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Atmospheric deposition and watershed nitrogen export along an elevational gradient in the Catskill Mountains, New York

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Abstract. Cumulative effects of atmospheric N deposition may increase N export from watersheds and contribute to the acidification of surface waters, but natural factors (such as forest productivity and soil drainage) that affect forest N cycling can also control watershed N export. To identify factors that are related to stream-water export of N, elevational gradients in atmospheric deposition and natural processes were evaluated in a steep, first-order watershed in the Catskill Mountains of New York, from 1991 to 1994.

Atmospheric deposition of SO_4^{2-}, and probably N, increased with increasing elevation within this watershed. Stream-water concentrations of SO_4^{2-} increased with increasing elevation throughout the year, whereas stream-water concentrations of NO_3^- decreased with increasing elevation during the winter and spring snowmelt period, and showed no relation with elevation during the growing season or the fall. Annual export of N in stream water for the overall watershed equaled 12% to 17% of the total atmospheric input on the basis of two methods of estimation. This percentage decreased with increasing elevation, from about 25% in the lowest subwatershed to 7% in the highest subwatershed; a probable result of an upslope increase in the thickness of the surface organic horizon, attributable to an elevational gradient in temperature that slows decomposition rates at upper elevations. Balsam fir stands, more prevalent at upper elevations than lower elevations, may also affect the gradient of subwatershed N export by altering nitrification rates in the soil. Variations in climate and vegetation must be considered to determine how future trends in atmospheric deposition will effect watershed export of nitrogen.

Introduction

Throughout most of the United States, concentrations of SO_4^{2-} in wet deposition have decreased since the early 1970's in response to reductions in SO_2 emissions (NAPAP 1993, Baier & Cohn, 1993). Emissions of nitrogen oxides, however, have decreased by less than 5% during this period (NAPAP 1993), and concentrations of NO_3^- in wet deposition have shown little change (Baier & Cohn 1993). Consistent with these deposition trends, SO_4^{2-} concentrations in surface waters of eastern North America have decreased since 1980, and NO_3^- concentrations have shown no clear trends (Driscoll et al. 1995, Likens et al. 1996).

Release of N from forest ecosystems to surface waters is regulated by biological processes that can result in nearly complete retention of N inputs (Hornbeck et al. 1997). Sustained, elevated atmospheric inputs of N, however, can lead to leaching of NO_3^- through increased nitrification rates and associated production of nitric acid (Emmett et al. 1995). The capacity of a watershed to retain N is, therefore, a function of how much N has accumulated in the ecosystem, a property determined by atmospheric inputs as well as short- and long-term biological cycling processes. McNulty et al. (1991) and Lovett & Rueth (1999) observed positive correlations between wet deposition of N and forest-floor N concentrations in forests in the northeastern U.S.A., which suggested that atmospheric deposition had increased N content in soils of this region. Murdoch & Stoddard (1992) documented increasing concentrations of NO_3^- in stream water since about 1960, in the Catskill Mountains of New York, a region that receives some of the highest rates of N deposition in the northeastern United States (Ollinger et al. 1993).

An understanding of N mobility in soils is essential for predicting future trends in surface-water quality, but the complexity of forest-N cycling (including spatial heterogeneity) makes quantification of a watershed’s capacity to retain atmospheric N inputs highly uncertain (Aber et al. 1995). Nitric acid, whether deposited from the atmosphere or produced by nitrification, can cause (1) leaching of base cations, which can reduce soil base saturation (Lawrence et al. 1997), and (2) leaching of Al, which is harmful to aquatic communities (Havas & Rosseland 1995). Little or no reversal of surface-water acidification has been observed in Canada or the United States over the last 15 years, a response that has been attributed to soil base depletion (Couture 1995, Driscoll et al. 1995, Likens et al. 1996).

With passage of the 1990 Clean Air Act Amendments, SO_2 emissions have been projected to decrease 27% by 2000, and another 7% by 2010 (NAPAP 1993); trends in N oxide emissions, however, could either increase or decrease in the next decade, depending on judicial interpretations of the Clean Air Act Amendments. These projections warrant further study of how atmospheric deposition of N effects N retention in forest watersheds. The purpose of this paper is to present the results of an analysis of the association between atmospheric N deposition and watershed N retention in a study of a first-order watershed in the Neversink River Basin, in the Catskill Mountains of New York. In this analysis, elevational gradients of atmospheric deposition and natural processes are used to identify factors that are related to watershed N export in stream water.

Methods

Site description

The study was conducted in Winnisook watershed (elevation 817 m to 1275 m, drainage area 205 ha), drained by a chronically acidic, first-order tributary of the West Branch Neversink River, in the Catskill Mountains of southeastern New York State. The bedrock consists of quartz-dominated sandstone, shale and siltstone overlain by intermittent layers of stones, boulders and till. Soils are Inceptisols with a mineral layer that ranges from 0 to 75 cm thick. The watershed is completely forested with sugar maple (*Acer saccharum* Marsh), yellow birch, (*Betula alleghaniensis* Britton), American beech (*Fagus grandifolia* Ehrh.), and stands of balsam fir (*Abies balsamea* (L.) Miller), which are most common near the ridgetops (Figure 1). The forest was selectively harvested up to an elevation of about 900 m before about 1950, but we found no physical or historical evidence that the forest was ever cleared or extensively burned (Kudish 1985). At the base of the watershed, mean annual air temperature is 4.3 °C, and average precipitation is 175 cm yr^{-1}, of which 23% falls as snow. Additional details of Winnisook watershed and the Neversink Basin are given in Lawrence et al. (1995a).

Data collection and analysis

Throughfall and bulk deposition

Throughfall was measured along an elevational gradient in Winnisook watershed at 14 stations located at ~50 m elevational intervals from 799 m to 1234 m, near the summit of Slide Mountain, from June 1993 through May 1995 (Figure 1) to obtain estimates of acidic deposition (Lovett et al. 1999). Our throughfall transect was restricted to the northwest facing slope of the watershed. Although we do not have throughfall measurements elsewhere, we have no information to indicate that the elevational patterns of deposition would be substantially different on the other half of the watershed, which has a southwest-facing slope. During June through September, throughfall at each station was collected by four 20-cm diameter funnels which drained through polyester filters and opaque tubing into 4 L polyethylene bottles partially buried in the ground. Each week, throughfall was collected, collectors were rinsed with deionized water, and the polyester filters were replaced.

