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Contrasting stream water NO_3^- and Ca^{2+} in two nearly adjacent catchments: the role of soil Ca and forest vegetation

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Abstract

Two nearly adjacent subcatchments, located in the Adirondack Mountains of New York State, US, with similar atmospheric inputs of N (0.6 kmol ha^{-1} yr^{-1}), but markedly different stream water solute concentrations, provided a unique opportunity to evaluate the mechanisms causing this variation. Subcatchment 14 (S14) had much greater stream water Ca^{2+} and NO_3^- concentrations (851 and 73 μmol_c L^{-1}, respectively) than Subcatchment 15 (S15) (427 and 26 μmol_c L^{-1}, respectively). To elucidate factors affecting the variability in stream water concentrations, soil and forest floor samples from each subcatchment were analyzed for total elemental cations and extractable N species. Mineral soil samples were also analyzed for exchangeable cations. Tree species composition was characterized in each subcatchment and potential differences in land use history and hydrology were also assessed. Compared with S15, soils in S14 had significantly higher total elemental Ca^{2+} in the forest floor (380 vs. 84 μmol g^{-1}), Bs horizon (e.g. 1361 vs. 576 μmol g^{-1}) and C horizon (1340 vs. 717 μmol g^{-1}). Exchangeable Ca^{2+} was also significantly higher in the mineral soil (64 μmol g^{-1} in S14 vs. 8 μmol g^{-1} in S15). Extractable NO_3^- was higher in S14 compared with S15 in both the forest floor (0.1 vs. 0.01 μmol g^{-1}) and Bs horizon (0.2 vs. 0.07 μmol g^{-1}) while extractable NH_4^+ was higher in S14 vs. S15 in the forest floor (7 vs. 5 μmol g^{-1}). The total basal area of 'base-rich indicator' tree species (e.g. sugar maple, American basswood, eastern hophornbeam) was significantly greater in S14 compared with S15, which had species characteristic of sites with lower base concentrations (e.g. American beech and eastern white pine). The disparity in stream water Ca^{2+} and NO_3^-, concentrations and fluxes between S14 and S15 were explained by differences in tree species composition and soil properties rather than differences in land use or hydrology. The marked difference in soil Ca^{2+} concentrations in S14 vs. S15 corresponded to the higher stream water Ca^{2+} and the larger contribution of base-rich tree species to the overstory biomass in S14. Soil under such species is associated with higher net mineralization and nitrification and likely contributed to the higher NO_3^- concentrations in the drainage waters of S14 vs. S15. Studies investigating differences in spatial and temporal patterns of the effects of chronic N deposition on surface water chemistry need to account for changes in tree species composition and how vegetation composition is influenced by soil properties, as well as climatic and biotic changes.

Keywords: acer saccharum, atmospheric deposition, calcium, catchment, hydrology, land use history, nitrate, nitrogen, tree species

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Introduction

During the last few decades, production and deposition of reactive forms of nitrogen (N) by humans has greatly increased because of increased agricultural activities (cultivation of N-fixing crops and production of fertili-

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zers) and combustion of fossil fuels (Galloway *et al.*, 2003). Atmospheric N deposition has increased five to 10 times since the preindustrial period in the northeastern US and has been chronically high for at least the last four and a half decades (Driscoll *et al.*, 2003c). As this increased N accumulates in forest ecosystems, N supply may approach or exceed biotic demand, a condition termed 'nitrogen saturation' (Aber *et al.*, 1989). Increased stream water NO_3^- concentrations are often associated with chronically high N deposition, and elevated surface water NO_3^- concentrations have been used as an indicator of N saturation (Aber *et al.*, 2003). However, recent studies across the northeastern US have indicated that chronically high N deposition has had variable effects on stream water NO_3^- concentrations. A long-term increase in stream water NO_3^- has been observed at the Fernow Experimental Forest, WV (Peterjohn *et al.*, 1996), while surface water NO_3^- concentration has declined since the 1970s within New Hampshire streams (Likens *et al.*, 1996; Goodale *et al.*, 2003) and several lakes in the Adirondack Park, NY (Driscoll *et al.*, 2003b). These inconsistent results suggest that factors in addition to N deposition are controlling N cycling and, therefore, temporal and spatial patterns of stream water NO_3^- concentrations (Campbell *et al.*, 2004; Ito *et al.*, 2005). These factors include those affecting atmospheric (Miller *et al.*, 1993; Ollinger *et al.*, 1993; Weathers *et al.*, 2000) and geological (Holloway & Dahlgren, 2001) sources of N; mineralization and nitrification of N as influenced by soil C:N ratios and tree species composition (Vitousek & Matson, 1985; Geary & Driscoll, 1996; Gundersen *et al.*, 1998a; Finzi *et al.*, 1998b; Lovett *et al.*, 2002, 2004; Lovett & Mitchell, 2004); and hydrological transport of N (Creed & Band, 1998; Inamdar *et al.*, 2000; Schiff *et al.*, 2002). Climatic variables (Mitchell *et al.*, 1996; Groffman *et al.*, 2001; Goodale *et al.*, 2003; Park *et al.*, 2003) and differences in land use history (Compton & Boone, 2000; Goodale & Aber, 2001) also have helped explain the spatial and temporal variability of stream water NO_3^- concentrations.

The Adirondack region of New York State receives among the highest rates of N deposition in the US For example, when comparing N deposition values from the Integrated Forest Study, southeastern, northeastern and northwestern US values were 0.4–0.7, 0.5 and 0.4 $\mathrm{kmol\,ha^{-1}\,yr^{-1}}$, respectively, while Adirondack values ranged from 0.7 to 1.1 $\mathrm{kmol\,ha^{-1}\,yr^{-1}}$ (Lovett & Lindberg, 1993). Surface waters in some parts of the Adirondacks are sensitive to acidic deposition because the shallow surficial geology results in soils with low pools of available nutrients and limited buffering capacity. Many studies have been conducted in the Adirondacks to determine the effects of acidic deposition on stream water chemistry and ecological variables (e.g. Driscoll *et al.*, 2003a, b; Ito *et al.*, 2005). Over the past 20 years, the Archer Creek Catchment, located in the center of the Adirondack Park, has been the site of several studies that explored biogeochemical and hydrological controls on various elements and their respective solutes (Mitchell *et al.*, 1996; Ohrui *et al.*, 1999; McHale *et al.*, 2000, 2002; Park *et al.*, 2003; Inamdar *et al.*, 2004; McHale *et al.*, 2004). From 1983 to 1998, although there was a net export of stream water solutes such as base cations and SO_4^{2-} from the catchment, atmospherically deposited N exceeded the loss in drainage waters, indicating that most of the N was retained or lost via denitrification within the catchment (Mitchell *et al.*, 2001). N retention within the Archer Creek Catchment was also controlled by seasonal variability of storage in near-stream wetlands (McHale *et al.*, 2004) while N mineralization and nitrification have been shown to vary with landscape position (Ohrui *et al.*, 1999). Interannual variability in NO_3^- loss in Archer Creek could be explained at least partly by climatic variables (Park *et al.*, 2003). Changes in sources of solutes among seasons, as well as variation of hydrologic flow paths during storm events, have also explained the temporal variability of stream water NO_3^- in the Archer Creek (McHale *et al.*, 2002; Inamdar *et al.*, 2004). As part of a preliminary survey for evaluating variation of surface water characteristics in the Archer Creek Catchment, we found two subcatchments that were in close proximity (Fig. 1), but differed substantially with respect to stream chemistry, providing a unique opportunity to ascertain the mechanisms causing this variation. Most notably, Subcatchment 14 (S14) had markedly higher NO_3^- and Ca^{2+} concentrations and pH than Subcatchment 15 (S15). The major objectives of this investigation were to further evaluate the surface water chemistry of S14 and S15 and to determine the underlying mechanisms that cause the marked difference in stream water chemistry between these two subcatchments with particular focus on the regulation of N cycling. To evaluate these differences, we gave particular attention to differences in tree species composition and soil chemistry as previous studies of forest ecosystems have suggested that these components have a major influence on N cycling (Vitousek & Matson, 1985; Gundersen *et al.*, 1998a; Finzi *et al.*, 1998b; Lovett *et al.*, 2004). We also considered the possible influences of other factors including atmospheric deposition, hydrology, storage and land use as these factors are also known to influence N biogeochemistry, as well as overall surface water–solute relationships (Mitchell *et al.*, 1992a, b; Miller *et al.*, 1993; Ollinger *et al.*, 1993; Creed & Band, 1998; Inamdar *et al.*, 2000; Weathers *et al.*, 2000; Goodale & Aber, 2001; Schiff *et al.*, 2002).

