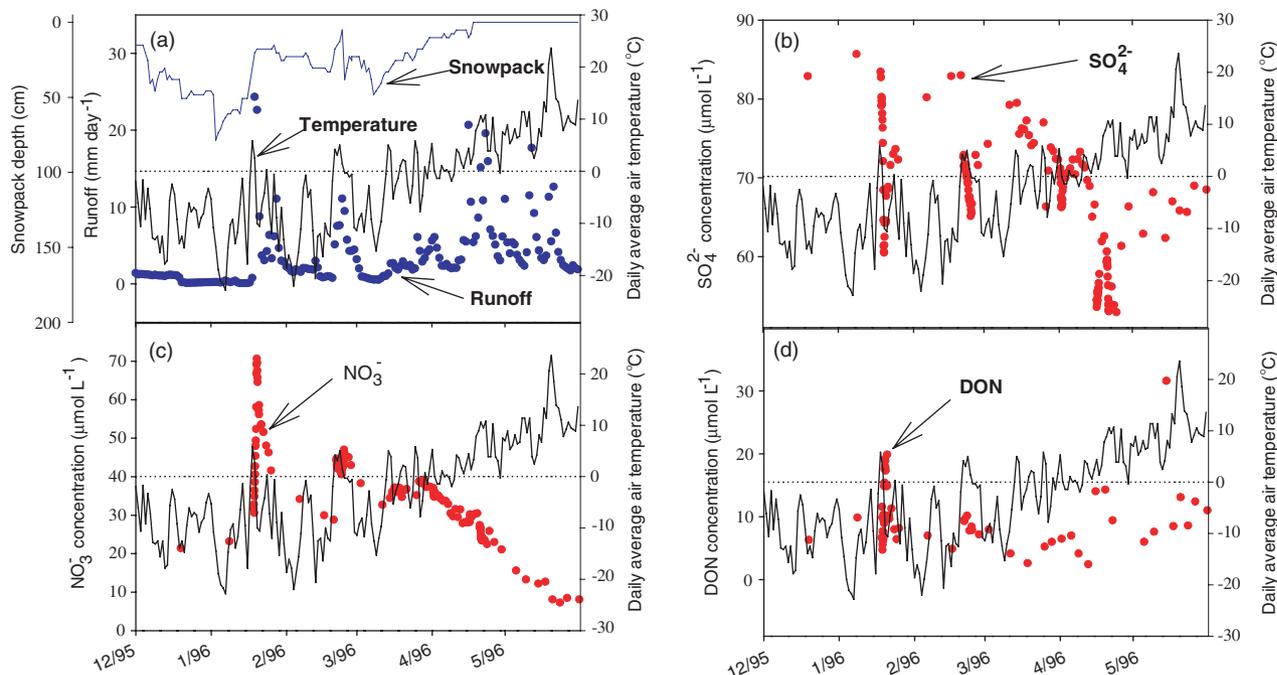


Fig. 3 Responses of snowpack depths, runoff amounts, and N and S solute concentrations in drainage water from the Archer Creek subcatchment to temperature changes from December 1995 to May 1996. The results on the response of runoff and NO_3^- concentrations were based on the published data of McHale *et al.* (2002). Changes in the daily average air temperature are depicted as a line plot and the 0 °C reference level is marked with a dotted line in all graphs.

spring snowmelt between 1984 and 2001 (Fig. 4). The relationship of temperature to NO_3^- export was strongest for the period from January to March ($R^2 = 0.72$), corroborating the idea that temperature fluctuations and snowmelt responses during these months play a key role in interannual variability in NO_3^- export from the watershed.