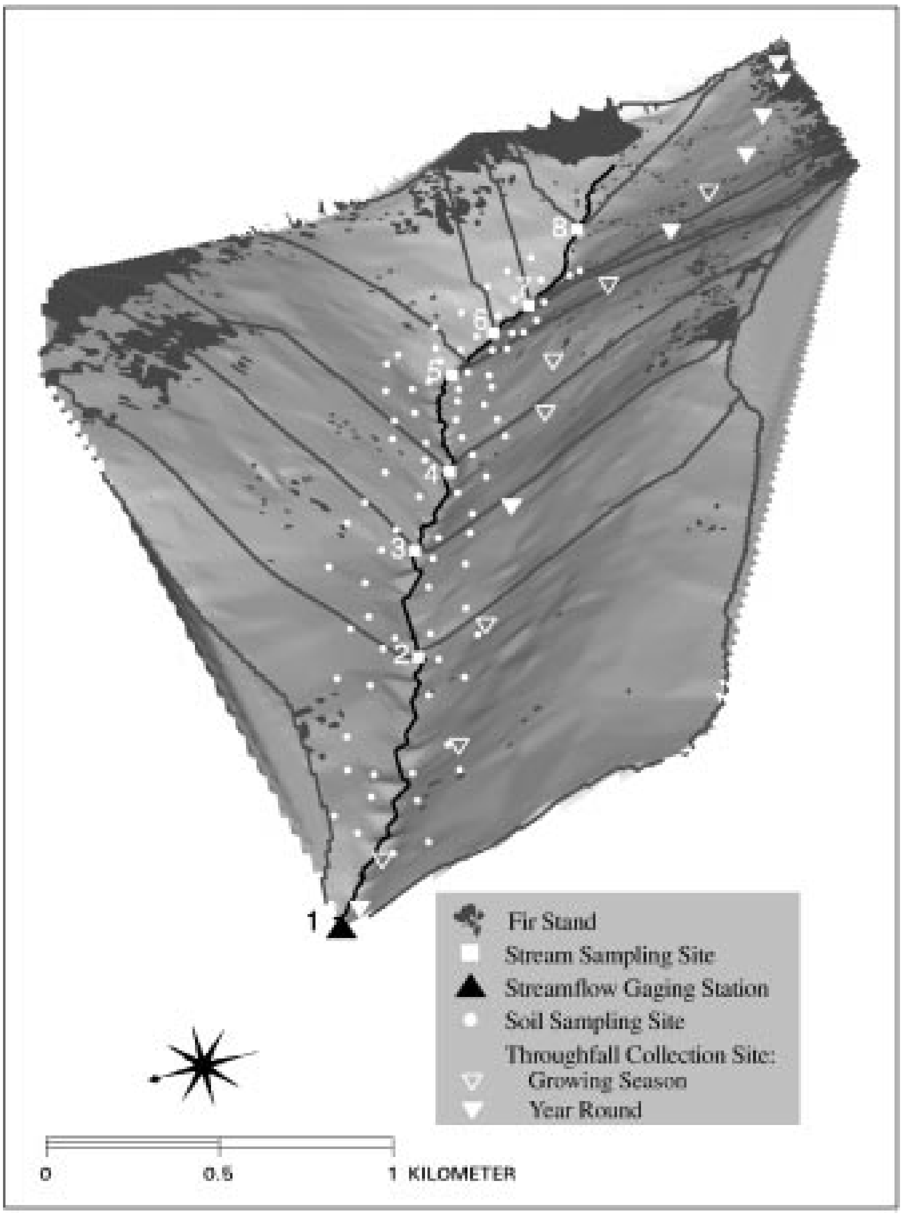

Figure 1. Three-dimensional analytically hillshaded view of Winnisook watershed. This perspective was generated with a light source at 280° from the north and 30° from the horizon. The vertical axis is exaggerated by a factor of 1.5. Subwatershed areas defined by stream sampling sites are delineated.

Table 1. Base elevation, drainage area, area of conifer stands, mean topographic index (ln(a/tanb); a = upslope drainage area, tanb = local slope), and nitrogen retention in percent ((input-output)input^{-1}), calculated from nominal and modeled deposition, for each subwatershed in Winnisook watershed.

Subwatershed	Base Elevation (m)	Drainage Area (ha)	Area of Conifer Stands (%)	Topographic Index	Nitrogen Retention	
					Nominal	Modeled
1	817	41.0	0.8	6.02	72	75
2	878	32.5	9.4	6.10	83	86
3	902	27.8	12.2	6.03	74	80
4	926	36.5	9.0	5.94	89	92
5	968	17.1	7.1	5.76	85	89
6	993	13.5	15.5	5.77	98	98
7	1010	28.5	13.1	5.97	87	92
8	1065	8.2	27.1	5.54	89	93

During October through May, each funnel collector was replaced by a 1.3-m high section of 20-cm diameter galvanized steel stovepipe lined with a polyethylene bag to facilitate collection of snow and ice. Only 7 of the 14 sites (Figure 1) were sampled in October through May because snow limited accessibility. Collections were made approximately biweekly. Sampling procedures were the same as for the June through September collections.

Bulk deposition was collected by two funnel collectors at one station in a clearing at 1164 m during the growing season, and by two lined stovepipe collectors during the nongrowing season. Samples from the two collectors were proportionally combined before analysis.

Water volume collected by the throughfall and bulk collectors was measured on site, and a subsamples from each station were saved for chemical analysis. Samples were preserved with 2 drops of chloroform per 60 ml of sample and stored in the dark until chemical analysis was completed. An ion chromatograph was used for analysis of SO_4^{2-} and NO_3^-; NH_4^+ was measured by the indophenol blue method (described in Lawrence et al. 1995a) on an Alpkem autoanalyzer. Total dissolved N was measured by persulfate digestion (Solarzano & Sharp 1980) by the method described in EPA (1987). Dissolved organic N was estimated by subtracting NO_3^- and NH_4^+ concentrations from total dissolved N concentrations.

Stream water sampling and chemical analysis

Stream-water samples were collected approximately weekly from June 1991 through May 1995 (a total of 242 samples) at the base of Winnisook watershed (site 1 in Figure 1), and biweekly to monthly at seven upstream sites (Figure 1; Table 1), from June 1991 through December 1994 (50–55 samples at each site). Additional samples were occasionally collected at all eight sites during periods of high flows (8 to 20 samples per site). All inorganic chemical analyses of stream samples were done according to Lawrence et al. (1995b). Total dissolved N and dissolved organic N concentrations were determined through persulfate digestion by the same procedure used for throughfall samples.

