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

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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$_4^{2-}$/C$_0$ in precipitation, SO$_4^{2-}$/C$_0$ 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 ($-2.1 \mu$eq L$^{-1}$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, 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 environmental 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;
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., 1993; Lovett, 1994). 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 (Solins & 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>
<thead>
<tr>
<th>Parameters</th>
<th>Measurement periods</th>
<th>Sampling frequency</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet-only precipitation</td>
<td>Volume, NH₄⁺, NO₃⁻, SO₄²⁻</td>
<td>1983–2001</td>
<td>Weekly</td>
</tr>
<tr>
<td>Dry deposition</td>
<td>Particulate NO₃⁻ and SO₄²⁻, HNO₃ vapor, SO₂</td>
<td>1986–1988</td>
<td>Weekly</td>
</tr>
<tr>
<td>Bulk precipitation and throughfall</td>
<td>Volume, NH₄⁺, NO₃⁻, DON, SO₄²⁻</td>
<td>1990–2001</td>
<td>Weekly</td>
</tr>
<tr>
<td>Lake inlet</td>
<td>Runoff, NH₄⁺, NO₃⁻, DON, SO₄²⁻</td>
<td>1995–2001</td>
<td>Weekly and irregular storm sampling</td>
</tr>
<tr>
<td>Lake outlet</td>
<td>Runoff, NH₄⁺, NO₃⁻, DON, SO₄²⁻</td>
<td>1983–1994</td>
<td>Monthly</td>
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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 Atmospheric 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-only 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 (NO₃⁻, SO₄²⁻, and Cl⁻) and cations (Ca²⁺, Mg²⁺, K⁺, Na⁺, and NH₄⁺). 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 (AIRMoN) 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 HNO₃ vapor, SO₂, and particulate NO₃⁻ and SO₄²⁻ 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 SO₂ (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). NH4+ was analyzed with an ammonia analyzer (Wescan, Model 360) up to March 2000 and subsequently by an autoanalyzer. Major anions including NO3−, SO42−, 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 μmol L−1 NO3 standard, 59 μmol L−1 NH4+ standard, and 50 μmol L−1 L-cysteine were used for the analyses of N species, including TDN digestion. DON was calculated by subtracting NO3− + NH4+ 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 Ca2+, Mg2+, 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 μmol 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, NH4+, and NO3−.

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 HNO3 vapor, SO2, and particulate NO3− and SO42−, 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 HNO3 vapor to account for the HNO3 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 NO3− 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 (NH4+ in precipitation, particulate NO3−, and HNO3 vapor) showed substantial variations and little overall change (Table 2). Concentrations of NO3− in wet-only precipitation exhibited a slightly decreasing trend (−0.32 μeq L−1 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 NOx 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 NO3− concentrations in precipitation during the late 1990s is not clear, because other N constituents did not exhibit any significant changes.

The concentrations of SO42− 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 SO42− 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), NO3− concentrations in the lake outlet increased substantially
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).

**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)

<table>
<thead>
<tr>
<th>Species</th>
<th>Wet-only or dry deposition</th>
<th>Drainage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>Slope (μeq L$^{-1}$ yr$^{-1}$ or µg m$^{-3}$ yr$^{-1}$)</td>
</tr>
<tr>
<td>N NH$_4^+$</td>
<td>0.481</td>
<td>0.075</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.016</td>
<td>–0.319</td>
</tr>
<tr>
<td>NO$_3^-$ (particulate)</td>
<td>0.649</td>
<td></td>
</tr>
<tr>
<td>HNO$_3$ (vapor)</td>
<td>0.131</td>
<td></td>
</tr>
<tr>
<td>S SO$_4^{2-}$</td>
<td>0.000</td>
<td>–0.785</td>
</tr>
<tr>
<td>SO$_4^{2-}$ (particulate)</td>
<td>0.003</td>
<td>–0.053</td>
</tr>
<tr>
<td>SO$_2$ (vapor)</td>
<td>0.001</td>
<td>–0.087</td>
</tr>
</tbody>
</table>

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.

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
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 precipitation and throughfall data are averages for the years 1996, 2000, and 2001. Values with boldface represent those involved in the actual input–output mass balance.

The deposition of $\text{SO}_4^{2-}$ 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 $\text{SO}_4^{2-}$) 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 $\text{SO}_4^{2-}$ (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).