Over-winter microbial activity under the continuous snow cover was found to be central in retaining N within forest soils of alpine watersheds in the Rocky Mountains of the western US (Brooks *et al.*, 1998). Thus, year-to-year changes in snow cover have been sug-

gested to explain most of the natural variability in N export from these watersheds (Brooks *et al.*, 1999). For forested watersheds in the northeastern USA, reduced snow cover, which often occurs under a milder winter climate, has been related to increased soil freezing damage that might increase N loss during the following growing season as a consequence of increased root mortality and disrupted soil structure (Fitzhugh *et al.*, 2001, 2003). However, the immediate responses of stream NO_3^- concentrations to temperature-induced water flow increases before spring snowmelt (Fig. 3) suggest that the frequency of snowmelts and the

amount of water flow before major spring snowmelts may play a central role in explaining the interannual variability in watershed NO_3^- export, most of which occurs during the dormant season in this watershed. Snowpack accumulation at this site has shown large year-to-year variations, generally starting between late October and early November and completely disap-

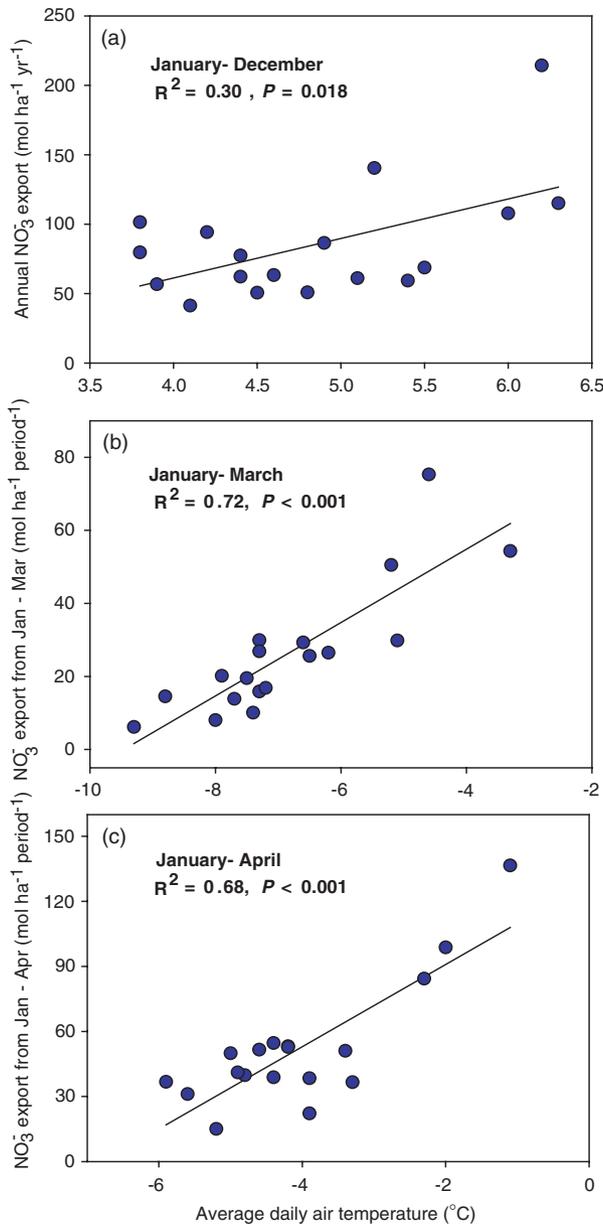


Fig. 4 Relationships between average air temperatures and NO_3^- export in lake outlet either for the entire year (a) or for the months preceding spring snowmelt (b: January–March; c: January–April) from 1984 to 2001. The line through the plot is the best-fit regression line and statistical significance is indicated by R^2 followed by P values.

pearing in May (data not shown). For the study period from 1983 to 2001, a significantly negative correlation was found between the average air temperature and snowpack depths during the months from January to March ($r = -0.50$; $P < 0.05$), supporting our assumption that interannual climate changes can significantly impact winter NO_3^- export mechanisms largely through changes in water flow derived from accumulated snowpacks.