Streamflow measurements

Streamflow was monitored at site 1 (Figure 1) throughout the study with an automatic recording stream-gaging station, in accordance to U.S.Geological Survey methods (Rantz et al. 1982). Flow meters were also used on nine dates to determine flow at each of the eight stream-water sampling sites. On these nine dates, flow ranged from 14 L $\sec^{-1}$ to 708 L $\sec^{-1}$ at the base of the watershed. The maximum flow measured at the base of the watershed with the flow meter was exceeded by average daily flows determined by the stage recorder only seven times from April 1991 through September 1995, indicating that the flow-meter estimates encompassed most of the upper range in flow that occurs in this watershed. The flow measurements at each stream-water sampling site were related to the monitored flow at site 1 (as calculated from stage measurements at the stream gage on the same date and time) by linear regression; R^2 values for these seven relations ranged from 0.96 to 0.99 ($P < 0.001$). These highly correlated relations allowed estimation of flow for any date and time at the seven sampling sites upstream from the gage.

Soil sampling

To characterize soil chemistry, 81 soil sampling sites were located longitudinally along the stream channel (Figure 1). Sampling locations along the stream channel were selected because these soils were assumed to be the most likely to affect stream chemistry. Subsurface water moving down the hillslope passes through these soils before discharging into the stream. At some locations, there was insufficient soil development for sampling. All samples were collected in hardwood stands, and Oa-horizon thickness was recorded at each sampling location. These samples were analyzed for total N and organic carbon content by the methods in Huntington et al. (1988). Bulk density of the forest floor was estimated by the model of Federer et al. (1993), which requires measurements of loss-on-ignition. In this study, loss-on-ignition was not measured, but the assumption was made that percent loss-on-ignition equaled twice the percent carbon (Federer, 1982). Net nitrification rates were measured in the organic soils under single-species stands of four major tree species by a buried-bag method (Eno 1960) in July 1993. Samples of forest floor (Oe and Oa horizons) were incubated *in situ* in gas-permeable polyethylene bags for 28 days (4 samples in each of 2 stands per species); samples collected before and after incubation were extracted with 2M KCl and analyzed for NO_3^- concentrations. Soils beneath American beech, sugar maple and yellow birch were compared at 790 m elevation, and balsam fir and yellow birch were compared at 1085 m elevation.

Calculations with spatially distributed data

A data base of digital hypsography was developed by scanning, editing, and coding topographic contours from USGS 1:24,000 Topographic Quadrangle maps. A Triangular Irregular Network (TIN) was developed to generate a topographic surface of Winnisook watershed. This surface was then sampled at 5 m intervals to produce a topographic grid of 25 m^2 cells. The boundaries of Winnisook watershed and interior subwatersheds were delineated according to the direction of flow from each cell, and the resulting flow-accumulation pathways. Regions where fir trees predominate were delineated by digitizing an aerial photograph. The areal percentage of fir vegetation was then calculated for each subwatershed.

A topographic index value (ln(a/tanb)) was calculated for each cell from the flow-accumulation grid (a = the upslope area contributing flow to cell, determined by surface topography) and the slope grid (b is the slope angle of the cell) to indicate the relative tendency of soil within each cell to become saturated; the higher the value of this index, the greater tendency for saturation. The distribution of topographic index values over a watershed can be used to identify areas where soils will be wet relative to other areas in a watershed. A watershed with well-drained soils will typically have cells with the highest index values in close proximity to stream channels, whereas watersheds with areas of poorly drained soils will have cells with high index values that appear in irregularly shaped polygons that extend away from defined stream channels.

Nitrogen budget calculations

Atmospheric deposition

We estimated atmospheric deposition of N to the watershed through our measurements of bulk deposition and throughfall, and dry deposition data available from an E.P.A. Clean Air Status and Trends Network (CAST-Net) monitoring station, located less than 10 km from Winnisook watershed

(720 m elevation). Because the CASTNet site did not operate prior to 1994, we used data from January 1994 through December 1995. The CASTNet network measures atmospheric concentrations of HNO_3 vapor and fine-particle NH_4^+ and NO_3^-, using a filterpack collected weekly. Atmospheric concentrations are converted to deposition rates by application of deposition velocities derived from a widely-used “big-leaf” model (Clarke et al. 1996). The model is parameterized with site-specific meteorological and canopy measurements, however, the estimates of dry deposition from the model must be considered approximate because the model assumes homogeneous canopies and flat terrain, clearly not the case in our watershed. Nonetheless, this approach is the most widely used method for measuring total N deposition to forests, and has been frequently applied in similar settings (Lovett & Lindberg 1993).

Estimating atmospheric deposition in mountainous terrain is a difficult problem (Lovett & Kinsman 1990, Lovett et al. 1999). Because we were unable to measure total atmospheric N deposition directly, we used two estimation methods that are likely to bracket the actual total N deposition in this watershed. The first method, referred to henceforth as the nominal deposition, is based on the assumption that deposition does not vary spatially within the watershed. The second method, referred to henceforth as the modeled deposition, is based on the assumption that N deposition increases with increasing elevation in direct proportion to the elevational increase in S deposition, which was measured directly by throughfall collection. Details of the two methods follow.

Nominal Deposition. The nominal N deposition was estimated by summing the average annual bulk deposition measured at our 1164 m site (548 mol N $ha^{-1}yr^{-1}$; 39% as NH_4^+, 61% as NO_3^-) plus the average annual dry deposition for the CASTNet site (361 mol N $ha^{-1}yr^{-1}$, of which 90% is attributed to HNO_3 vapor). The mean HNO_3 vapor concentration for the site was 2.68 μg m^{-3}. Dissolved organic N concentrations were about 3% of the total N measured in bulk deposition, and are not included in the nominal deposition estimate. The nominal deposition for the watershed estimated by this method was thus 909 mol $ha^{-1}yr^{-1}$. Cloud-water deposition may also contribute some N to this watershed, but cloud immersion is infrequent (we estimate $<$10% of the time based on visual observations) and generally limited to the area over 1000 m elevation (Lovett et al. 1999). Nevertheless, inclusion of cloud deposition would have increased the nominal deposition estimate somewhat. The nominal deposition estimate also did not include an elevational increase in dry deposition, which has recently been identified in this watershed (Lovett et al. 1999). Because cloud deposition and the dry deposition gradient are not accounted for in the nominal deposition estimate, this value probably underestimates the actual total N deposition for the overall watershed.

Modeled Deposition. To account for spatial variability in our measurements, we relied on data from the array of throughfall collectors. Throughfall measurements in Winnisook watershed showed that N deposition was not statistically related to elevation either during the growing season or annually ($P > 0.10$), but a distinct upslope increase in SO_4^{2-} deposition was measured for both of these periods (Lovett et al. in 1999). Deposition of SO_4^{2-} in throughfall has been determined to be a reliable estimate of total sulfur deposition (Lindberg & Garten 1988, Lindberg & Lovett 1992, Lawrence & Fernandez 1993, Lovett et al. 1999), but uptake and release of N by forest canopies precludes the use of throughfall to estimate total N deposition. Spruce and fir canopies are particularly efficient at retaining N (Lovett & Lindberg 1993), which suggests that canopy retention of N may increase with elevation in Winnisook watershed (Figure 1).

