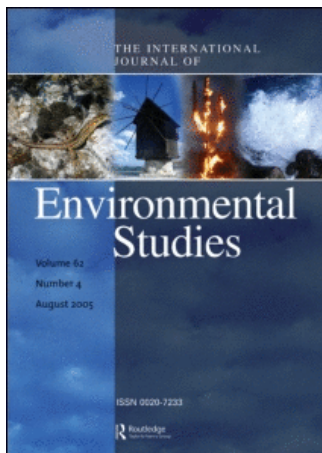


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Nitrogen deposition and cycling across an elevation and vegetation gradient in southern Appalachian forests

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We studied nitrogen (N) cycling pools and processes across vegetation and elevation gradients in the southern Appalachian Mountains in SE USA. Measurements included bulk deposition input, watershed export, throughfall fluxes, litterfall, soil N pools and processes, and soil solution N. N deposition increased with elevation and ranged from 9.5 to 12.4 kg ha⁻¹ yr⁻¹. In all sites canopies retained inorganic N and lost organic N; net canopy retention varied among vegetation types. The high elevation site had the greatest litterfall N, soil N transformations, soil solution N, and greater stream N exports (0.60 kg ha⁻¹ yr⁻¹). Low elevation sites had lower litterfall N, soil N transformations, and soil solution N. Low stream N exports (0.14 kg ha⁻¹ yr⁻¹) suggested N limitation. Multivariate analyses showed that abiotic variables account for up to 63% of the variation in biotic site characteristics.

Keywords: Elevation gradient; N cycling; N deposition; Coweeta Hydrologic Laboratory; Soil nitrogen; Litterfall

Introduction

SO₄ and NO₃ deposition peaked in 1970 just before the passage of the Clean Air Act (The Clean Air Act (CAA); 42 U.S.C. s/s 7401 et seq., 1970). Since then, SO₄ emissions have declined while NO₃ concentrations in bulk deposition have remained stable or even slightly increased [1]; cloud water NO₃ concentrations have shown no patterns. N deposition gradients exist regionally and locally. For example, within the contiguous USA, N deposition is greatest in the northeastern (NE) part of the country; and across the eastern USA, N deposition tends to increase with elevation largely due to increased precipitation. In some regions deposition increases at more local scales due to proximity of N producing industry or metropolitan areas with car exhaust inputs. Although nitrogen (N) often limits forest productivity, there are concerns in many parts of the world about forest ecosystem N saturation.

N saturation occurs when N availability exceeds the uptake capabilities of site vegetation and soil microorganisms and results in increased NO₃-N leaching from the system [2, 3]. This situation may occur following site disturbance for a short time but in undisturbed

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ecosystems mainly occurs due to chronic N deposition or declining vegetation growth rates. In order to understand and predict the vulnerability of forest ecosystems to N saturation, we need a fundamental understanding of the interactions among N-cycling components and how these vary over space (e.g. environmental gradients, vegetation types, etc.) and time.

Responses to N deposition differ with forest vegetation types and watershed characteristics such as hydrology, and land use history. For example, Mansson and Falkengren-Grerup [4] found that N deposition had a greater impact on deciduous forests compared to other forest types. They attributed the difference to the mass of forest floor material normally present in coniferous forests. Forest floor material acts as a physical buffer to N deposition, preventing direct input to the mineral soil, and also as a chemical buffer because the mass of the forest floor allows increased time to incorporate and process the additional N. Martin *et al.* [5] examined a watershed near Hubbard Brook in the NE USA. In a comparison of 1973–1974 and 1994–1997, they found that stream NO₃ concentrations had decreased in this mature forested watershed. This was contradictory to findings within Hubbard Brook where stream NO₃ concentrations increased over the same period of time. Similarly, Christopher *et al.* [6] found significant differences between two adjacent watersheds in NO₃ and Ca export via stream water. Differences were attributed to slight differences in vegetative composition. Campbell *et al.* [7] examined net retention of inorganic N in 24 watersheds in the NE. They found that differences among watersheds were unrelated to N deposition patterns. Instead, watershed characteristics such as hydrology, vegetation, and land use history were the primary factors controlling N export and retention. At Coweeta, Swank and Vose [8] summarized 23 years of inorganic N deposition and loss for an extensive network of mature mixed hardwood watersheds. They also assessed watershed N saturation in the context of responses associated with management practices and natural disturbances. Stages of N saturation were related to the dynamics of microbial transformations of N and vegetation uptake.