Seasonal variations

Seasonal patterns were found for some N and S compounds in air or precipitation (Fig. 5). Compared with the relatively constant monthly mean concentrations of NO_3^- in particles and precipitation, concentrations of HNO_3 vapor and precipitation NH_4^+ tended to be higher either during the dormant season or during

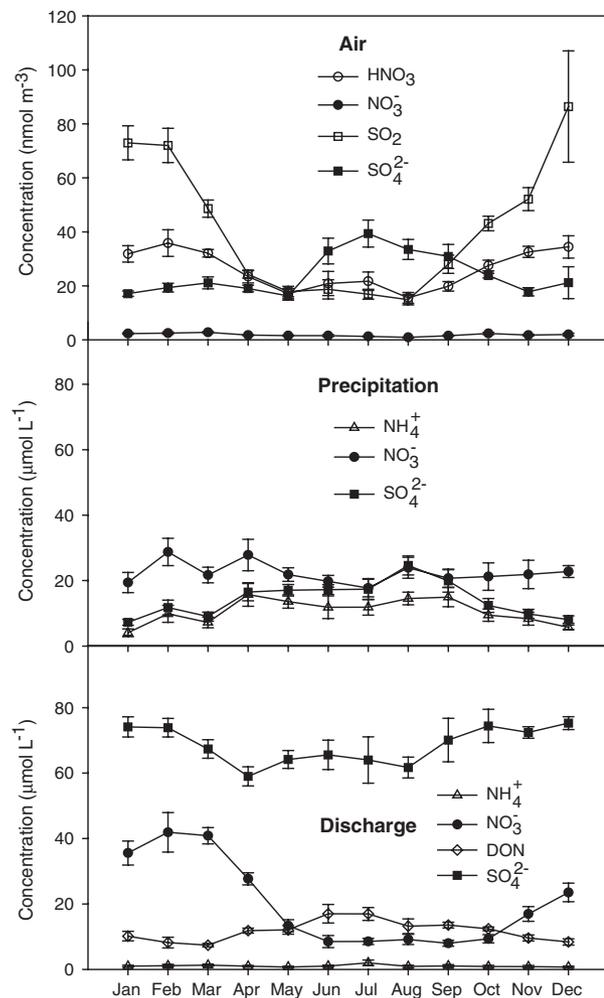


Fig. 5 Volume-weighted monthly mean concentrations of N and S compounds in air, precipitation, and discharge water from the Archer Creek from 1995 to 2000 (mean \pm 1 SE).

the growing season, respectively. While SO_4^{2-} concentrations both in particles and precipitation were higher during the growing season, atmospheric SO_2 concentrations were significantly elevated during the dormant season. This type of seasonality in S deposition has often been observed at the AIRMoN monitoring sites in the northeastern USA and explained by the highest power demand in winter and a rapid conversion of SO_2 to SO_4^{2-} in summer (Hicks *et al.*, 2001).

Higher dormant-season concentrations were observed for SO_4^{2-} and NO_3^- in discharge water from the Archer Creek subcatchment (Fig. 5). By contrast, DON concentrations in discharge were slightly higher during the growing season. The contrasting seasonal patterns observed for NO_3^- and DON were related to temperature differences among seasons, as illustrated by a significant positive (DON) or negative (NO_3^-) relationship between the average air temperatures and volume-weighted monthly mean concentrations of each solute (Fig. 6). At relatively high temperatures (mostly during the growing season), NO_3^- concentrations decreased but DON concentrations generally increased.

Low growing-season NO_3^- concentrations in drainage water suggest that biological N demands exceed the N supply in this watershed (Stoddard, 1994). Higher DON concentrations during warm summer months may indicate that DON does not simply 'leak' from biologically unavailable pools of organic N (Hedin *et al.*, 1995), but can be produced by microbial transformations of organic matter in forest soils (Kalbitz *et al.*, 2000; Park *et al.*, 2002). DON concentrations in drainage water were not significantly related to stream discharge ($R^2 = 0.04$, $P = 0.11$), suggesting that higher DON concentrations during summer months might reflect enhanced biological production rather than the simple concentration effect of lower stream discharge.