Although we were unable to directly measure spatial patterns of total N deposition, evidence from other studies suggests that atmospheric deposition of S and N are likely to covary in Winnisook watershed because the sources, transport and deposition mechanisms for S and N tend to be very similar in this region. Wet deposition of inorganic N (NO_3^- and NH_4^+) is positively correlated with wet deposition of SO_4^{2-} ($P < 0.001$; $R^2 = 0.73$) for 8 NADP (National Atmospheric Deposition Program) stations in New York plus the 3 stations in southern Vermont, northeastern Pennsylvania and western Massachusetts (data available at http://nadp.sws.uiuc.edu.). Furthermore, the processes that cause wet, dry and cloud-water deposition to increase with elevation have been shown to apply equally well to N and S in other studies (Lovett & Kinsman 1990). Estimates of deposition made through measurements of air concentrations and modeled deposition velocities at Whiteface Mountain, N.Y., showed an increase with increasing elevation for NO_3^- plus NH_4^+ ($R^2 = 0.90$), and SO_4^{2-} ($R^2 = 0.88$) (Miller et al. 1993). The deposition of N and S were also found to vary almost identically ($R^2 = 0.999$) over elevations that ranged from 600 to 1350 m, in the study of Miller et al. (1993).

Therefore, we used the elevational pattern of SO_4^{2-} deposition to estimate total N deposition in the watershed. We assumed that NO_3^- and NH_4^+ deposition in Winnisook watershed was likely to increase with elevation in direct proportion to the measured increase in SO_4^{2-}deposition in throughfall. In this approach, we calculated the ratio of throughfall deposition of SO_4^{2-} at each elevation to the nominal deposition of SO_4^{2-} for the watershed (302 mol SO_4^{2-} $ha^{-1}yr^{-1}$ measured by the bulk deposition collector at 1164 m plus 100 mol

SO_4^{2-} $ha^{-1}yr^{-1}$ dry deposition from the CASTNet data). We then regressed these throughfall:nominal ratios vs elevation to determine an equation for the elevational increase in relative SO_4^{2-} deposition for the 7 throughfall sites that were collected throughout the year. The regression equation is

$$D_i/D_n = 0.002379(\text{elevation}) - 1.121825 \qquad (1)$$
$$(adj.r^2 = 0.63, P = 0.02, n = 7)$$

where D_i is the throughfall SO_4^{2-} flux at a given elevation, D_n is the nominal deposition, and elevation is in m.

We then used equation (1) to estimate total N deposition for each cell in the GIS layer based on the cell's elevation and the nominal deposition of N (909 mol $ha^{-1}yr^{-1}$). Subwatersheds were then delineated on the basis of the eight stream sampling sites, and deposition values for the individual cells were summed to provide deposition estimates for each subwatershed. Throughfall deposition was measured for 2 years (June 1993–May 1995); the data are reported as annual averages.

The difference between annual SO_4^{2-} deposition measured at the 7 year-round stations and values calculated from equation 1 ranged from +18.6% to –25.0% (mean difference –2.6%). Throughfall fluxes at the 14 growing-season stations yielded a regression model ($D_i\ D_n^{-1}$ = 0.00247elev – 1.1848; adj. r^2 = 0.63; $P < 0.001$) similar to that based on data from the annual 7 year-round stations.

Stream water export

Estimation of net N export in stream water for each subwatershed (determined by subtracting the value determined at the upstream site from that determined at the immediate downstream site) entailed the development of relations between measured NO_3^- concentrations and instantaneous flows for the dates and times that stream samples were collected. Seasonal variability in these relations was accounted for by developing concentration-discharge relations for the snowmelt period (March 1 to April 30), summer (May 1 to September 30), fall (October 1 to December 15) and winter (December 16 to February 28). If no relation was found for a particular season at an individual site, the mean NO_3^- concentration was assigned for each day of that season. Export of N in stream water was determined from NO_3^- concentrations; therefore, total N loss in stream water was somewhat underestimated because dissolved organic N and NH_4^+ were not included. In a subset of samples collected at site 1, over the entire stream-sampling period, dissolved organic N (91 samples) plus NH_4^+ (233 samples) represented 10–15% of total N in stream water. No seasonal trends were apparent in DON or NH_4^+ concentrations. The concentration-discharge relations and mean daily flows were then

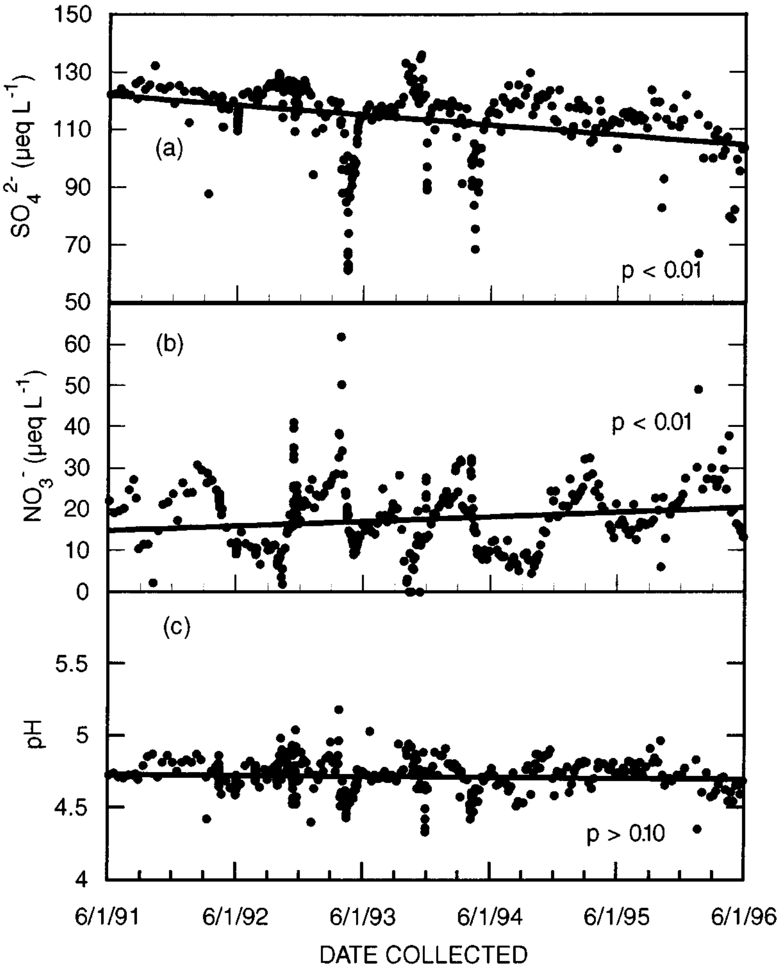

Figure 2. Concentrations of SO_4^{2-} and NO_3^-, and pH, in stream water at the base (site 1) of Winnisook watershed, 1991–96. Statisical significance of trends was determined from Kendall Tau.