The complexity of interactions among N deposition, vegetation, watershed characteristics, climate, land use history, and N cycling processes makes it difficult to generalize response patterns for any given watershed. To examine the role of N deposition and other abiotic and biotic factors in regulating N availability and cycling we established plots across an elevation, topographic, and vegetation gradient in the southern Appalachians. On these plots, we measured N deposition, abiotic driving variables (e.g. rainfall, soil moisture, air and soil temperature), soil nutrient pools and associated N cycling variables (e.g. total soil N and C; litterfall and forest floor N, throughfall N), and N availability (e.g. nitrogen mineralization and nitrification, soil solution N) over a three-year period. Our objectives were 1) to characterize spatial and temporal variation in N deposition, streamwater N outputs, and N pools and cycling processes, and 2) to examine relationships among N deposition, abiotic variables, biotic variables, and N cycling processes and availability. Due to the strong environmental and topographic gradients, we hypothesized that most of the variation in N cycling processes and availability would be explained by abiotic variables.

Materials and methods

Site description

This study was conducted at the Forest Service, US Department of Agriculture, Coweeta Hydrologic Laboratory in the southern Appalachians of western North Carolina, USA. Annual precipitation is ~1900 mm and is >100 mm in most months. The growing season

extends from early May to early October. Mean monthly temperatures are highest in June through August ($\sim 20^{\circ}\text{C}$) and lowest in December through January ($\sim 5^{\circ}\text{C}$).

The sites examined represent a gradient in vegetation, elevation, climate, and N deposition. All sites are located on reference watersheds 18 and 27 (with no cutting since 1929) and represent the major vegetation community types within the Coweeta basin. Watershed 18 is 13 ha with an elevation range from 726 m at the weir to a maximum elevation of 993 m. Watershed 27 is 39 ha; elevation at the weir is 1061 m, maximum elevation is 1454 m. Sites include dry mixed-oak pine (oak-pine), cove hardwoods (cove), low elevation mesic mixed-oak (oak-low), high elevation mesic mixed-oak (oak-high), and northern hardwoods vegetation community types. We established 20×40 m plots at each site in 1991. Intensive measurements included throughfall chemistry, soil solution chemistry, forest floor mass and chemistry, aboveground productivity, root phenology and productivity, and many other parameters. Table 1 provides information about dominant vegetation, elevation, aspect, slope, and soils. See the Coweeta LTER website (<http://coweeta.ecology.uga.edu/webdocs/1/index.htm>) for additional site information.

Measurements

Abiotic characteristics, precipitation inputs and stream outputs. Temperature was monitored on each plot with a climate station located just outside the plot boundary. Measurements included air temperature (1 m above the surface) and soil temperature at 5 cm and 20 cm below the surface. Precipitation inputs were measured using standard rain gauges located within the Coweeta Hydrologic Laboratory basin. Precipitation input for each site was corrected using established relationships between specific locations within the basin and individual or multiple rain gauges [9]. Bulk precipitation samples were collected weekly for chemical analysis using 16 cm diameter funnels and 1 L bottles containing preservatives (mercuric acetate) to prevent microbial transformations. Total Kjeldahl N (TKN) concentration in precipitation was determined on monthly weighted composite samples collected at two low elevation climate stations in Coweeta. Total organic N (TON) input was calculated from the TKN values minus NH_4 concentration. Stream discharge was measured using 120° V-notch weirs with continuous flow level recorders and weekly grab samples were collected above the weir for chemical analysis. $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ analyses are conducted on weekly samples using ion chromatography and the alkaline phenol method on an autoanalyzer [10], respectively. We used monthly inputs of NO_3 , NH_4 , and TON in g N ha^{-1} for all statistical analyses.