Implications of changing biogeochemistry of N and S

Nitrogen

The pools and internal fluxes of N within the watershed were much greater than the relatively small atmospheric input and drainage loss (Fig. 7). However, assuming that the annual N accumulation rate

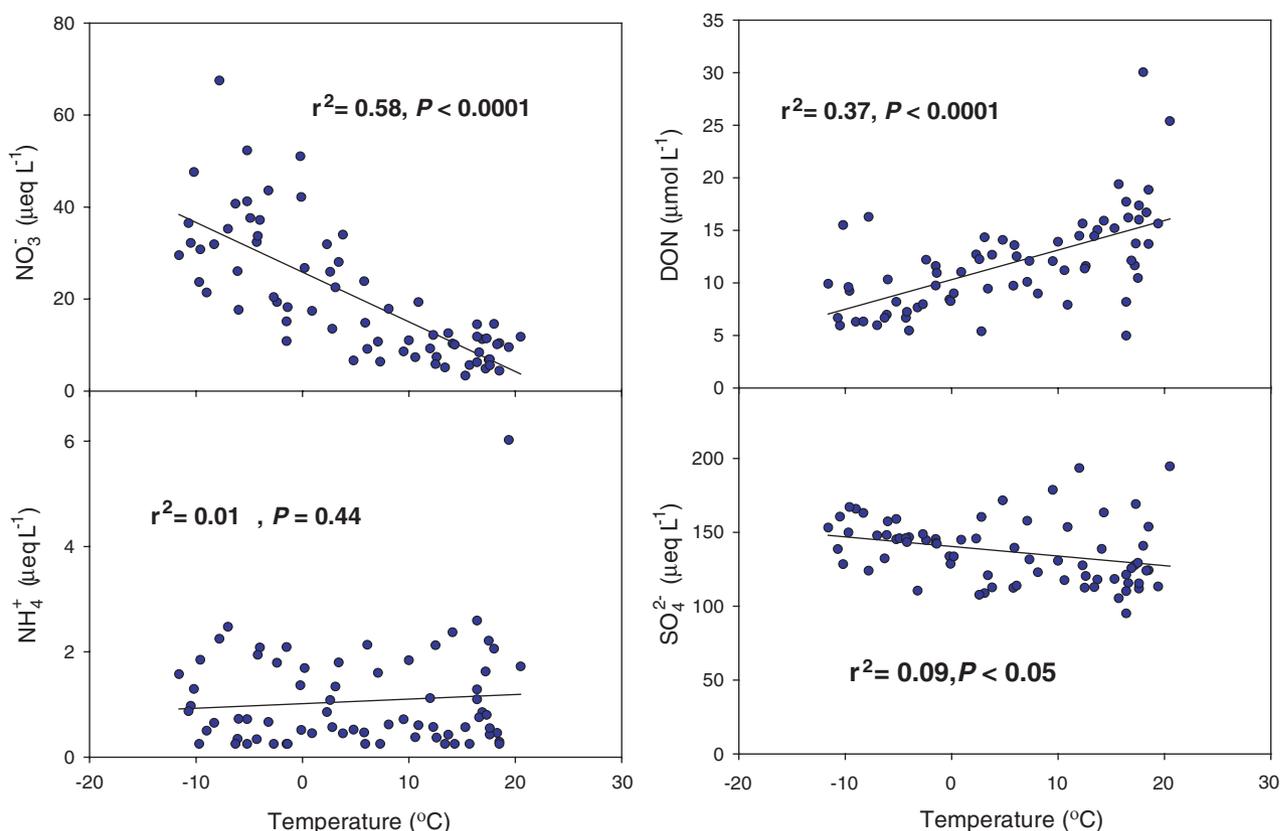


Fig. 6 Relationships between the average daily air temperature and volume-weighted monthly mean concentrations of NH_4^+ , NO_3^- , DON, and SO_4^{2-} in discharge water from the Archer Creek during the period from 1995 to 2000. The line through the plot is the best-fit regression line and statistical significance is indicated by R^2 followed by P values.