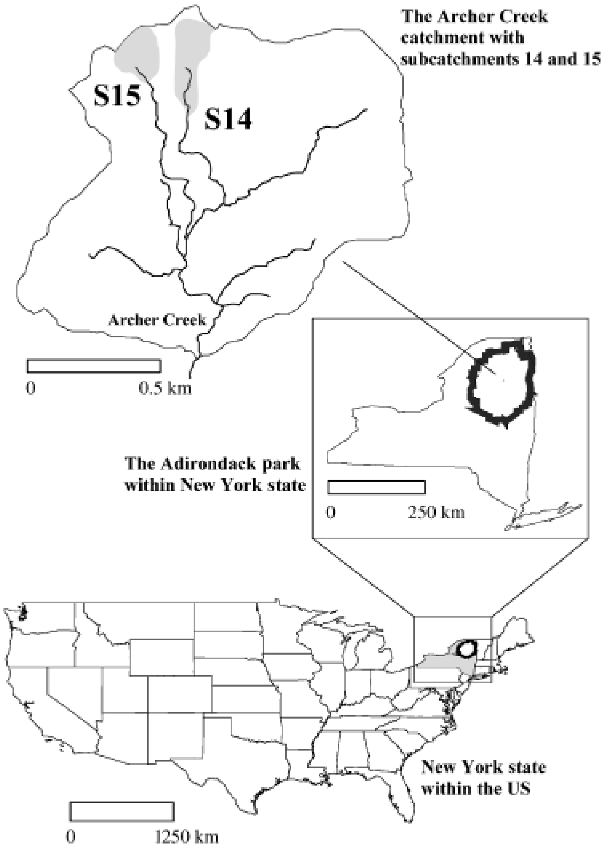

Fig. 1 Subcatchments 14 and 15 in the Archer Creek Catchment located in the Adirondack Park, New York.

Methods

Site description

Subcatchment 14 (3.5 ha) and Subcatchment 15 (2.5 ha) are located in the 135 ha Archer Creek Catchment (43°58′N, 74°14′W) within the 6066 ha Huntington Forest near the center of the Adirondack Park, US (Fig. 1). The bedrock consists of Precambrian rock composed primarily of granitic gneiss with some gabbro-amphibolite. Archer Creek is also located within the Anorthosite Massif, a large igneous intrusion composed of up to 90% calcium-rich feldspar (Driscoll *et al*., 1991). The surficial geology is dominated by glacial till deposited during the recession of the Wisconsin glacier ~ 14 000 years ago. Glacial till in the Adirondacks has a high sand (~ 75%) and low clay (<10%) content, with an abundance of cobbles and boulders. Upland catchment soils are generally less than 1 m in depth and include the Becket-Mundall series sandy loams (course-loamy, mixed, frigid, typic Haplorthods). Upland soils typify temperate forest spodosols with an O horizon to a depth of approximately 5 cm, a large Bs horizon (approximately 80 cm) and a C horizon. An E horizon is sporadically present and there is no A horizon. Greenwood mucky peats are found in valley bottom wetlands (Sommers, 1986). Overstory vegetation at lower elevations includes eastern hemlock (*Tsuga canadensis* (L.) Carr.), yellow birch (*Betula alleghaniensis* Britt.), speckled alder (*Alnus incana* (L.) Moench), red spruce (*Picea rubens* Sarg.) and scattered balsam fir (*Abies balsamea* (L.) Mill.). Upper slopes are dominated by American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), red maple (*Acer rubrum* L.), yellow birch and eastern white pine (*Pinus strobus* L.). A detailed description of the vegetation in each subcatchment is given in the results and discussion section.

Precipitation and air temperature have been measured hourly at a meteorological station 2.5 km from the subcatchments since 1940. The climate is cool and moist and the mean annual temperature and precipitation were 4.4 °C and 1010 mm, respectively, from 1951 to 1980 (Shepard *et al*., 1989).

Physiographic and hydrologic characteristics of the subcatchments

We examined physiographic properties of S14 and S15 and used these as surrogates for assessing hydrological similarity (after Lovett *et al*., 2000). We delineated the subcatchment boundaries of S14 and S15 using a 3 m digital elevation model (DEM) that was ground-truthed using a field-delineated boundary. We also used the DEM to calculate various physiographic features of the subcatchments: (1) total watershed area; (2) minimum (stream sampling point at the subcatchment outlet), maximum and mean elevation; (3) total relief (maximum–minimum elevation); (4) length (distance from stream sampling point to the farthest point in the subcatchment); (5) mean slope (in degrees); (6) mean aspect (expressed in positive degrees from 0 to 360, measured clockwise from the north); and (7) the topographic index (TI) described as $\ln(a/\tan\beta)$, where a is the upslope contributing area per unit contour and $\tan\beta$ is the local slope angle (see Wolock, 1993). Areas in the subcatchments that drain large upslope contributing areas or that are flat in slope give rise to high index values. One of the main assumptions of this index is that all points with the same value respond similarly hydrologically (Beven *et al*., 1995; Beven, 1997) meaning points with the same TI value will wet and dry (i.e. watertable rise and fall) similarly. Points in a catchment having high index values tend to saturate first and will, therefore, indicate potential subsurface or surface contributing areas (i.e. source areas of solutes that would be carried to the stream). The expansion and contraction of such areas as the catchment wets and dries is then indicated by the pattern of the cumulative frequency distribution of TI values for any particular catchment. Catchments having the same cumulative frequency distributions should show similar hydrological responses to wetting and drying. The cumulative frequency distributions of the TIs for each subcatchment were compared and used to assess hydrologic similarity between the subcatchments.

Stream stage height was monitored at 20 min intervals at the outlets of S14 and S15 using water-height capacitance probes (± 1 mm resolution, Tru Track, New Zealand) housed in stilling wells. Stage height was related to discharge using a rating curve based on data collected over a range of stream stages. Hourly and daily discharge rate was computed by summing 20 min discharge measurements.

Atmospheric deposition

Although atmospheric deposition was not measured directly within S14 and S15, it is measured at a site 2.5 km southeast of the two subcatchments. At this site, wet-only deposition has been monitored since November 1978 by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN, site location NY20). More details about site monitoring can be found on the NADP/NTN website (http://nadp.sws.uiuc.edu/sites/siteinfo.asp?id=NY20&net=NADP). We used the weekly NADP data to calculate total annual (June 12, 2002–June 11, 2003) precipitation and precipitation-weighted mean annual N solute concentrations. Annual solute fluxes were obtained by multiplying the total precipitation amount for the study period by the precipitation-weighted mean annual concentration.

Dry deposition (HNO_3 vapor and particulate NO_3^- and NH_4^+) also has been monitored since June 2002 by the US Environmental Protection Agency (EPA) as part of the Clean Air Status and Trends Network (CASTNET). More detailed information on dry deposition sampling can be found at the CASNET website (http://www.epa.gov/castnet/overview.html). Many factors can control the rate of atmospheric dry deposition. These factors range from meteorology and air chemistry to those associated with forest composition such as tree canopy structure and leaf physiology. For instance, significant differences in dry deposition rates can be expected between coniferous and deciduous canopies (Weathers *et al*., 2000). Therefore, after calculating the mean annual N solute concentrations using the weekly CASNET dataset, we estimated mean annual (June 12, 2002–June 11, 2003) dry deposition of S14 and S15 based on tree species composition. We multiplied CASNET mean annual concentration data by individual mean annual dry deposition velocities for coniferous and deciduous forests to acquire flux values for hardwoods and conifers trees. Estimates of annual dry N deposition for each subcatchment were obtained as follows:

$$\mathrm{TF}_i = \mathrm{HF}(\%\mathrm{H}) + \mathrm{CF}(\%\mathrm{C}), \qquad (1)$$

where TF_i is total flux in subcatchment i, HF and CF are hardwood and conifer fluxes, respectively, and %H and %C are percent hardwoods and conifers, respectively. For deciduous forests, we used dry deposition velocities of $2.14\,\mathrm{cm\,s^{-1}}$ for HNO_3 vapor and $0.12\,\mathrm{cm\,s^{-1}}$for NH_4^+ and NO_3^- particles (Lovett & Rueth, 1999). These deposition velocities were based on an average of seven sites across the northeastern US (69–765 m elevation) calculated from a model parameterized with site-specific canopy and meteorological data (Clarke *et al*., 1997). For conifer forests, we used dry deposition velocities of $2.9\,\mathrm{cm\,s^{-1}}$ for HNO_3 and $0.09\,\mathrm{cm\,s^{-1}}$ for fine particles (Johnson & Lindberg, 1992). These values were the average dry deposition velocities from two northeastern conifer sites studied as part of the Integrated Forest Study (IFS) (Johnson & Lindberg, 1992). One site was on Whiteface Mountain (elevation 950–1100 m), also located in the Adirondack Park while the other site was in Howland, Maine (elevation 65 m). Dry deposition velocities for deciduous and conifer sites used in this study were based on sites with a range of elevations. Higher elevation sites tend to have greater deposition velocities than lower sites (Lovett, 1994). However, many other studies have used average values to estimate deposition velocities especially when other site characteristics (such as vegetation) are similar (Lindberg *et al*., 1986; Ollinger *et al*., 1993; Lovett & Rueth, 1999).