used to calculate daily NO_3^- export in stream water for each subwatershed. (For this calculation, the assumption was made that the relations between instantaneous gage-recorded flow and metered flow at upstream sites would not change if mean daily flow measurements were substituted for instantaneous flow measurements). The resulting daily NO_3^- fluxes were summed to yield annual fluxes. As with the atmospheric deposition estimates, this analysis was done for two years (June 1993 through May 1995); data are reported as annual averages.

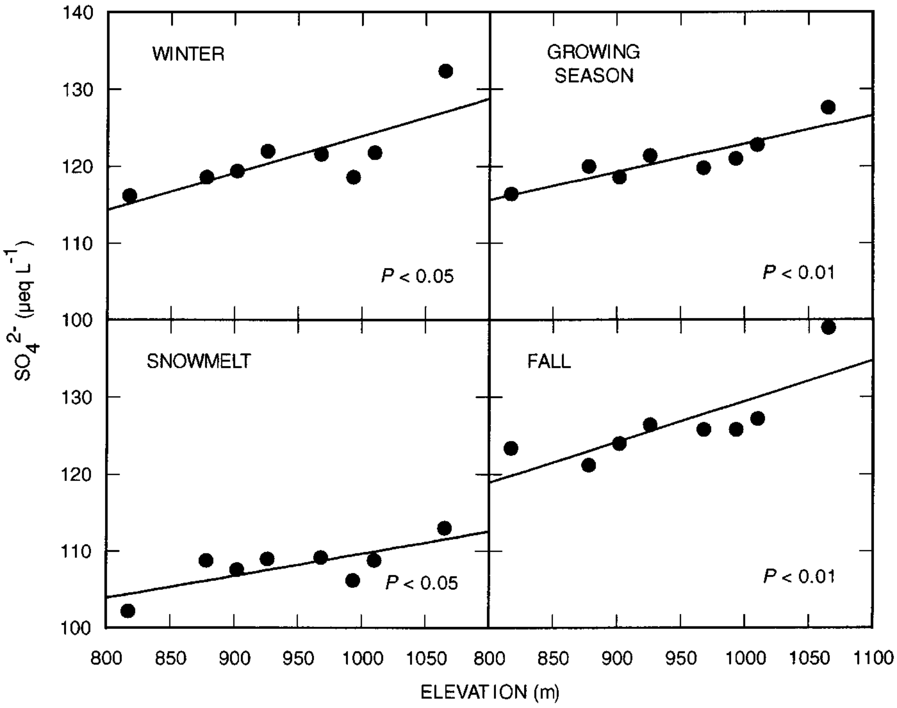

Figure 3. Seasonal mean concentrations of SO_4^{2-} in stream water along an elevational gradient in Winnisook watershed. Data represent a four-year sampling period. Winter is December 16 to February 28; snowmelt is March 1 to April 30; the growing season is May 1 to September 30; fall is October 1 to December 15.

Results

Stream water

Concentrations of SO_4^{2-} in stream water at site 1 decreased at a rate of 3.4 μeq $L^{-1}yr^{-1}$ from 1991 through 1996, whereas NO_3^- concentrations increased at a rate of 1.0 μeq L^{-1} yr^{-1} and pH showed no trend (Figure 2). Both pH and SO_4^{2-} concentrations were negatively correlated with flow ($P < 0.01$) throughout the year at this site. Concentrations of NO_3^-, however, were negatively correlated with flow during the summer ($P < 0.01$), positively correlated during the fall ($P < 0.01$) and unrelated to flow during the winter ($P > 0.1$). During snowmelt, NO_3^- concentrations were negatively correlated with flows less than 450 L sec^{-1} ($P < 0.01$), but unrelated to flows above this level ($P >$ 0.1). Concentration-discharge relations at the seven upstream sampling sites were generally similar to those at site 1, although no correlation was observed for about one third of these relations.

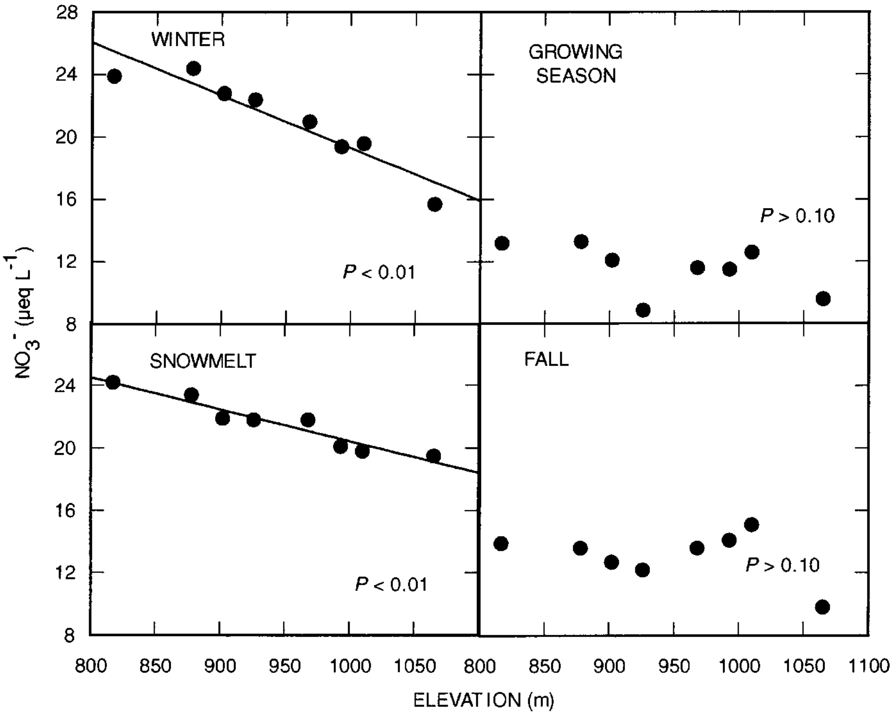

Figure 4. Seasonal mean concentrations of NO_3^- in stream water along an elevational gradient in Winnisook watershed. Data represent a four-year sampling period. Winter is December 16 to February 28; snowmelt is March 1 to April 30; the growing season is May 1 to September 30; fall is October 1 to December 15.