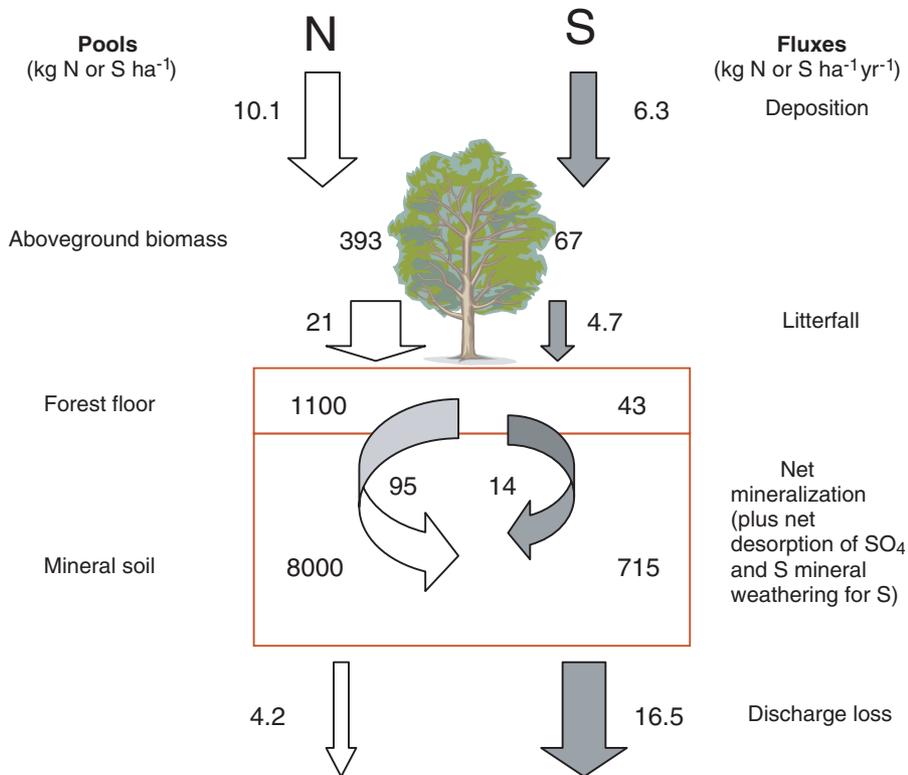


Fig. 7 Pools (kg N or S ha⁻¹) and fluxes (kg N or S ha⁻¹ yr⁻¹) of N and S in the Archer Creek subcatchment. Inputs and outputs of N and S are 6-year (1995–2000) average fluxes from Table 3. Measurements of N pools, litterfall N, and N mineralization rates were made for some upslope areas of the Archer Creek (Ohri *et al.*, 1999; Bischoff *et al.*, 2001). Data on S pools, litterfall S, and S mineralization are from a study conducted at a hardwood stand adjacent to the watershed (David *et al.*, 1987).

(approximately 6 kg N ha⁻¹ yr⁻¹) has not greatly changed, the total accumulated N from atmospheric deposition amounts to 120 kg N in the past two decades. N loss through denitrification is not thought to influence this accumulation rate significantly, considering that relatively low annual fluxes of N₂O (generally not greater than 0.4 kg N ha⁻¹ yr⁻¹) have been measured for most temperate forests under moderate levels of N deposition (Brumme *et al.*, 1999; Bowden *et al.*, 2000). Recent measurements of the forest biomass at the IFS site, which is adjacent to the Arbutus watershed and with a vegetation similar to that within the watershed, have shown that the forest is not exhibiting any net increase in biomass (Forrester *et al.*, 2003), suggesting that the majority of N accumulation has probably occurred in soil pools. Site-specific factors, including soil N status and forest species composition, have been suggested to affect the high degree of variation in N retention among forested watersheds with similar amounts of N inputs (Fenn *et al.*, 1998; Lovett *et al.*, 2000).

Given that the maturity of a forest is considered to be an important predisposing factor of N saturation

(Stoddard, 1994; Fenn *et al.*, 1998), a question can be raised regarding how long the forest in the Arbutus watershed can sustain the accumulation of both organic and inorganic N inputs in the absence of any substantial increase in forest biomass. According to the classification of watershed N saturation by Stoddard (1994), the Arbutus watershed was assessed to be at 'Stage 1', in which drainage water from the watershed has peak NO₃⁻ concentrations during winter and snowmelt, but negligibly low concentrations during the growing season (Mitchell *et al.*, 1996a). Low summer concentrations (<10 μmol L⁻¹) have persisted through the 1990s (Figs 1 and 5). This low level of summer NO₃⁻ concentrations was characterized as a 'Stage 1' symptom in a survey study conducted for Catskill streams (Lovett *et al.*, 2000). These results lead us to believe that the watershed has not yet transitioned into more advanced stages of N saturation.