N cycling measurements. Each gradient plot had 10 lysimeters, five located 15 cm in the soil and five placed in the lower portion of the B horizon (ranging from 30 to 85 cm) on all sites. Lysimeters were sampled each week; solutions were composited monthly for analysis. Throughfall (TF) solution was collected in six 0.15×2.0 m troughs located randomly within each site. Samples for each trough were collected weekly and composited monthly by volume yielding six weighted composite samples. Solution analyses for NH_4 and NO_3 were conducted on monthly composites as described above; TKN analyses were conducted on composited samples quarterly during the calendar year; TON was calculated as above. We used the annual average TF TON concentration and the total TF volume to calculate TON fluxes through the canopy.

Soil N transformations and N concentrations. Net rates of N transformations were measured using an *in situ* closed core method modified from Adams and Attiwill [11]. These

Table 1. Selected characteristics of the elevation gradient sites. Data compiled from Coweeta Long-term Ecological Research Program records.

Site	Mixed oak/pine	Cove hardwood	Mixed oak-low	Mixed oak-high	No. hardwood
Elevation (meters)	788	801	860	1094	1389
Aspect (degrees)	180	340	15	75	20
Slope (degrees)	34	21	34	33	33
Vegetation type	oak-pine	cove hardwoods	mixed oak	mixed oak	northern hardwoods
Dominant species	<i>Pinus rigida</i> <i>Quercus coccinea</i> <i>Quercus prinus</i> <i>Carya</i> spp. <i>Kalmia latifolia</i>	<i>Liriodendron tulipifera</i> <i>Quercus prinus</i> <i>Carya</i> spp.	<i>Quercus prinus</i> <i>Carya</i> spp. <i>Quercus rubra</i> <i>Rhododendron maximum</i>	<i>Quercus prinus</i> <i>Quercus rubra</i> <i>Carya</i> spp. <i>Rhododendron maximum</i>	<i>Betula allegheniensis</i> <i>Quercus rubra</i> <i>Betula lenta</i> <i>Tilia heterophylla</i>
Moisture regime	xeric	mesic	mesic	mesic	mesic
Soil series	Evard/Cowee Chandler Edneyville/Chestnut	Saunook Tuckaseegee	Trimont	Chandler	Plott
Soil texture	Fine-loamy Coarse-loamy Coarse-loamy	Fine-loamy Fine-loamy	Fine-loamy	Coarse-loamy	Coarse-loamy
Soil subgroup	Typic Hapludults Typic Dystrubrepts	Humic Hapludults Typic Haplumbrepts	Humic Hapludults	Typic Dystrubrepts	Typic Haplumbrepts

determinations were made bimonthly in 1994 and monthly from April to October in 1995 and 1996; one winter measurement was made each year in January or February. Two 15-cm long, 4.3-cm inside diameter, PVC cores were driven 10 cm into the mineral soil within 25 cm of each other. One PVC core was removed immediately for the time zero determination of soil NH_4^- and NO_3^- -N concentrations. The second core of each pair was capped and retrieved after incubating in the field for 28 days. All collected soil cores were kept cool until returned to the laboratory and stored in a refrigerator at 4°C until analyzed, within 24 hours. Soils were moist sieved to < 6 mm. One subsample (20 g) was placed in a 105°C oven for > 12 hours to obtain the oven-dry weight. One 5 g subsample was shaken with 20 ml of 2 M KCl for 1 hour to extract NH_4^- and NO_3^- -N. The soil/ KCl mixture was centrifuged for 15 minutes at 6000 rpm. The supernatant was analyzed for NH_4^- and NO_3^- -N on an autoanalyzer using alkaline phenol [10] and cadmium reduction [12] techniques, respectively. Net N mineralization rates were calculated as soil $\text{NH}_4^- + \text{NO}_3^-$ -N concentrations at 28 days minus $\text{NH}_4^- + \text{NO}_3^-$ -N concentrations at time zero. Net nitrification rates equaled soil NO_3^- -N concentrations at 28 days minus NO_3^- -N concentrations at time zero. Soil bulk density was determined on all samples collected during 1994; by weighing the sieved soil (< 6 mm) in each $t = 0$ soil core, the mean bulk density value was used for mass calculations for each site. We used 28 day N mineralization and nitrification data in g N ha^{-1} (0–10 cm) on an oven dry weight basis in all statistical analyses. The percent volumetric soil moisture of $t = 0$ soil samples for each site were calculated using average soil bulk density values for each site. Soil moisture was used as an abiotic variable in multivariate analyses.