Mineral soil elemental analysis

Soil samples for total elemental analyses were collected from two replicate plots within each subcatchment. In each subcatchment, one plot was located on the eastern side of the stream while the other plot was located on the western side of the stream. At each plot, three samples were collected from the Bs (15 and 50 cm) and C horizons for a total of 18 samples from each subcatchment. Soil samples were digested using a microwave acid digestion procedure (EPA, 1996) and the digests were analyzed for total elemental Ca, Mg, Na, K and Al on an inductively coupled plasma atomic emission spectrometer (ICP-AES). A randomized split-plot analysis of variance (ANOVA) was performed using SAS statistical software (SAS Inst., 1985) to detect differences in total elemental analyses between subcatchments. Within our study, all statistical comparisons were assessed at $\alpha = 0.05$.

Soil extractions and forest floor elemental analyses

Samples for soil extractions were collected from each subcatchment. Horizontal transects (20 m wide) were established perpendicular to the main slope and extending the entire width of each subcatchment (Fig. 2). Each transect was comprised of adjacent $20 \times 20\,m^2$ ($400\,m^2$) sampling plots. In a randomized split-plot sampling design with repeated measures, soil was sampled on October 29, 2002 (after leaf-fall), May 29, 2003 and July 28, 2003. On each date, we sampled from the forest floor (Oe and Oa horizons) and the mineral soil (Bs horizon) at 17 and 13 plots in S14 and S15, respectively, for a total of 60 samples per sampling date. The number of plots sampled in each catchment was based on sampling approximately 30% of the surface area; because S14 is larger, more plots were included. Samples were transported in coolers containing ice packs and were stored at 4 °C until analyzed.

All forest floor and mineral soil samples were extracted with 2 M KCl within 3 days of collection. The extracts were filtered (pore size 2.5 μm) and analyzed at the Biogeochemistry Laboratory at the State University of New York College of Environmental Science and Forestry (SUNY-ESF) for NH_4^+ and NO_3^- using continuous flow colorimetry and total dissolved N (TDN) by persulfate oxidation. DON was calculated by subtracting dissolved inorganic nitrogen ($NH_4^+ + NO_3^-$) from TDN. Subsamples of each soil sample were oven dried for 2–3 days at 65 °C, until the mass was constant, to determine the moisture content during each sampling date. Additional subsamples also were separated during the May and July sampling dates to analyze for pH using a 1 : 2 ratio of soil to 0.01 M $CaCl_2$. Cation analyses for the forest floor and mineral soil were performed on subsamples from the October sampling date. Mineral soil subsamples were extracted with 2 N ammonium acetate. The extracts were filtered and analyzed for exchangeable Ca^{2+}, Mg^{2+}, Na^+ and K^+ by ICP-AES. Subsamples from the forest floor were combusted in a muffle furnace at 470 °C for 16 h and the residual ash was dissolved in 6 M HCl. The solution was evaporated to dryness on a hot plate, rinsed a second time with 6 M HCl, and filtered before being analyzed for total elemental Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions as described for the mineral soil. A randomized split-plot ANOVA with repeated measures was performed in SAS (SAS Inst., 1985) to determine differences in extractable N species and pH between subcatchments, depths and seasons. A randomized split-plot ANOVA also was performed to determine differences in extractable and total elemental Ca^{2+}, Mg^{2+}, Na^+ and K^+ between subcatchments.

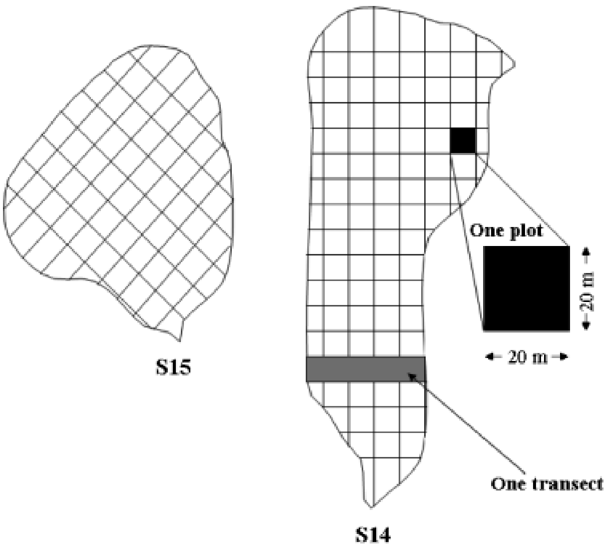

Fig. 2 Transect and plot delineation in S14 and S15. The subcatchments were divided into horizontal adjacent transects (20 m wide) perpendicular to the main slope and extending the entire width of each subcatchment (e.g. gray rectangle shown in S14). Each transect was comprised of adjacent $20 \times 20\ m^2$ ($400\,m^2$) sampling plots (e.g. black square shown in S14). Transects and plots are not to drawn to scale and are under-represented.

Vegetation and litter sampling

We sampled vegetation in every plot along six randomly selected horizontal transects (Fig. 2). The diameter at breast height (dbh) and species of trees greater than 5 cm dbh were recorded in each of 33 plots in S14 and 26 plots in S15, for a total of 59 plots. The basal area was calculated by species and per unit catchment area. ANOVA was performed (SAS Inst., 1985) to determine differences in tree species between subcatchments.

To determine litterfall biomass, we placed one $0.25\,m^2$ wooden trap on the ground in the center of each of the 30 plots used in the soil extraction analyses. Square traps were $50 \times 50 \times 15$ cm with a 2 mm mesh base suspended approximately 3 cm above the forest floor to inhibit decomposition. We collected early reproductive litterfall from May 11 to July 15, 2003 and senescent leaves along with mast were collected from July 15 to November 19, 2003. Total surface area covered by litter traps was 0.012% and 0.013% in S14 and S15, respectively. Mass of air-dried samples was calculated per unit area. ANOVA was performed (SAS Inst., 1985) to determine differences in leaf litter biomass between subcatchments.

Surface water chemistry

Stream samples were collected from the subcatchment outlets (Fig. 1) at least once per month from June 12,

Table 1 Physiographic characteristics of Subcatchments 14 and 15

Physical characteristic	S14	S15
Catchment area (ha)	3.5	2.5
Mean elevation (m)	619	614
Minimum elevation (subcatchment outlet) (m)	572	594
Maximum elevation (m)	672	632
Total relief (maximum–minimum elevation) (m)	100	38
Length (distance from subcatchment outlet to the farthest place in the catchment.) (m)	374	223
Mean slope (deg)	16	10
Mean aspect (expressed in positive degrees from 0 to 360, measured clockwise from the north)	200	168

2002 to June 11, 2003, with more intensive sampling carried out during hydrologic events. Samples from S14 and S15 were collected at approximately the same dates and times throughout the study period. Storm samples at subcatchments outlets were collected with an automatic sampler triggered at specified time intervals. Stream samples were transported on ice to the Biogeochemistry Laboratory at SUNY-ESF and generally were analyzed within 2 weeks following collection. Samples were analyzed for Cl^-, SO_4^{2-} and NO_3^- by ion chromatography; Ca^{2+}, Mg^{2+}, K^+, Na^+ and total Al using ICP-AES; NH_4^+ using continuous flow colorimetry; TDN by persulfate oxidation; and pH using glass electrode potentiometry. Concentrations of DON also were analyzed as described for soil extracts. The contribution of organic acids to solution charge was estimated using the following two equations:

$$[\mathrm{RCOO}^-] = \frac{\mathrm{p}K_\mathrm{a} m[\mathrm{DOC}]}{\mathrm{p}K_\mathrm{a} + [\mathrm{H}^+]} \qquad (2)$$

and

$$\mathrm{p}K_\mathrm{a} = a + (b\mathrm{pH}) - (c\mathrm{pH}^2), \qquad (3)$$

where $[\mathrm{RCOO}^-]$ is the organic anion concentration, $\mathrm{p}K_\mathrm{a}$ is the dissociation constant of humic acid, m is the concentration of acidic functional groups per mole C of DOC, [DOC] is the dissolved organic carbon concentration and a, b and c are operationally defined by model calibration (Driscoll *et al.*, 1989). We used $a = 0$, $b = 1.45$, $c = 0.08$ and $m = 0.17$, values established by Driscoll *et al.* (1989) for Adirondack Lakes. DOC concentrations were determined by ultra violet-persulfate oxidation after being filtered through a precombusted glass fiber filter (Whatman GF/F, 0.7 μm). The Biogeochemistry Laboratory at SUNY-ESF follows an extensive QA/QC procedure and participates in the US Geological Survey (USGS) audit program. Every analysis has calibration QCs, detection limit QCs, analytical blanks, and analytical replicates. Samples having concentrations above calibration standards were diluted and rerun.

Flow-weighted mean annual stream water concentrations for all solutes were calculated using daily stream concentrations and discharge (SAS Inst., 1985) for the subcatchments. For days when there were multiple collections (during hydrologic events), flow-weighted concentrations were determined to obtain a daily concentration value. For days when chemical concentrations were not available, concentrations were computed by averaging the two measured concentrations closest to that day. Daily fluxes were calculated by multiplying solute concentration by discharge. Monthly and annual fluxes were then determined by summing daily solute fluxes.