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

<table>
<thead>
<tr>
<th></th>
<th>NH$_4^+$-N (kg N ha$^{-1}$ yr$^{-1}$)</th>
<th>NO$_3^-$-N (kg N ha$^{-1}$ yr$^{-1}$)</th>
<th>DON (kg N ha$^{-1}$ yr$^{-1}$)</th>
<th>SO$_4^{2-}$-S (kg S ha$^{-1}$ yr$^{-1}$)</th>
<th>DOS (kg S ha$^{-1}$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet-only precipitation</td>
<td>1.6 (1.9)</td>
<td>3.3 (2.6)</td>
<td>NA</td>
<td>5.0 (5.7)</td>
<td>NA</td>
</tr>
<tr>
<td>Dry deposition</td>
<td>NA (0.2)</td>
<td>2.6 (3.2)</td>
<td>NA</td>
<td>1.3 (2.1)</td>
<td>NA</td>
</tr>
<tr>
<td>Bulk precipitation</td>
<td>3.0 (2.5)</td>
<td>4.4 (3.4)</td>
<td>2.4 (1.7)</td>
<td>8.1</td>
<td>NA (0.0)</td>
</tr>
<tr>
<td>Throughfall</td>
<td>1.6 (1.2)*</td>
<td>4.3 (3.9)*</td>
<td>2.8 (1.8)*</td>
<td>9.1</td>
<td>NA (0.8)</td>
</tr>
<tr>
<td>Estimated total input</td>
<td>1.8 (2.1)</td>
<td>5.9 (5.8)</td>
<td>2.4</td>
<td>6.3 (7.8)</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Output</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Runoff to lake inlet</td>
<td>0.1</td>
<td>2.9</td>
<td>1.2</td>
<td>15.2</td>
<td>NA (1.3)</td>
</tr>
<tr>
<td>Balance</td>
<td>1.7</td>
<td>3.0</td>
<td>1.2</td>
<td>−8.9</td>
<td>−1.3</td>
</tr>
</tbody>
</table>

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 $\text{SO}_4^{2-}$ 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 $\text{SO}_4^{2-}$) 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 $\text{SO}_4^{2-}$ (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).
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 $\delta^{34}$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.
concentrations (Fig. 1). The differences among years in NO$_3^-$ concentrations were not related to NO$_3^-$ concentrations in precipitation $(r = -0.03; \text{Table 4})$. 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 NO$_3^-$ concentrations among years. Significant correlations between NO$_3^-$ concentrations in lake outlet and annual average air temperature $(r = 0.51, P < 0.05; \text{Table 4})$ and total precipitation $(r = 0.53, P < 0.05; \text{Table 4})$ suggested possible climatic controls on long-term variations in surface water NO$_3^-$ concentrations. In a forested watershed within the Catskill Mountains of New York State, Murdoch et al. (1998) also found a positive correlation between stream NO$_3^-$ 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 NO$_3^-$ concentrations was found for the Hubbard Brook subcatchment (McHale et al., 2002) indicated that snowmelt, in a mixture with high N soil water, first charges till groundwater rather than being directly flushed to the stream.

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 ($n = 18$)

<table>
<thead>
<tr>
<th></th>
<th>Annual mean temperature</th>
<th>Annual total precipitation</th>
<th>Concentrations in precipitation</th>
<th>Ca$^{2+}$ in lake discharge</th>
<th>Mg$^{2+}$ in lake discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4^+$</td>
<td>-0.05</td>
<td>0.35</td>
<td>0.19</td>
<td>-0.14</td>
<td>-0.14</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.51*</td>
<td>0.53*</td>
<td>-0.03</td>
<td>0.15</td>
<td>0.23</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>-0.40</td>
<td>-0.20</td>
<td>0.64**</td>
<td>0.86**</td>
<td>0.85**</td>
</tr>
</tbody>
</table>

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

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**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 ($n = 18$)

<table>
<thead>
<tr>
<th>Correlations with</th>
<th>NO$_3^-$ (Jan–Mar)</th>
<th>NO$_3^-$ (Jan–Apr)</th>
<th>SO$_4^{2-}$ (Jan–Mar)</th>
<th>SO$_4^{2-}$ (Jan–Apr)</th>
<th>Runoff (Jan–Mar)</th>
<th>Runoff (Jan–Apr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average daily air temperature</td>
<td>0.84**</td>
<td>0.74**</td>
<td>-0.23</td>
<td>-0.27</td>
<td>0.80**</td>
<td>0.62**</td>
</tr>
<tr>
<td>Number of days with average temperature $&gt;1$ °C</td>
<td>0.59*</td>
<td>0.45</td>
<td>-0.05</td>
<td>-0.17</td>
<td>0.74**</td>
<td>0.58*</td>
</tr>
<tr>
<td>Runoff</td>
<td>0.75**</td>
<td>0.50*</td>
<td>-0.15</td>
<td>-0.09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

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**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.
amount of water flow before major spring snowmelts may play a central role in explaining the interannual variability in watershed NO₃⁻ 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-

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 NO₃⁻ 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 NO₃⁻ in particles and precipitation, concentrations of HNO₃ vapor and precipitation NH₄⁺ tended to be higher either during the dormant season or during

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**Fig. 4** Relationships between average air temperatures and NO₃⁻ 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.

**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 ± 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...
(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 N\(_2\)O (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 NO\(_3\)\(^-\) concentrations during winter and snowmelt, but negligibly low concentrations during the growing season (Mitchell et al., 1996a). Low summer concentrations (<10 \(\mu\)mol L\(^{-1}\)) have persisted through the 1990s (Figs 1 and 5). This low level of summer NO\(_3\)\(^-\) 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 transited into more advanced stages of N saturation.

In the late 1980s, increased NO\(_3\)\(^-\) 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,
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 snowmelt 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 kg S ha$^{-1}$ 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).
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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References