Seasonal mean concentrations of SO_4^{2-} decreased with decreasing elevation throughout the year; concentrations were lowest during snowmelt, and were similar in the fall, winter and summer seasons (Figure 3). In contrast, seasonal mean NO_3^- concentrations increased with decreasing elevation during the winter and snowmelt seasons, but showed no consistent spatial trends during the summer and fall (Figure 4). The lowest NO_3^- concentrations occurred during the growing season, and highest concentrations occurred during winter or spring snowmelt (Figure 4). At all sites, seasonal mean concentrations of NO_3^- were equal to or greater than 16 μmol L^{-1} during the winter and snowmelt period, but less than 16 μmol L^{-1} during the summer and fall (Figure 4).

Vegetation and soils

Prevalence of fir stands, relative to hardwood stands (expressed as a percentage of areal coverage), was greatest in subwatershed 8, least in subwatershed

1, and similar among the remaining subwatersheds (Figure 1; Table 1). A statistically significant relation was observed between the areal extent (as percent) of conifer stands in each subwatershed and elevation ($P < 0.01$; adj. $R^2 = 0.67$). The prevalence of conifer stands at upper elevations may have increased atmospheric deposition in this part of the watershed relative to areas of hardwood stands (Lovett et al. 1999). Net nitrification rates in soils were higher in hardwood stands than fir stands, and the rates in yellow birch stands were higher at low elevations than high elevations (Figure 5). The concentration of total N was not related to elevation ($P > 0.05$) in either the Oa or the mineral soil horizon of hardwood stands, but the thickness of the Oa horizon increased with increasing elevation ($P < 0.01$), as did the total N content of this horizon (Figure 6). The spatial distribution of the topographic index (ln(a/tanb)) showed that soils most likely to become saturated were near the primary stream channel or along narrow tributary flowpaths (Figure 7), which indicates that soils throughout the watershed are well drained. Index values, if averaged for each subwatershed, decrease with increasing elevation ($P < 0.05$; $R^2 = 0.64$), a suggestion that residence time of subsurface water decreases with increasing elevation.

Nitrogen fluxes and pools

Atmospheric deposition of N was estimated to be 909 mol ha-1 yr^{-1} by the nominal method. The modeled deposition increased from 1013 mol ha-1 yr^{-1} in the lowest subwatershed to 1430 mol ha-1 yr^{-1} in the highest subwatershed, and averaged 1226 mol ha-1 yr^{-1} for the watershed as a whole (Figure 8). Export of N in stream water decreased with increasing elevation ($P < 0.05$; $R^2 = 0.55$; Figure 8), which resulted in an increase in N retention with increasing elevation. Retention of N in the eight subwatersheds ranged from 72% to 98% if calculated with the nominal N input, and 75% to 98% if calculated with modeled N inputs (Table 1). Inclusion of dissolved organic N export in stream water would have decreased these retention estimates by less than 3 percent. Export of N in stream water for the overall watershed was 150 mol ha^{-1} yr^{-1}, which represented 17% of the nominal N input or 12% of the modeled N input, and N stored within the Oa horizon was 93,300 mol ha^{-1}.

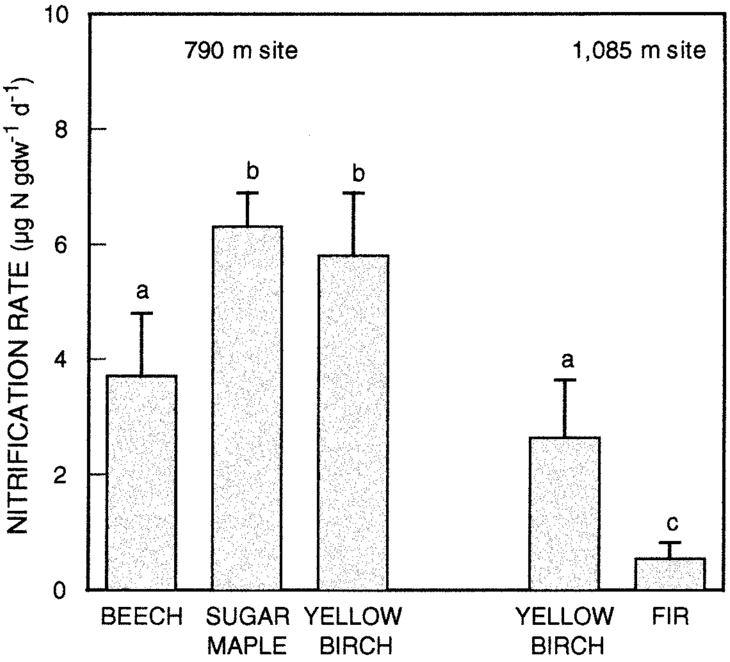

Figure 5. Mean rates of net nitrification under single-species stands of beech, sugar maple, and yellow birch, at 790 m elevation, and under yellow birch and balsam fir at 1085 m elevation. Vertical bars are standard errors. Within an elevation group, different letters indicate statistical differences at $P < 0.05$. The yellow birch values also differed significantly between elevations.

Discussion

Controls of watershed nitrogen export

Year-round similarity between the elevational patterns of SO_4^{2-} deposition and stream-water concentrations suggests that export of SO_4^{2-} is closely tied to atmospheric inputs. This finding is consistent with other research in the Catskill Mountains that has linked decreases in SO_4^{2-} concentrations in stream water over the past 2 decades to decreases in S deposition (Lawrence et al. 1999). In marked contrast, annual N export from these watersheds decreases with elevation, which corresponds to neither the nominal N deposition estimate (constant with elevation) nor the modeled N estimate, for which N deposition increases with elevation. Our data indicate that retention of N increases with elevation within this watershed regardless of which deposition estimate is used.