We calculated an index of N availability (N index) as the ratio of N mineralization to total soil N concentration. This index accounts for site variability and focuses on the environmental regulation of N availability [13].

Soil and forest floor N pools. We analyzed $t = 0$ soil samples collected for N transformation measurements for total N and C. Soils were sieved to < 2 mm and ground to a powder; total N and C were determined by combustion using a Perkin Elmer 2400 CHN analyzer. We used soil bulk density values to calculate total N and C in g ha^{-1} for all statistical analyses.

We determined forest floor mass and nutrient concentrations in October 1994 and May 1995. Samples were collected using a 0.09 m² quadrant. Samples were collected along four transects located at each corner and parallel to the long axis of the 20 × 40 m gradient plot, outside the main plot due to the destructive nature of forest floor sampling. Samples were collected at either four (October 1994) or two (May 1995) random locations along each transect. At each location the quadrant was placed on the forest floor and the material cut, using a soil knife, to mineral soil. Forest floor material was collected by layer, Oi, Oe, and Oa, wood (1–10 cm diameter) was collected separately; each layer was put in a paper bag and dried at 60°C in a forced air oven to a constant weight. Material was weighed and ground to < 1 mm. Total N and C were determined on ground material using a Perkin Elmer 2400 CHN analyzer.

Litterfall was collected monthly from six, 0.9 × 0.9 m litter traps throughout the year and biweekly during October to November. Samples were dried at 60°C to a constant weight and weighed. Samples were composited quarterly, ground to < 1 mm, and analyzed for total C and N using a Perkin Elmer 2400 CHN Analyzer.

Statistics

Significant effects of SITE and sampling MONTH on temperature, precipitation amount, soil moisture, N deposition, throughfall, lysimeter solution concentrations, soil N transformations,

and soil N and C pools were determined by repeated measures analysis using the MIXED procedure in SAS [14]. We used mean monthly values from each site for all three years of sample collection in the analysis. Significant differences among sites and among months within a site were determined using Tukey adjusted LSMEANS. Effects of SITE on variables not collected on a monthly basis (litterfall and forest floor data) were determined using the GLM procedure of SAS [14], using the Tukey adjusted LSMEANS.

We used the stepwise procedure of SAS [15] to explore interactions of variables. We examined the interactions between biotic site characteristics such as total soil N and C, litterfall mass and percent N and soil N index with abiotic site climatic variables. We also explored the interactions between abiotic and biotic site characteristics with nutrient cycling processes such as, soil N transformations, net canopy N retention, and N movement in the soil solution. We used the standard stepwise method with a minimum significance level of 0.10 for entering into or remaining in the final model.

Results and discussion

Abiotic characteristics

Sites differed significantly in mean climatic characteristics. The northern hardwood site received significantly greater rainfall (268 cm) than the oak-pine site (210 cm), other sites did not differ (table 2). Sites also differed in volumetric soil moisture content. The northern hardwood and cove sites had the greatest moisture (0.44 and 0.49 g cm⁻³, respectively), the two oak sites, high and low elevation, were similar with 0.30 and 0.25 g cm⁻³ while the oak-pine site was driest with 0.18 g cm⁻³. The temperature characteristics on the sites also differed with the oak-pine being warmest for both air (15.1°C) and soil temperature (14.8°C) and the northern hardwood site being coolest (11.8°C air and 10.8°C soil temperature).