Results and discussion

Physiographic and hydrologic similarities

There were differences in some of the physiographic features between S14 and S15 mostly because of the larger size of S14 (3.5 ha) vs. S15 (2.5 ha) suggesting hydrologic residence time might be greater in S14 (Table 1). Mean, minimum and maximum elevation differed 5, 22 and 40 m, respectively. There was a 32° (9%) difference in mean aspect while mean slope differed by 6°. Total relief and total length differed by 62 and 151 m, respectively.

The topographic distributions ranged from 3 to 13 in S14 and from 3 to 15 in S14 (Fig. 3). There was very little difference in the pattern of the topographic index distributions between S14 and S15. S14 had a slightly higher percentage (1%) of area having index values of 9–11 vs. S15 (5 vs. 4%). Values between 9 and 11 have a higher propensity for the water table to reach the ground surface and form surface and subsurface contributing areas to the stream during hydrologic events. These two subcatchments, therefore, would be expected to have similar hydrologic responses to precipitation. Solute transport should be quite similar during hydrologic events because of similarity in stream water and, therefore, stream solute source areas in the landscape.

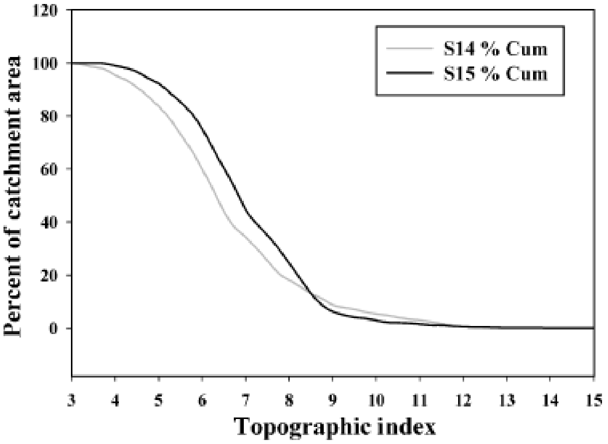

Fig. 3 The topographic index cumulative frequency distribution within S14 and S15.

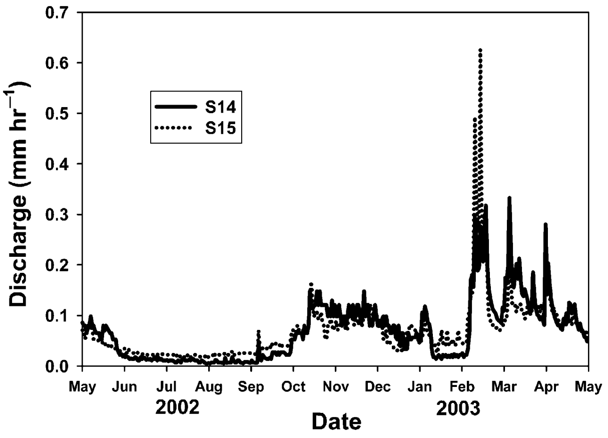

Fig. 4 Discharge (mm hr^{-1}) at S14 and S15 from June 12, 2002–June 11, 2003.

Total discharge for the study period (June 12, 2002–June 11, 2003) was 600 mm for both S14 and S15. The patterns of stream discharge were similar between S14 and S15 (Fig. 4). However, during hydrologic events, S15 had more of a 'flashy' hydrologic response, with stream discharge peaks occurring more rapidly than S14; however, this was expected because of its smaller size compared with S14 (Christopher, 2004).

Atmospheric deposition

There was no difference in estimated atmospheric N deposition between S14 and S15. Both catchments had total N deposition of 0.6 kmol ha^{-1} with 0.2, 0.1, and 0.2 kmol ha^{-1} yr^{-1} from NO_3^- (wet-only deposition), NH_4^+ (wet-only deposition), and DON, respectively (Table 2). Dry deposition estimates were also identical with S14 and S15 having 0.1, 0.002, and 0.02 kmol ha^{-1} yr^{-1} HNO_3 vapor, particulate NO_3^-, and particulate NH_4^+, respectively.

Differences in mineral soil total cation chemistry

Total mineral soil Ca^{2+} and Mg^{2+} concentrations were significantly and markedly higher in S14 vs. S15 (Table 3, $P<0.001$ and $P=0.014$ for Ca^{2+} and Mg^{2+} comparisons, respectively), while there were significantly greater mineral soil Al concentrations in S15 vs. S14 ($P=0.006$). These data suggest that there were larger internal sources of Ca^{2+} and Mg^{2+} and lower sources of Al in S14 vs. S15. There were no significant differences in mineral soil Na^+ and K^+ concentrations between the two subcatchments.

Differences in soil and forest floor extractable N

There were marked differences between S14 and S15 in soil extractable inorganic N (NO_3^- and NH_4^+), but very little difference in extractable DON (Fig. 5). Extractable DON was only marginally different in the summer when S15 values were actually greater than S14 ($P=0.031$) (Fig. 5a). S14 soil extractable NH_4^+ was significantly greater than S15 during both the fall and the spring ($P=0.020$ and $P<0.001$, respectively) (Fig. 5a) although the difference between S14 and S15 extractable NH_4^+ concentration was more pronounced during the spring. Significant differences in S14 and S15 extractable NH_4^+ concentration occurred only in the forest floor (Fig. 5b). Soil extractable NO_3^- in S14 was higher in both the forest floor and mineral soil ($P<0.001$ and <0.001, respectively), as well as during both the spring ($P<0.001$) and summer ($P<0.001$) (Fig. 5a,b). Differences between the S14 and S15 soil extractable NO_3^- during the summer were significantly greater than those in the spring. Soil extractable TDN was significantly higher at S14 compared with S15 only during the spring (Fig. 5a, $P<0.001$).

Differences in soil and forest floor base cation chemistry and pH

The total elemental Ca $^{2+}$, Mg^{2+} and K^+ concentrations were significantly and markedly higher in S14 vs. S15 in the forest floor (Table 4, $P<0.001$ for Ca^{2+} and Mg^{2+} and $P=0.002$ for K^+). Exchangeable Ca^{2+} was also much higher in S14 vs. S15 in the mineral soil (Table 4, $P=0.053$) and was the dominant exchangeable cation in both subcatchments. There was a significantly higher pH in S14 vs. S15 in both the forest floor (Fig. 6, $P<0.001$) and mineral soil ($P<0.001$) although the disparity in catchment means (between S14 and S15) was

Table 2 Atmospheric N deposition in S14 and S15 (June 11, 2002–June 10, 2003)

	Dry deposition			Wet-only deposition		DON* deposition	Total N deposition
	HNO_3 vapor	Particulate NO_3^-	Particulate NH_4^+	NO_3^-	NH_4^+		
Flux to deciduous (kmol ha^{-1} yr^{-1})	0.1	0.002	0.02	n/a	n/a	n/a	n/a
Flux to conifers (kmol ha^{-1} yr^{-1})	0.1	0.001	0.01	n/a	n/a	n/a	n/a
S14 flux (kmol ha^{-1} yr^{-1})	0.1	0.002	0.02	0.2	0.1	0.2	0.6
S15 flux (kmol ha^{-1} yr^{-1})	0.1	0.002	0.02	0.2	0.1	0.2	0.6

*DON deposition from Park *et al*. (2003).

Table 3 Mineral soil elemental Ca, Mg, Na, K and Al in S14 and S15

	S14			S15		
Element (µmol g^{-1} dry soil)*	15 cm Bs horizon	50 cm Bs horizon	C horizon	15 cm Bs horizon	50 cm Bs horizon	C horizon
Ca	1306 a (153)	1361 a (153)	1340 a (153)	422 b (153)	576 b (153)	717 b (153)
Mg	779 a (184)	967 a (184)	915 a (184)	162 b (184)	222 b (184)	266 b (184)
Na	472 a (53)	643 a (53)	740 a (53)	606 a (53)	748 a (53)	855 a (53)
K	439 a (19)	465 a (19)	534 a (19)	493 a (19)	560 a (19)	598 a (19)
Al	2028 a (109)	2224 a (109)	2335 a (109)	2476 b (109)	2725 b (109)	2796 b (109)

*Values are means with SE of the group means given in parentheses ($N = 6$). Values with different letters between S14 and S15 for each element within a horizon are significantly different ($P < 0.05$).

significantly greater in the forest floor. Soil pH also was greater in S14 in both the spring and summer ($P < 0.001$ for both comparisons).