In the late 1980s, increased NO₃⁻ concentrations were observed in many surface waters of the northeastern US, raising concerns over N saturation of watersheds in this region (Driscoll & van Dreason, 1993; Stoddard,

1994). It was suggested that forested watersheds in the Adirondack and Catskill Mountains were exhibiting early stages of nitrogen saturation (Stoddard, 1994). Sullivan *et al.* (1997) contended that the role of NO_3^- as an agent for surface water acidification in Adirondack lakes was becoming increasingly important not only for episodic acidification events but also for chronic acidification. In a recent regional analysis, however, Driscoll *et al.* (2003) observed significant decreases in NO_3^- concentrations in some of the Adirondack Long-Term Monitoring lakes (15 of the 48 lakes) over the period from 1992 to 2000. Similar to the synchronous patterns of stream water NO_3^- concentrations across the northeastern USA from 1983 to 1993 as observed by Mitchell *et al.* (1996a), decreasing concentrations of NO_3^- during the 1990s have been reported for many different watersheds in this region (Lawrence *et al.*, 2000b; Martin *et al.*, 2000; Aber *et al.*, 2002; Goodale *et al.*, 2003). Model simulations have demonstrated that interannual climatic variations, in combination with other physical and chemical disturbances (e.g., rising atmospheric CO_2 concentrations), can account for much of the observed decadal variability in NO_3^- drainage loss from several forested watersheds in New Hampshire, although the PnET model application was not successful in simulating decreasing stream NO_3^- concentrations during the 1990s (Aber & Driscoll, 1997; Aber *et al.*, 2002). In an attempt to explain the unexpected recent NO_3^- decline in some other New Hampshire streams, Goodale *et al.* (2003) suspected that the effects of interannual climatic variations on biotic N retention may have masked the response of watershed N loss to chronic N deposition.

Our results demonstrated the importance of climatic variability in explaining long-term temporal variations in NO_3^- export from the watershed. The relationship between the mean annual temperature and watershed N export suggests that soil microbial processes, such as nitrification (Murdoch *et al.*, 1998) and litter decomposition (Lawrence *et al.*, 2000a), play a crucial role in the loss or retention of N within watersheds. Our results also suggest that the production and release of NO_3^- in soils sensitively respond to variations in temperature and runoff during the months preceding spring snowmelt. Recent studies have linked winter temperature variability in the northeastern USA to decadal trends in North Atlantic–Arctic Oscillation (NAO–AO), showing a positive relationship between NAO–AO indexes and temperature averages or maxima (Hurrell, 1995; Wettstein *et al.*, 2002). Although recent studies have focused on the response of NO_3^- release to soil freezing that is projected to occur more frequently under a warmer climate (Mitchell *et al.*, 1996a; Fitzhugh *et al.*, 2001), our results suggest that the

response of snowmelts and hydrologic flushing to winter climate variability (e.g., warming) might be more important in explaining long-term patterns of watershed NO_3^- export than soil freezing itself.

Sulfur

In contrast to the relatively high retention of N, the watershed is losing large amounts of S (about $10 \text{ kg S ha}^{-1} \text{ yr}^{-1}$), which comprised a much higher percentage of the total soil S storage than N fluxes do for the soil N stocks (Fig. 7). Surface water responses to decreasing S deposition have been observed since the 1980s across most of Europe and North America, but the most marked declines in the northeastern US have generally been found in the 1990s (Stoddard *et al.*, 1999; Lawrence *et al.*, 2000b). Consistent with this regional trend, considerable decreases in SO_4^{2-} concentrations occurred at the Arbutus Lake through the 1990s. It is still unknown whether the declining S deposition will reverse the large negative S balance in this watershed in the future. The potential for this reversal might be dependent on the relative importance of internal S sources vs. atmospheric inputs.