Bulk N deposition

Mean annual bulk deposition estimates for total N ranged from 9.4 kg ha⁻¹ yr⁻¹ on oak-pine site and 12.6 kg ha yr on northern hardwood (table 3); a 25% increase in N deposition across the gradient. Total N inputs consisted of 40% NO₃, 39% NH₄, and 21% TON. The two high elevation sites, northern hardwood and oak-high, had significantly greater NO₃ deposition than the low elevation sites. NH₄ deposition was greatest on the northern hardwood site; significantly greater than all low elevation sites. Bulk deposition estimates for

Table 2. Climatic characteristics of the mixed oak-pine (OP), cove hardwood (CH), mixed-oak low elevation (MO-L), mixed oak high elevation (MO-H) and northern hardwood site (NH). Data shown are three-year means of annual averages of monthly means collected 1994 through 1996. Different letters within a row designate significant differences among sites.

	OP	CH	MO-L	MO-H	NH
Rainfall (cm)	210.2 b	212.4 ab	222.9 ab	264.9 ab	267.6 a
Soil water content (g cm ⁻³)	0.18 c	0.49 a	0.25 b	0.30 b	0.44 a
Air temperature (1 m)	15.1 a	14.5 ab	15.0 a	13.6 b	11.8 c
Soil temperature (20 cm)	14.8 a	14.0 b	13.5 bc	12.8 c	10.8 d

NO₃ and NH₄ (table 3) are likely to be conservative. Previous work at Coweeta [8] suggests that bulk deposition underestimates total deposition; 40% for NO₃ and 20% for NH₄ inputs resulting in an underestimate in total N deposition; this work did not include estimates of TON inputs.

Boggs *et al.* [16] also studied an N deposition gradient in the southern Appalachians, for sites that varied in vegetation and elevation; N deposition ranged from 9 to 15 kg ha⁻¹ yr⁻¹. Their geographic area was, however, much greater and included sites from North Carolina to Virginia. Most N deposition gradients studied result from proximity to N pollutant sources [17–19].

Examination of intra-annual variation in nitrogen inputs showed significant differences in NO₃ and NH₄-N inputs ($p = 0.02$) among months. November and December had the least NO₃-N g ha⁻¹ input, while most other months were significantly greater (figure 1). There were few significant differences among months in NH₄ inputs but late winter (February and March) and summer (May and June) were greater than November and December. TON inputs did not differ significantly among months ($p = 0.19$).

The short time frame of this study did not allow analyses of interannual variation in N deposition; previous studies at Coweeta suggest increasing N deposition over time [8]. Swank and Vose [8] regressed bulk precipitation average annual NO₃ and NH₄ concentrations from 1972 to 1994 and found that both were increasing significantly over the time period; largely due to increased concentrations in dry deposition. We repeated this analysis, including the years 1995–2004 and found that the change in NO₃ concentrations over time was no longer significant ($r^2 = 0.05$; $p = 0.23$); NH₄ concentrations continue to increase significantly ($r^2 = 0.51$; $p < 0.001$) with slope of 0.003 mg L⁻¹ yr⁻¹. Cornell *et al.* (2003) reviewed organic N deposition amounts and trends over time. They found that organic N is an important component of the total N in bulk precipitation; ranging from 11% to 56% of the total N deposition. Our TON is 16% of the total N deposition. They found little evidence for temporal trends in bulk precipitation amounts of organic N.

Throughfall

Throughfall fluxes of NO₃ and NH₄ differed significantly among the sites (table 3). Throughfall NO₃ concentrations were greatest in the high and low elevation mixed oak sites; significantly greater than the oak-pine and cove sites. Throughfall NH₄ concentrations were greatest in the two high elevation sites, oak-high and northern hardwood, they differed significantly from the oak-pine and the cove site. TON analyses on TF solutions were conducted quarterly and calculated flux (g ha⁻¹) did not differ significantly among sites.