Differences in vegetation species and similarities in vegetation biomass

Although the total basal area of S14 and S15 were nearly identical (with S14 having 37.6 m^2 ha^{-1} and S15 having 37.8 m^2 ha^{-1}), species composition was markedly different between the subcatchments (Fig. 7). S14 had higher mean basal areas of sugar maple ($P = 0.001$), American basswood (*Tilia americana* L.) ($P < 0.001$), and eastern hophornbeam (*Ostrya virginiana* (Mill.) K. Koch) ($P < 0.001$) while S15 had higher mean basal areas of American beech ($P = 0.001$) and eastern white pine ($P = 0.022$). S14 had 96% hardwood species while S15 had 79%. There were no significant differences in leaf litter biomass between S14 and S15 with S14 having 3587 (± 1 SE = 128) kg ha^{-1} and S15 having 3241 (± 1 SE = 185) kg ha^{-1} ($P = 0.125$).

Differences in stream chemistry

From June 12, 2002 to June 11, 2003, S14 and S15 had markedly different stream water solute concentrations (Table 5). Although S15 had greater concentrations of some base cations (103, 69, and 7 μmol_c L^{-1} for Mg^{2+}, Na^+ and K^+, respectively) vs. S14 (73, 32 and 4 μmol_c L^{-1} for Mg^{2+}, Na^+ and K^+, respectively), for Ca^{2+}, the dominant base cation, the mean concentration of S14 (851 μmol_c L^{-1}) was nearly twice the concentration of S15 (427 μmol_c L^{-1}). The S14 mean SO_4^{2-} concentration (198 μmol_c L^{-1}) was nearly identical to that of S15 (203 μmol_c L^{-1}). DON and NH_4^+ concentrations were very similar in S14 and S15 (S14 and S15 having 6 and 10 µmol L^{-1} DON and 4 and 4 μmol_c L^{-1} NH_4^+, respectively). Concentrations of NO_3^- and TDN were two to three times higher in S14 (73 μmol_c L^{-1} and 83 µmol L^{-1}) vs. S15 (26 μmol_c L^{-1} and 39 µmol L^{-1}) and the mean pH value also was substantially higher in S14 (7.3) compared with S15 (6.7).

There were also substantial differences in the annual flux of solutes between S14 and S15 (Fig. 8). S14 and S15 both had relatively large and nearly identical SO_4^{2-} export (~ 1.2 $kmol_c$ ha^{-1} yr^{-1}). A high loss of SO_4^{2-} in surface waters has been observed within the Adirondack region even though SO_4^{2-} atmospheric deposition has decreased during the last 20 years (Driscoll *et al*., 2003b). High losses of SO_4^{2-} within the northeastern US, including the Adirondacks, have been attributed to internal sources of sulfur (S) such as SO_4^{2-} desorption,

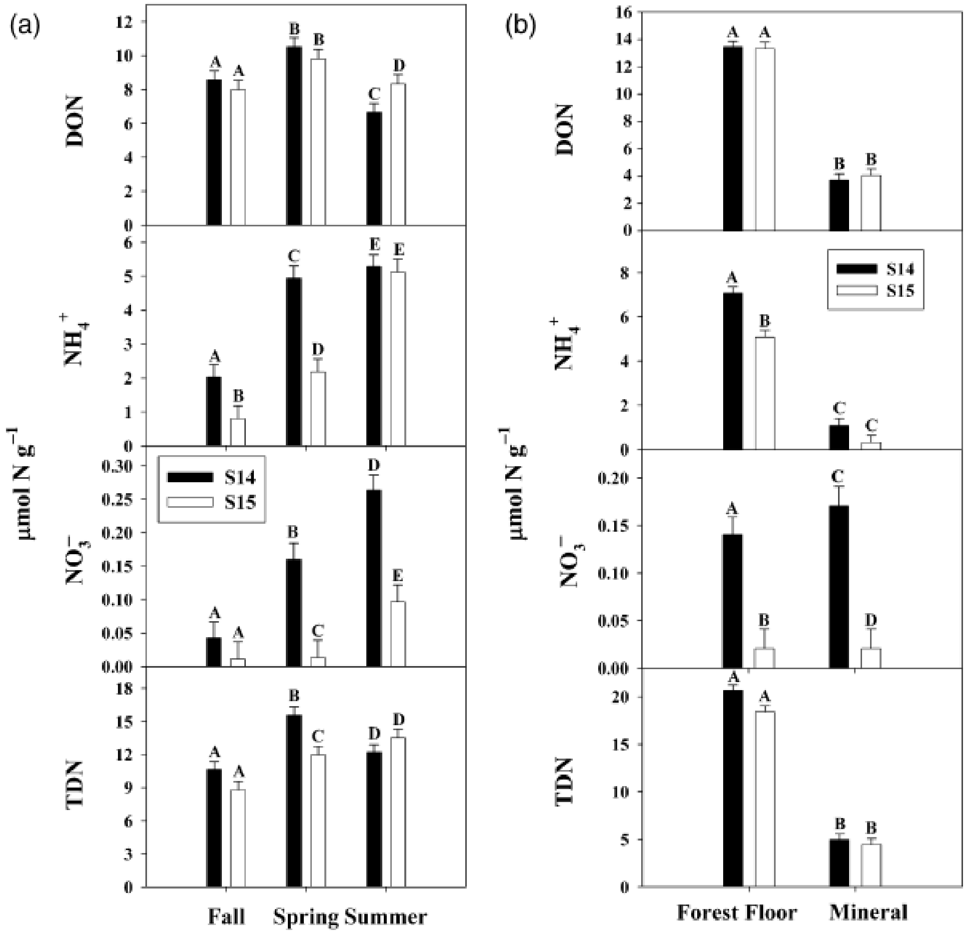

Fig. 5 Mean soil extracts (DON, NH_4^+, NO_3^- and TDN) in S14 and S15 (+ SE of the group means) for different seasons (a) and soil horizons (b). Letters that differ within a season (a) or soil horizon (b) indicate a significant difference between catchments at the 0.05 level.

S mineral weathering or net mineralization of organic S pools (Mitchell *et al.*, 2001; Likens *et al.*, 2002; Bailey *et al.*, 2004b). Stream water NO_3^- export was twofold greater from S14 (0.4 kmol$_c$ ha^{-1} yr^{-1}) than from S15 (0.2 kmol$_c$ ha^{-1} yr^{-1}). Similarly drainage loss of Ca^{2+} from S14 (5.1 kmol$_c$ ha^{-1} yr^{-1}) was two times that of S15 (2.5 kmol$_c$ ha^{-1} yr^{-1}). As a function of their relative concentrations, S15 exported greater amounts of the other base cations including Mg^{2+} (0.6 kmol$_c$ ha^{-1} yr^{-1}) and Na^+ (0.4 kmol$_c$ ha^{-1} yr^{-1}) vs. S14 (exporting 0.4 and 0.2 kmol$_c$ ha^{-1} yr^{-1} Mg^{2+} and Na^+, respectively). The higher loss of Ca^{2+} in S14 was a function of its high Ca^{2+} concentrations on soil exchange sites (Table 3) combined with high concentrations of mobile anions (NO_3^-, SO_4^{2-} and HCO_3^-) (Reuss & Johnson, 1986).

Much of the stream water charge imbalance between measured ions (Fig. 8; Table 5) is likely attributed to bicarbonate (HCO_3^-) anion that was estimated by difference in calculated charge balances between measured anions and cations. Thus, the major mobile anions are HCO_3^-, SO_4^{2-} and NO_3^- for S14 (658, 198, 73 μmol$_c$ L^{-1}, respectively) and S15 (355, 203, 26 μmol$_c$ L^{-1}, respectively) with HCO_3^- being the dominant anion in both subcatchments. The greater contribution of HCO_3^- in S14 would be a function of its higher base cation concentrations and higher pH (7.3) compared with S15 (6.7) (Morel & Haring, 1993).

What are the factors controlling the variability in stream water chemistry, especially Ca^{2+} and NO_3^-, between S14 and S15?

Physiographic and hydrologic characteristics

As hydrologic characteristics (TI distribution, stream discharge quantity and stream discharge pattern) were quite similar between S14 and S15 and there were only minor differences in physiographic characteristics (slope, aspect, relief and length), our results suggest that hydrology alone cannot explain the overall differences in the surface water chemistry between these two subcatchments. Major differences in features such

Table 4 Forest floor elemental and mineral soil exchangeable Ca^{2+}, Mg^{2+}, Na^+ and K^+ in S14 and S15

	S14		S15	
Element (μmolg^{-1} dry soil)*	Forest floor	Mineral	Forest floor	Mineral
Ca^{2+}	380 a (17)	64 a (19)	84 b (20)	8 b (20)
Mg^{2+}	57 a (4)	7 a (4)	25 b (4)	2 a (4)
Na^+	5 a (0.5)	0.9 a (0.6)	5 a (0.6)	1 a (0.6)
K^+	17 a (0.6)	3 a (0.7)	14 b (0.7)	3 a (0.7)

*Values are means with SE of the group means given in parentheses. Values with different letters between S14 and S15 for each extract within a horizon are significantly different ($P < 0.05$).