Greater N retention at high elevations than at low elevations is probably related to the increasing thickness of the Oa horizon with increasing eleva-

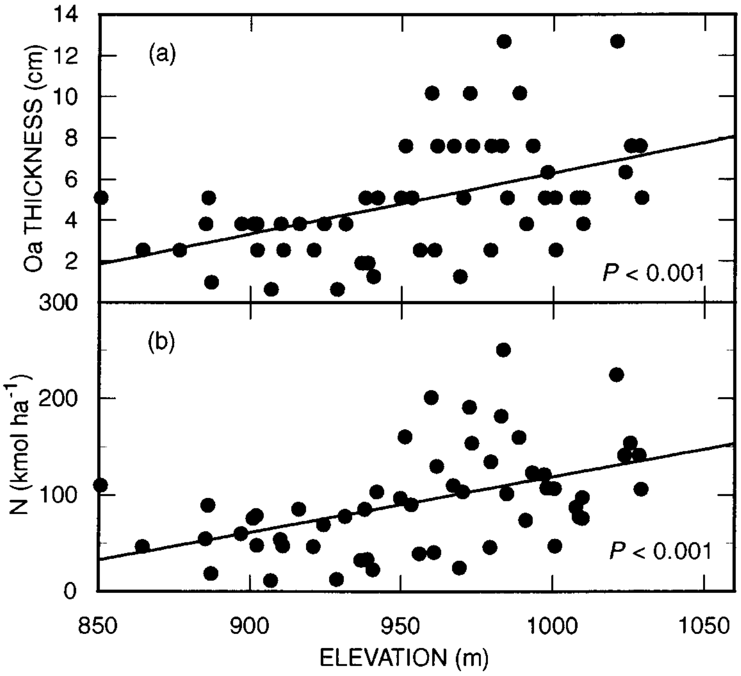

Figure 6. Thickness and total nitrogen content of Oa horizons along an elevational gradient in Winnisook watershed.

tion. This trend in Oa-horizon thickness can be attributed to a gradient in decomposition rates that results from an elevational temperature gradient. It should be noted that the soil sampling design did not include areas of the watershed with fir stands, where the forest floor is probably thicker than in hardwood stands. Because these areas tended to be at upper elevations near the ridgetops (Figure 1), a stronger upslope gradient in N retention might have been measured if sampling locations were selected randomly. Decomposition rates are likely to be lowest at the highest elevations, where soil temperatures are also lowest. This interpretation is supported by a climatic gradient study in Maine, where forest-floor thickness and carbon storage at colder northern sites were greater than at warmer, southern sites with similar soils and vegetation (Simmons et al. 1996). Average N content of the Oa horizon in Winnisook watershed was 93.3 kmol N ha^{-1}, somewhat higher than the value of 62.1 measured at the Hubbard Brook Experimental Forest, N.H. (Huntington et al. 1988).

The gradient of Oa horizon N content shown in Figure 6 was not a result of the spatial distribution of conifer and hardwood stands, because all of the soil sampling sites were in stands of mixed hardwoods. A lower net nitrific-

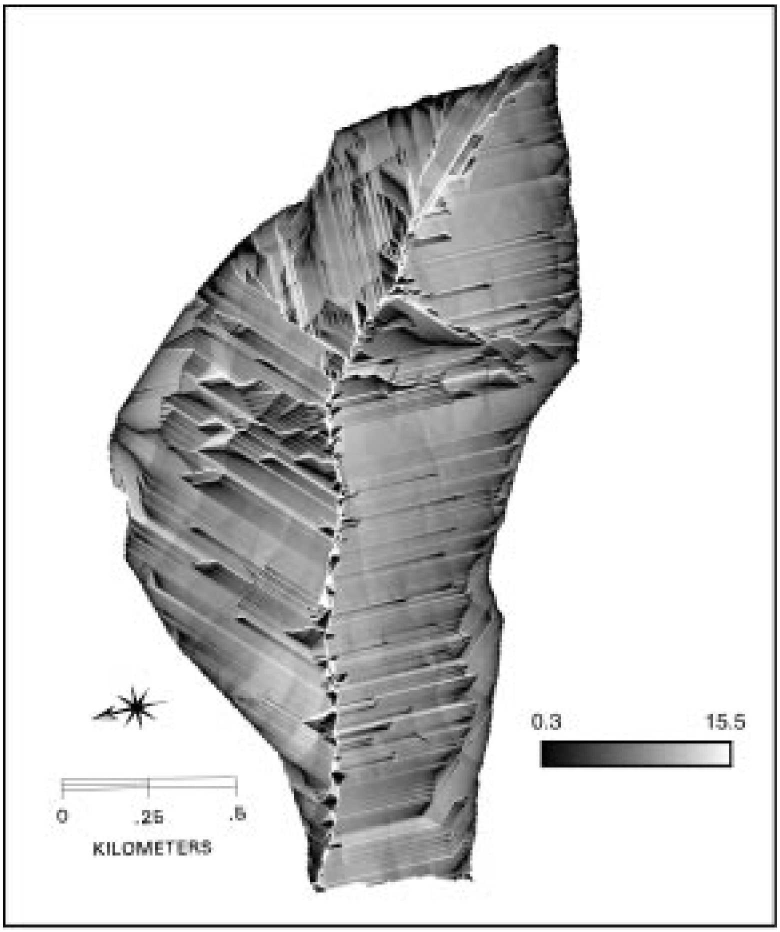

Figure 7. Distribution of topographic index (ln(a/tanb)) values for 5 m^2 grid cells in Winnisook watershed, shown in two dimensions. Darkest shading indicates least tendency for soils to become saturated. The linear patterns and lack of lightly shaded polygons indicates well drained soils throughout the watershed.

ation rate in yellow birch stands at upper elevations than at lower elevations, however, suggests that an elevational gradient in nitrification may have contributed to the spatial pattern of watershed N export. Even though balsam fir stands may not affect the soil measurements, the increasing importance of these stands at upper elevations may have affected stream-water export of N. Balsam fir trees are also commonly found in the understory of hardwood stands in this watershed, suggesting that the influence of this tree species may be increasing. Beech trees in this watershed, by contrast, are in decline from beech bark disease (*Nectria* sp.) transmitted by an introduced insect

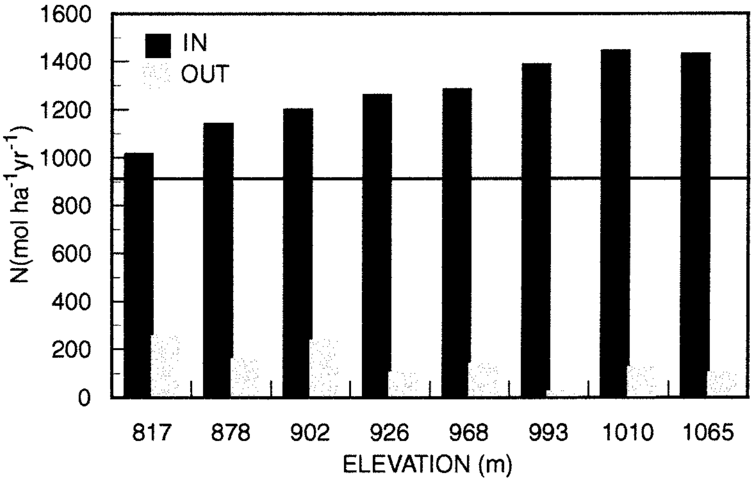

Figure 8. Atmospheric inputs (in) and watershed export of nitrogen in stream water (out) for 8 individual subwatersheds in Winnisook watershed. The horizontal line is the nominal deposition value of 909 mol ha^{-1}yr^{-1}. Values are the averages of 2 years.