Throughfall chemistry also varied significantly among sample months (figure 2). Concentrations of NO₃ were greatest in summer months; August and September were greatest, significantly greater than most months of the year. NH₄ concentrations did not have a significant seasonal pattern, but November and December concentrations were significantly lower than most months.

We calculated net canopy effects on TF chemistry by subtracting TF fluxes from bulk precipitation inputs. Positive values represent net canopy retention of nutrients and negative values suggest net N canopy loss by leaching or wash-off of N from the canopy surface (table 3 and figure 2). Sites differed significantly in the interaction of precipitation NO₃ with the canopy (table 3). Net canopy retention of NO₃ occurred on all sites; oak-pine and northern hardwood had the greatest NO₃ retention in the canopy, significantly greater than mixed oak-low (table 2). Throughfall fluxes of NH₄ differed significantly among sites but

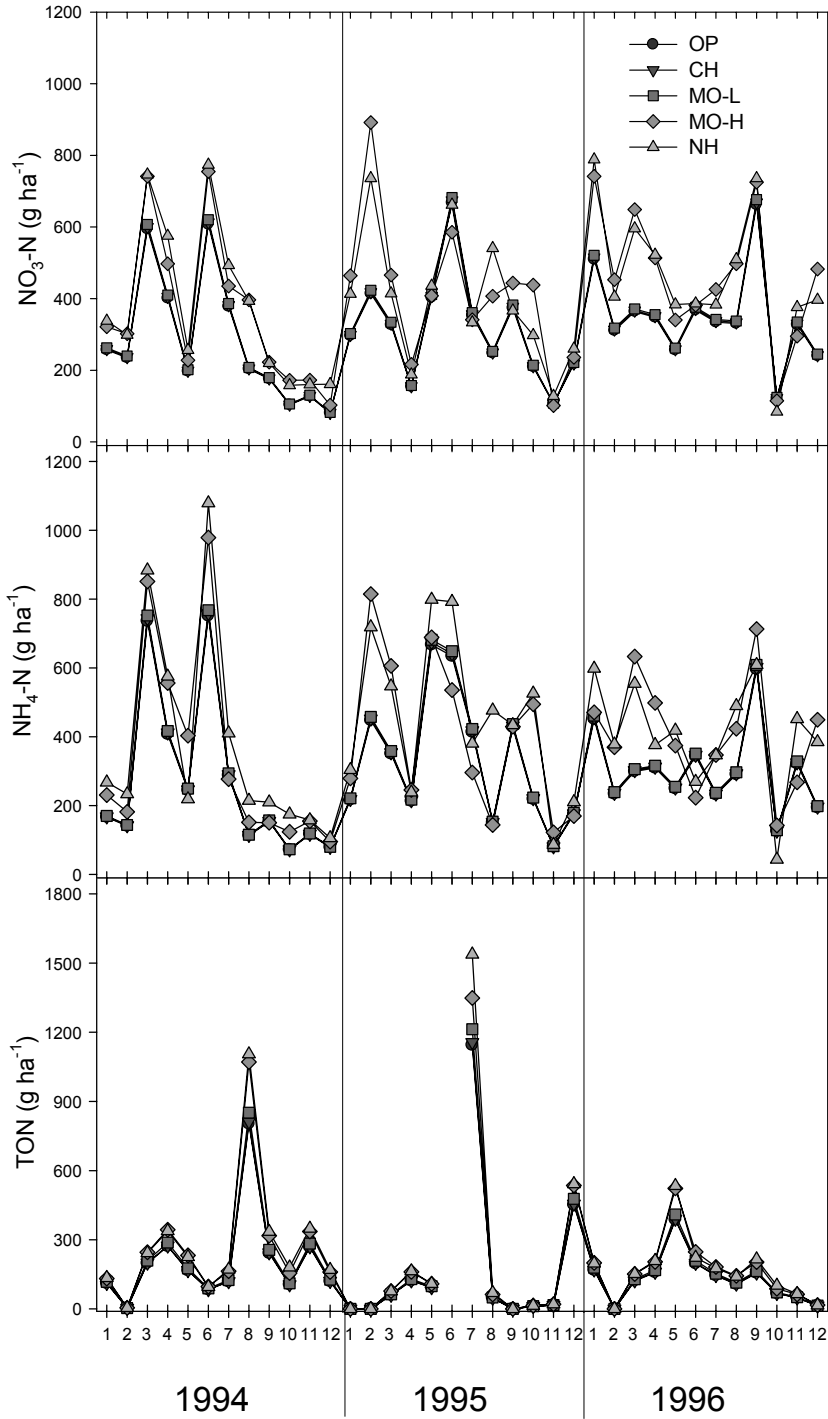


Figure 1. Total monthly bulk precipitation inputs of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and TON to five sites; mixed oak-pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH) for 1994 through 1996.

Table 3. Bulk precipitation, throughfall (TF) flux and net canopy retention or loss of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and TON ($\text{g ha}^{-1} \text{yr}^{-1}$) for sites along an elevation gradient. Site vegetation is: mixed oak-pine (OP), cove hardwood (CH), mixed oak-low elevation (MO-L), mixed oak-high elevation (MO-H), and northern hardwood (NH). Values represent mean annual input or flux for 1994–1996. Precipitation, TF, or canopy retention values followed by different letters are significantly different among sites. TON values for TF were calculated using the seasonal mean concentration for 1994–1996 and the total TF volume.