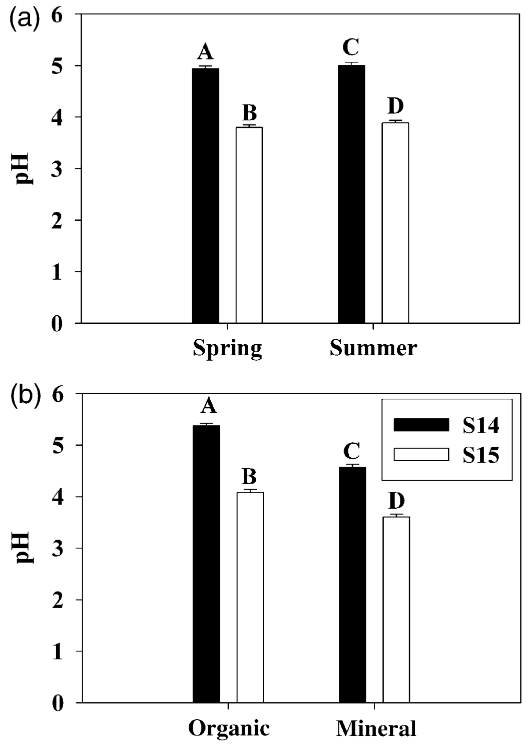

Fig. 6 Mean soil pH in S14 and S15 (+ SE of the group means) for different seasons (a) and soil horizons (b). Letters that differ within a season (a) or soil horizon (b) indicate a significant difference between catchments at the 0.05 level.

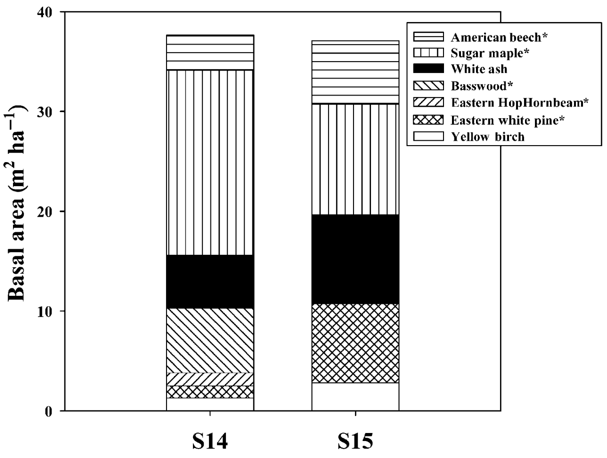

Fig. 7 Total basal area (m^2 ha^{-1}) of S14 and S15. Asterisks indicate significant differences ($P < 0.05$) between S14 and S15 within a species.

as slope and topography have explained the temporal variability in stream water chemistry in catchments located in Ontario, Canada (Creed & Band, 1998; Schiff *et al*., 2002). For example, the variability of stream water NO_3^- was controlled by topography and its influence on the variable source area (VSA-Creed & Band, 1998). Differences in the VSA controlled the flushing of NO_3^- within the landscape, resulting in a sixfold difference among 13 catchments. In our study, there was little difference in topography between the subcatchments (e.g. a 5, 22 and 40 m difference in mean, minimum and maximum catchment relief, respectively, and a 1% difference in TIs between 9 and 11). The variability of NO_3^- export in two other catchments within Ontario was explained by differences in hydraulic gradients associated with differences in slope between two catchments (Schiff *et al*., 2002). There was only a 6° difference in mean slope between S14 and S15.

Land use history

Land use history can have a profound effect on stream water NO_3^- concentrations for some catchments and can mask or enhance other factors such as differences in atmospheric deposition, vegetative and soil properties, as well as hydrological characteristics. For example, agricultural practices in some areas of New England (US) resulted in previously cultivated soil having lower C : N ratios and higher rates of nitrification a century after agricultural abandonment compared with relatively undisturbed sites (Compton & Boone, 2000). In the White Mountain National Forest, NH, US, Ratios of C : N were relatively high and nitrification rates and export of stream water NO_3^- remained depressed

Table 5 Solute concentrations in stream water at the outlets of S14 and S15 from June 12, 2002–June 11, 2003

Sub-catchment	pH	Solute ($\mu mol_c\,L^{-1}$)*									Solute ($\mu mol\,L^{-1}$)*			
		Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	Cl^-	NO_3^-	$HCO_3^{-\dagger}$	NH_4^+	TDN	DON	DOC	Al
S14	7.3	851 (4.7)	73 (0.2)	32 (0.3)	4 (0.1)	198 (2.1)	12 (0.04)	73 (0.8)	658 (4.3)	4 (0.09)	83 (1.0)	6 (0.9)	135 (2.1)	0.2 (0.01)
S15	6.7	427 (7.6)	103 (1.8)	69 (1.0)	7 (0.1)	203 (2)	12 (0.05)	26 (0.4)	355 (8.6)	4 (0.4)	39 (0.8)	10 (0.6)	88 (1.2)	0.7 (0.02)

*Values are volume weighted means with 1 SE given in parentheses.

[†] Estimated by differences in calculated charge balances.

TDN, total dissolved N.

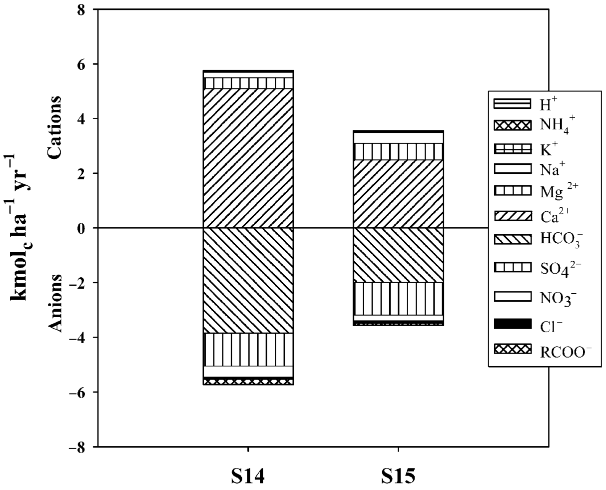

Fig. 8 Mean annual stream water flux of ions ($kmol\,ha^{-1}\,yr^{-1}$) from S14 and S15. Cation concentrations are represented as positive values while anion concentrations are represented as negative values. Flux of HCO_3^- was estimated by differences in calculated charge balances.

100 years after timber harvests and fire disturbances (Goodale & Aber, 2001). Similarly, soil C : N ratios in the Cone Pond watershed, NH, that experienced a fire 175 years ago, had higher C : N ratios compared with unburned watersheds in the same region (Hornbeck & Lawrence, 1997). Both of the latter two studies resulted in lower NO_3^- export in disturbed vs. undisturbed sites.

Historic land use has been very similar between S14 and S15 for the past two centuries (Gooden, Property Forester, Huntington Forest, personal communication). From 1815 to 1833, there was a farm (~ 18 h) located in both S14 and S15. Most of the area was used for pasture and a small amount of the surrounding forest was used for firewood. In 1977, there was a small commercial partial-cut of mostly hardwoods that covered approximately only 0.4 ha near the highest elevations of both S14 and S15. Because S14 and S15 have had relatively similar land use history and similar aged forest stands, differences in land use history cannot explain their marked differences in stream water chemistry.

Atmospheric deposition

Estimated total N deposition of S14 and S15 were nearly identical. Wet-only and dry annual deposition values were similar to those calculated for the entire Archer Creek Watershed from 1995 to 2000 by Park *et al.* (2003, Table 3) having values of 0.1, 0.2 and 0.2 $kmol\,ha^{-1}\,yr^{-1}$ NH_4^+ (wet-only), NO_3^- (wet-only) and NO_3^- (total dry), respectively (vs. values in the current study of 0.1, 0.2, 0.1 $kmol\,ha^{-1}\,yr^{-1}$ NH_4^+ (wet-only), NO_3^- (wet-only) and NO_3^- (total dry), respectively). Park *et al.* (2003) used data from NADP/NTN for wet-only deposition; dry deposition values were obtained from the Atmospheric Integrated Research and Monitoring Network (AIRMoN) of the National Oceanic and Atmospheric Administration (NOAA), which was also located at the Huntington Forest.

Cloud deposition can also contribute significantly to total N (wet and dry) deposition above 1000 m elevation in the Adirondacks (Miller *et al.*, 1993). There is no evidence that cloud deposition is an important contributor to total deposition as S14 and S15 have elevations much less than 1000 m. This is further supported by the IFS results that found no direct cloud inputs measured at another site in the Huntington Forest at an elevation similar (530 m) to S14 and S15 (Johnson & Lindberg, 1992).

It is not surprising that these two subcatchments had identical estimates of N inputs from atmospheric dry deposition. S14 and S15 were separated by less than 200 m, and both were dominated by a deciduous overstory. Although S15 had a higher percentage of conifers (21% for S15 vs. 4% for S14), this was not sufficient to cause a marked difference in dry or total N deposition. Furthermore, other features such as mean elevation and mean aspect were similar between the two subcatchments (Table 1) resulting in similar atmospheric deposition values (Weathers *et al.*, 2000). Another study in the Adirondacks that examined N input–output budgets for 52 lake-containing catchments found that only a small portion of the N drainage losses could be explained by differences in atmospheric deposition (Ito *et al.*, 2005). Other noted factors explaining NO_3^- loss included differences in landscape features such as elevation and percentage of wetlands; in-lake processes; and hydrologic flow paths. There was also no significant relationship between N deposition and NO_3^- leaching in ecosystem-scale NITREX (NITRogen saturation EXperiments) sites in Europe (Bredemeier *et al*., 1998; Gundersen *et al*., 1998b).