Despite declines in SO_4^{2-} concentrations, SO_4^{2-} has been the predominant anion in surface waters of this watershed (Figs 1 and 5). Although earlier predictions suggested that NO_3^- would replace SO_4^{2-} as the dominant agent of soil and surface water acidification, recent analyses of long-term surface water data have led to the conclusion that SO_4^{2-} is still the predominant anion in most surface waters throughout eastern North America (Stoddard *et al.*, 1999; Driscoll *et al.*, 2001). Above all, long-term changes in SO_4^{2-} concentrations have affected the loss rates of base cations. The concentrations of Ca^{2+} and Mg^{2+} in lake outlet were strongly related to SO_4^{2-} concentrations, whereas there was no correlation with NO_3^- (Table 4). While the correlation between the concentrations of SO_4^{2-} and Ca^{2+} was significant throughout the whole monitoring period, the concentrations of both ions concomitantly decreased in the late 1990s relative to the previous periods, pointing to the recent trend of declining base cation leaching from the watershed and its relation to changing SO_4^{2-} release (Fig. 8). Although decreases in base cation leaching have been related to various factors, including declining atmospheric deposition of base cations and depletion of soil cation pools (Hedin *et al.*, 1994; Likens *et al.*, 1996), our results imply a dominant role of declining concentrations of SO_4^{2-} as a counter anion leaching base cations. Declining surface water concentrations of base cations will have a great impact on future trends in surface water recovery from acidification (Likens *et al.*, 1996; Lawrence *et al.*, 1999).

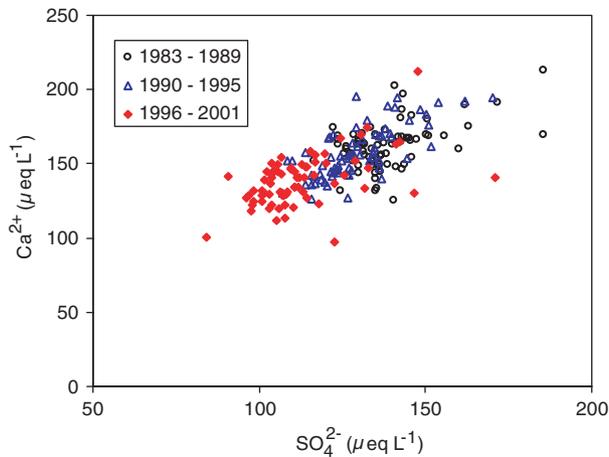


Fig. 8 Relationships between the concentrations of SO_4^{2-} and Ca in drainage water from the Arbutus Lake outlet over the three time periods (1983–1989; 1990–1995; 1996–2001).

Conclusions

Over 19 years of monitoring, contrasting patterns were observed for changing atmospheric inputs and hydrologic losses of N and S in the Arbutus watershed. Despite the concerns over N saturation based on increasing surface water NO_3^- concentrations in the late 1980s, no long-term trend in NO_3^- loss was found in the 1990s. In contrast to the relatively constant concentration levels observed for the 1980s, SO_4^{2-} concentrations in lake discharge markedly decreased in the 1990s, reflecting declining patterns of both wet and dry deposition of S. The inclusion of both dry deposition and organic N flux substantially elevated N retention in this forested watershed. This result, along with very low summer NO_3^- concentrations in drainage water, suggests that a strong biological retention of both organic and inorganic N still prevails in this watershed. As demonstrated by the close relationships between temperature and hydrologic losses of NO_3^- and DON, biotic processes affecting N transformations and fluxes may be especially sensitive to future climatic changes. Unlike previous predictions, responses of watershed N export to chronic N deposition were hardly detectable in drainage waters across the northeastern USA during the 1990s (Driscoll *et al.*, 2003; Goodale *et al.*, 2003). Our results suggest that climatic variability, especially during the months preceding spring snowmelt, might play a crucial role in decadal variations in watershed NO_3^- export across the northeastern USA. Despite concomitant decreases in atmospheric deposition and hydrologic losses, SO_4^{2-} was still the dominant anion in drainage water. Our results showed that dry deposition cannot account for the large

negative balance of S and thus internal S sources are important contributors to the S balances of this watershed. More research effort is needed to understand how long the retention of N and the loss of S will continue and what direct and indirect influences the projected climatic change will exert on the long-term patterns of N and S retention within watersheds.

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