Site	$\text{NO}_3\text{-N}$ $\text{g ha}^{-1} \text{yr}^{-1}$	$\text{NH}_4\text{-N}$ $\text{g ha}^{-1} \text{yr}^{-1}$	TON $\text{g ha}^{-1} \text{yr}^{-1}$	Total Input, TF, Retention
OP				
Bulk precip	3767 b	3635 b	2000	9402
TF	1041 c	545 c	4525	6111
Canopy retention	2726 a	3090	-2525	3291
CH				
Bulk precip	3807 b	3673 b	2021	9501
TF	1600 c	1031 bc	3987	6618
Canopy retention	2207 ab	2642	-1966	2883
MO-L				
Bulk precip	3850 b	3715 b	2120	9685
TF	2772 ab	1719 ab	6219	10710
Canopy retention	1078 b	1996	-4099	-1025
MO-H				
Bulk precip	4989 a	4630 ab	2536	12155
TF	2946 ab	2000 a	7879	12825
Canopy retention	2043 ab	2630	-5343	-670
NH				
Bulk precip	4973 a	4989 a	2641	12603
TF	1744 bc	1923 a	6590	10257
Canopy retention	3229 a	3066	-3949	2346

canopy retention did not. Calculated estimates of canopy effects on TON suggest net losses of TON from the canopy for all sites; sites were not significantly different.

Monthly patterns of net canopy N retention suggested seasonal controls. Canopy retention of NO_3 and NH_4 was greatest in the spring and early summer and lowest in the fall and winter (figure 2a and 2b). TON also varied by season, but in the opposite direction (figure 2c). TON was leached from the canopy in the spring and summer, and retained by the canopy in the fall and winter. This pattern of N removal from precipitation by the canopy coincides with seasonal patterns of foliar N concentration measured in a low elevation forest at Coweeta by Day and Monk [20] in the 1970s. They found that % foliar N was greatest early in the summer, declining through the summer but increasing again prior to leaf fall.