Soil and vegetation

There was little difference between S14 and S15 in leaf litter biomass (S14 having 3587 kg ha^{-1} and S15 having 3241 kg ha^{-1}) and tree basal area (Fig. 7). Due to differences in tree species composition as well as differences in nutrient availability, litter concentrations of Ca and N are likely greater in S14 vs. S15 while vegetation Ca and N uptake are likely similar between the subcatchments. Uptake could only explain 15% of the variation in NO_3^- leaching among sites while N mineralization alone could explain up to 44% across the 16 northeastern IFS sites (Johnson & Lindberg, 1992). Variation in mineralization is highly dependent on differences in the *quality* of litter (Melillo *et al*., 1982; Finzi *et al*., 1998b) and can be considered a more important factor controlling the variability of NO_3^- leaching than litter quantity (Mitchell *et al*., 1996; Emmett *et al*., 1998a, b; Finzi *et al*., 1998b; Gundersen *et al*., 1998b; Emmett, 1999; Lovett *et al*., 2000, 2002, 2004). For example, the NITREX sites in Europe that received variable N inputs responded differently depending on the internal N status of the ecosystem. N retention among sites varied considerably depending on the N content and rate of N cycling in the leaf litter and forest floor at the onset of increased N deposition (Emmett *et al*., 1998a; Gundersen *et al*., 1998b).

Variability of litter quality can be controlled by differences in tree species composition. The role of species is less important in Europe where most forests are managed stands of Norway spruce (*Picea abies*) (Bredemeier *et al*., 1998). However, nitrate export from 39 Catskill, NY US catchments was strongly associated with the soil C : N ratio, which was driven by differences in tree species composition among the catchments (Lovett *et al*., 2002, 2004). Many studies, conducted in North America, have suggested that species such as sugar maple, eastern hophornbeam, and white ash (*Fraxinus americana* L.) are associated with soil having low C : N ratios while soil under species such as red oak (*Quercus rubra* L.), American beech, and various conifers have higher C : N ratios in the litter (Pastor *et al*., 1984; Mitchell *et al*., 1992b; 2003; Finzi *et al*., 1998b; Lovett & Mitchell, 2004; Lovett *et al*., 2004). The relationship between vegetation and soil C : N ratios are likely driven by the ligni : N ratio (Lovett & Mitchell, 2004). Lower lignin : N ratios in soil often result in higher rates of net carbon mineralization (Melillo *et al*., 1982; Pastor & Post, 1986; McGee *et al*., 2005) that can result in lower C : N ratios. Lower C : N ratios and the higher rates of NO_3^- production (i.e. net nitrification) result in elevated NO_3^- leaching (Melillo *et al*., 1982; Gundersen *et al*., 1998a; Finzi *et al*., 1998b; Lovett & Rueth, 1999; Lovett *et al*., 2004).

Species such as sugar maple, eastern hophornbeam and white ash are associated with base-rich sites. Kolb & McCormick (1993) found liming increased exchangeable Ca^{2+} and Mg^{2+} in the upper soil horizons resulting in increases in survival, crown vigor, diameter and basal area growth of sugar maple in the Allegheny Plateau of north central Pennsylvania (US). American beech and black cherry (*Prunus serotina* Ehrh.) did not respond to liming. Further investigations within the Allegheny Plateau suggested declining sugar maple stands were located on unglaciated upper landscape positions where soils had very low exchangeable Ca^{2+} and Mg^{2+} (Bailey *et al*., 2004a). Sugar maple in northwestern Connecticut, US was most dominant on sites with moderate to high exchangeable cations such as Ca^{2+} and Mg^{2+} (shallow mineral soil) while soils associated with species such as beech, red oak and hemlock had much lower exchangeable Ca^{2+} and Mg^{2+} (Finzi *et al*., 1998a).

There are two explanations indicating why ‘base-rich indicator’ tree species (Burns and Honkala, 1990; Whitney & Decant, 2003; McGee *et al*., 2005) are found on sites with higher exchangeable base cations: (1) the vegetation affects site characteristics (Finzi *et al*., 1998a; Fujinuma *et al*., 2005) and/or (2) the site controls the colonization of tree species (Kobe *et al*., 1995; van Breemen *et al*., 1997; Walters & Reich, 1997). The latter explanation was supported by work done in stands of northwestern Connecticut suggesting that the variability in the distribution of tree species was governed by the distribution of Ca content in the parent material, with species such as white ash colonizing sites with high elemental and exchangeable base cation content (van Breemen *et al*., 1997). Support for the former explanation is twofold. First, there may be differences in the production of organic acids from decomposing litter among species that change the relative quantities of exchangeable base cations (Finzi *et al*., 1998b; Fujinuma *et al*., 2005). Higher organic acid production has been noted in species such as eastern hemlock, resulting in slower litter decomposition and the formation of a highly acidic forest floor. Low soil pH increases the solubility of Al and Fe, which displace base cations on soil exchange sites, resulting in base cation leaching. Second, there may be differences among species in base cation inputs to the forest floor, via canopy exchange in throughfall, resulting in differences in Ca^{2+} and Mg^{2+} uptake and allocation to biomass pools with varying turnover times (Finzi *et al.*, 1998b; Fujinuma *et al.*, 2005). Ca^{2+} and Mg^{2+} inputs in throughfall under sugar maple are higher than under species such as eastern hemlock resulting in a larger soil base cation pool under sugar maple vs. other species (Fujinuma *et al.*, 2005).

A definitive explanation for describing the distribution of tree species relative to exchangeable base cations in soils, however, remains unclear and may likely vary with tree species and site characteristics. However, recent studies have found that sites containing high exchangeable base cations, and therefore, species such as sugar maple, also have high rates of net nitrification and elevated NO_3^- leaching from the soil (Finzi *et al.*, 1998b; Lovett & Mitchell, 2004; McGee *et al.*, 2006). For example, in a study comparing four sites having similar foliar N storage pools but different stand ages and soil nutrient pools in the Adirondack Park of New York State, one old growth site (Ampersand) with predominantly base-rich indicator tree species (e.g. hophornbeam, basswood, and sugar maple) had soils with lower lignin : N ratios and higher soil solution Ca^{2+} and NO_3^- than the other sites with lower base cation availability (McGee *et al.*, 2006). Higher concentrations of available Ca^{2+} in soils are generally associated with higher soil pH. Numerous studies in both North America and Europe have reported a positive correlation between soil pH and both nitrification and leachable NO_3^- (Nyborg & Hoyt, 1978; Vitousek & Matson, 1985; Johnson *et al.*, 1994; Nilsson & Tyler, 1995; Geary & Driscoll, 1996; Simmons *et al.*, 1996; Watmough & Dillon, 2003a) although in some cases these relationships were confounded by other factors (Finzi *et al.*, 1998a; Lovett *et al.*, 2004).

Thus, the differences in S14 and S15 stream water base cations (particularly Ca^{2+}) and NO_3^- can be explained by the combined effects of the differences in vegetation and soil characteristics. A greater internal source of Ca in S14 resulted in much higher soil exchangeable Ca^{2+} (Table 4) and stream water Ca^{2+} export (Fig. 8). This high base status also resulted in the greater predominance of base-rich indicator species including sugar maple (Fig. 7) compared with S15. The greater production of NO_3^- in S14 was likely a function of the abundant sugar maple trees producing a forest floor with lower lignin : N, lower C : N and higher pH. Thus, there likely were higher net mineralization and nitrification rates resulting in a greater flux of stream water NO_3^- from S14 compared with S15. In contrast, S15 had a greater proportion of American beech. American beech litter has a lignin : N ratio and net nitrification rates similar to red oak (Finzi *et al.*, 1998b; Melillo *et al.*, 1982) and variation in abundance of beech may explain significantly lower stream water NO_3^- concentrations of catchments in which oak is not present. Furthermore, in sites examined across eastern North America, it was suggested that high NO_3^- leaching was observed in stands having 50% or greater sugar maple (Lovett & Mitchell, 2004). S14 had 50% sugar maple while S15 had only 29% (Fig. 7). In addition, Lovett *et al.* (2004) found that the forest floor under sugar maple with lower C : N ratios and 2–12 times higher extractable NO_3^- concentrations had two to six times higher net nitrification rates vs. forest floor under other species (such as American Beech, Hemlock, and Yellow Birch). In our study, S14 had over 10 times more extractable NO_3^- in the forest floor vs. S15 further suggesting S14 had higher nitrification rates vs. S15. Forest floor extractable NH_4^+ concentrations were also significantly greater in S14 vs. S15, notably three times higher during spring, further suggesting that net mineralization rates were greater in S14 vs. S15.