(*Cryptococcus fagisuga* Lindinger) (Houston 1994). The combined effect of these changing vegetation patterns on watershed N export is unknown.

Aquic soils, which (1) promote denitrification and (2) enhance N retention through slowed decomposition, may also affect watershed export of N. An increase in either of these processes with increasing elevation could explain decreased N export in stream water in the upper subwatersheds. The topographic index values, however, give no indication of an elevational trend in hydrologic convergence areas that would result in aquic soils. This conclusion is supported by field reconnaisance and mapping by the Natural Resources Conservation Service (formerly the Soil Conservation Service; Tornes 1979). The deeply incised stream channel in this watershed also minimizes the extent of perennially wet riparian soils adjacent to the stream. Thus, the effect of aquic soils on N cycling in this watershed is probably limited to the few areas where ground water discharges at slope breaks near the main channel before becoming channelized overland flow.

Watershed nitrogen export and stream-water acidification

In Winnisook watershed, the elevational gradient of stream-water NO_3^- concentrations did not correspond spatially to atmospheric N deposition, even during the snowmelt period, when soil-water flux is at the annual maximum. In another recent study conducted in the Neversink River Basin, Murdoch et al. (1998) found that annual mean NO_3^- concentrations in stream water were unrelated to annual atmospheric deposition of NO_3^-, but positively correlated with air temperature. The positive relationship between NO_3^- concentrations in stream water and air temperature was probably related to a positive correlation between net nitrification rates and soil temperature, also observed by Murdoch et al. (1998). Results of Boutin & Robitaille (1995) and Mitchell et al. (1996) indicate that extremely low temperatures that freeze soils can enhance N release to surface waters as well. Analyses of ^{15}N and ^{18}O of NO_3^- in stream water, soil water, and snowmelt provided additional evidence that atmospherically deposited N is cycled within forest ecosystems of the Neversink River Basin before entering the stream (Kendall et al. 1995). Lovett et al. (in press) found over a 20-fold variation NO_3^-concentrations in streams draining forested watersheds throughout the Catskills, and concluded that variations were related to differences in vegetation and land-use history among the watersheds, rather than differences in atmospheric N deposition. Further evidence of internal control of NO_3^- release to surface waters was observed in Bear Brook watershed, Maine, where addition of $(^{15}NH_4)_2SO_4$ increased concentrations of $^{14}NO_3^-$ in stream water, but the added ^{15}N was retained within the watershed (Norton et al. 1994).

Our analysis did not reveal a direct effect of atmospheric deposition on NO_3^- concentrations in stream water. This finding is in contrast to results of Johnson et al. (1992) and Dise & Wright (1995), which showed positive correlations between N export from forests and atmospheric inputs of N at sites with high rates of N deposition. The decrease in N export with increasing elevation in Winnisook watershed is also in contrast to the generalization of Fenn et al. (1998), that N export tends to be greater at higher elevations than lower elevations.

The seemingly inconsistent findings of these studies may be, in part, related to differences in the amounts of N deposited from the atmosphere. Although the Catskill Mountains receive high levels of N deposition relative to the eastern United States, sites in Europe and southern California receive substantially higher levels than the Catskill Mountains. In forest ecosystems that receive high rates of N deposition, export in drainage waters may be more closely tied to deposition than in forest ecosystems that receive relatively low N inputs, such as the Catskill Mountains, where soil and vegetation are the most obvious control.

Watersheds in the Catskill Mountains have the highest rates of N export in the northeastern United States (Stoddard 1994), however, in Winnisook watershed, only about 12% (modeled) to 17% (nominal) of atmospheric N inputs are exported in stream water. Under the assumption that there is minimal loss of N from the watershed other than in stream water, accumulation of N was about 759 to 1067 mol N $ha^{-1}yr^{-1}$ – less than 1% per year of the

Oa horizon N pool. Annual export of N in stream water was about 0.2% of the Oa-horizon pool and, if expressed as a percentage of the total N pool for the watershed, the percentage would be considerably smaller. Nevertheless, this amount of N export in the form of HNO_3 significantly contributes to decreased pH and elevated concentrations of toxic Al in this chronically acidified stream. Much of the large pool of soil N is associated with organic matter that is resistant to decay. Outputs of N are likely to be derived from a smaller, more labile pool of N. Spatial and temporal correspondence between N inputs and outputs will depend on the size of this labile pool and how its effected by N deposition.

Although SO_4^{2-} concentrations in the Neversink River have steadily declined since 1983 (Murdoch & Stoddard 1993), and in Winnisook stream water since at least 1991, SO_4^{2-} remains the primary acid anion associated with the chronic acidification of stream water in the Neversink Basin. Concentrations of NO_3^- in Winnisook stream water during exceptionally high flows approach SO_4^{2-} concentrations (when expressed as μeq L^{-1}). During more typical flow conditions, however, NO_3^- concentrations are only about 1/5 as high as SO_4^{2-} concentrations. Similar ratios of SO_4^{2-} to NO_3^- concentrations have been observed in Biscuit Brook, a tributary of the Neversink River (Murdoch & Stoddard 1992). The high ratio of SO_4^{2-} to NO_3^- concentrations in streamwater, indicates that most leaching of soil base cations into drainage waters in Winnisook watershed is currently attributable to SO_4^{2-}, although the relative importance of NO_3^- has increased.

Conclusion

We conclude that N retention increases with elevation in this watershed, and that this relationship is likely to be caused by elevational increases in (1) organic horizon thickness, and (2) the prevalence of conifers. Accurate predictions of future trends in watershed N export are necessary for estimating future rates of soil-base cation leaching and neutralization of acidified surface waters, but these predictions will need to include the effects of changing temperature and vegetation, as well as the effects of atmospheric deposition. The elevational gradient of N content in the Oa horizon in hardwood stands in Winnisook watershed suggests that increases in temperature will reduce soil storage of N. Forest N cycling therefore must be viewed as a function of climate, which is highly variable and may be changing in response to increasing concentrations of atmospheric CO_2 (IPCC 1996). Future trends in N cycling will also be affected by changes in forest composition, such as those underway in Winnisook watershed, which are common in the northeastern United States (Canham & Pacala 1995). Research on the biogeochemical effects of atmospheric deposition need to be further integrated with studies of the interactions among climate, vegetation and forest N cycling to develop a quantitative understanding of how atmospheric deposition of N affects the release of NO_3^- to surface waters.

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