Summary conceptual model

A conceptual model considering the interaction between parent material, soil processes, vegetation and surface water chemistry illustrates the dominant factors controlling the variation in stream water NO_3^- and Ca^{2+} across sites with similar hydrology, land use and atmospheric deposition (Fig. 9). Mobilization of NO_3^- and Ca^{2+} is governed by the *quality* of the parent material and the litter. A site with parent material rich in Ca (e.g. S14) results in the formation of a soil with high exchangeable Ca^{2+} and the generation of calciphilic vegetation communities including tree species such as sugar maple, American basswood and eastern hophornbeam. The forest floor produced from this vegetation has lower lignin : N ratios likely resulting in higher net soil mineralization and nitrification and increased leaching of NO_3^- and associated cations including Ca^{2+}. Both high soil NO_3^- and Ca^{2+} concentrations and a species composition with higher requirements of this element result in greater amounts of fine-root uptake and NO_3^- and Ca cycling through the vegetation. In contrast, a site with lower amounts of Ca in the parent material (e.g. S15) has lower soil exchangeable Ca^{2+}. The forest vegetation has a different species composition and produces a forest floor that has biochemical characteristics (e.g. higher lignin:N ratios) less conducive to nitrification. The lower availability of Ca, as well as the forest vegetation contributes to lower rates of biotic Ca cycling. As a result, there is less leaching of NO_3^- and Ca^{2+}, less fine-root uptake of these solutes, and litter having a higher C : N ratio.

Negative feedback loop to the acidification process

Although both S14 and S15 leached varying amounts of Ca^{2+} and NO_3^-, these catchments both have received elevated fluxes of N and S deposition in the last four and a half decades (Driscoll *et al*., 2003c). Chronically high acidic deposition and subsequent acid leaching can increase base cation losses from soils above the inputs from soil weathering and atmospheric deposition (Miller *et al*., 1993; Kirchner & Lyderson, 1995; Likens *et al*., 1996; Friedland & Miller, 1999; Ouimet *et al*., 2001; Tomlinson, 2003; Watmough & Dillon, 2003a). Such losses of base cations, especially Ca^{2+}, have been reported in the Archer Creek Catchment (Mitchell *et al*., 2001; Watmough *et al*., 2005), as well as in other forested catchments located in the northeastern US (Likens *et al*., 1998; Fernandez *et al*., 2003), the Allegheny Plateau, US (Bailey *et al*., 1996), Canada (Johnson *et al*., 2000; Watmough & Dillon, 2003a–c), and Europe (Bredemeier *et al*., 1998; Watmough *et al*., 2005). A large percentage of the loss has been attributed to lower base cation deposition (Driscoll *et al*., 1989; Hedin *et al*., 1994; Likens *et al*., 1996) and/or a reduction of the cation exchangeable pool (soil calcium available for root uptake and leaching) (Kirchner & Lydersen, 1995; Likens *et al*., 1996; Lawrence *et al*., 1999; Watmough *et al*., 2005).

Declining plant-available calcium levels have been associated with a number of adverse effects on trees including perturbation of plant nutrition resulting in reduced growth and/or related secondary stresses such as diseases, insect defoliation, and freezing stress (Cronan & Grigal, 1995). Dieback has been observed particularly in species such as Norway and red spruce (Shortle *et al*., 1995; Boxman *et al*., 1998; DeHayes *et al*., 1999), as well as sugar maple (Kolb & McCormick, 1993; Houle *et al*., 1997; Horsley *et al*., 2000; Duchesne *et al*., 2002; Watmough, 2002; Bailey *et al*., 2004a). Increased dieback of tree species is of particular concern in North America (Bailey *et al*., 1996; Likens *et al*., 1996; Lawrence *et al*., 1997; Tomlinson, 2003; Watmough & Dillon, 2003a) because changes in nutrient status of sites may change species composition in natural forests (McNulty *et al*., 1996). Although further investigation is needed, our results suggest that at sites where a significantly large depletion of base cations occurs there could be a reduction of base-rich indicator species. Colonization of species such as American beech and red oak produce lower quality litter having less NO_3^- production. Thus, a shift in species composition toward American beech and red oak could result in a negative feedback to the acidification process. Such negative feedback loops would not necessarily be apparent in Europe where differences in tree composition are not

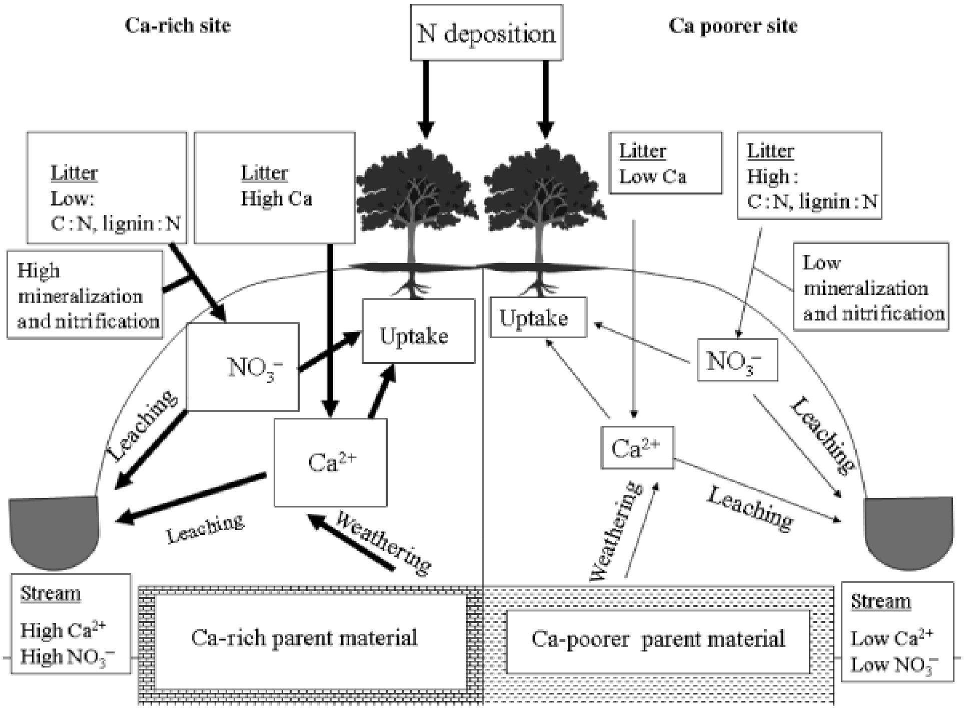

Fig. 9 Conceptual model indicating the dominant factors controlling the variation in stream water chemistry across sites with similar hydrology, atmospheric deposition and land use but varying parent material, vegetation and soil processes. Thicker arrows indicate relatively greater fluxes and larger boxes indicate relatively larger pools.

found because of the predominance of Norway spruce plantations.

Conclusions

The disparity in stream water Ca^{2+} and NO_3^-, concentrations and fluxes between S14 and S15 can be largely explained by differences in tree species composition, soil properties and their interactions. There was a marked difference in the soil Ca^{2+} concentrations in S14 vs. S15, which corresponded to the higher stream water Ca^{2+} and the larger contribution of sugar maple (and other species associated with base-rich sites such as American basswood and eastern hophornbeam) to the overstory biomass in S14. Soil under sugar maple is associated with higher net nitrification (Lovett *et al.*, 2004) and thus, would contribute to the higher NO_3^- concentrations in the drainage waters of S14 vs. S15 especially during the spring and summer seasons. We are currently in the process of further quantifying nitrification and N mineralization rates, as well as soil lignin : N and C : N ratios in these catchments to further corroborate our findings.

Our results suggest that tree species composition has a major influence on N cycling in these two subcatchments and thus, any alteration of the vegetation composition by changes in climate, soil chemistry or invasive species would likely alter nutrient cycling. For example, nutrient cation depletion by acidic deposition could result in the lowering of soil base status and possible dominance of species, such as American beech, that produce litter with lower net mineralization and NO_3^- production potential, resulting in a negative feedback loop to the soil acidification process. Disease may also alter tree species composition in forested ecosystems. Beech bark disease is altering size classes of American beech relative to sugar maple at a site within 2 km of the Archer Creek catchment (Forrester *et al.*, 2003) and the Asian long-horned beetle is attacking sugar maple in parts of New York and Illinois (Lovett & Mitchell, 2004). Clearly, future research investigating the effects of chronic N deposition on stream chemistry in ecosystems should account for possible changes in vegetation species composition and how vegetation composition is influenced by soil properties, as well as biotic and climatic changes. The role of spatial and temporal patterns of atmospheric pollutants and how these interactions are altered by abiotic and biotic ecosystem properties is clearly of high importance. Further studies are needed that evaluate how the interactions among climate, atmospheric pollutants and species composition affect biogeochemical processes. Such studies will be useful for predicting the impact of global change on forested watersheds over a range of spatial and temporal scales.

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