The effect of vegetation on net canopy retention or leaching of N is evident in other studies as well. Johnson and Lindberg [21] summarized precipitation-canopy interactions across a range of sites in the US and found that forest canopies retained NO_3 and NH_4 from bulk precipitation and dry deposition and lost TON. Data from two sites at Coweeta were included in this study [22], a white pine plantation and a mixed-oak hardwood reference site, both followed this pattern, as did the sites included in our study. In contrast, Hermann *et al.* [23] examined TF in seven forested sites, oak-birch and pine stands, in northwest Germany. They found TF concentrations of NO_3 and $\text{NH}_4\text{-N}$ were greater than wet deposition, suggesting foliar leaching, in all forests. Balestrini *et al.* [24] measured mass balance and N cycling in

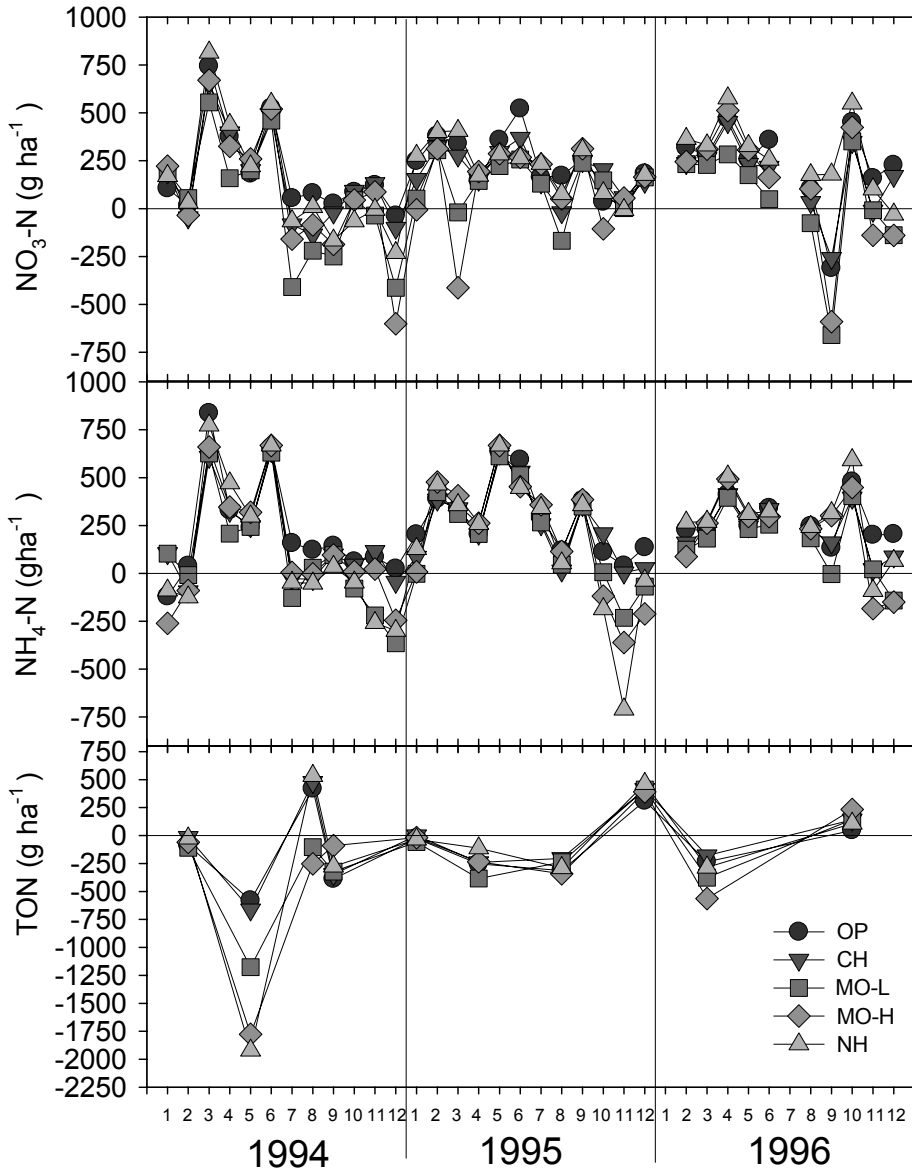


Figure 2. Net canopy exchange of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and TON in five study sites, mixed oak pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH). Plotted values represent mean monthly total bulk precipitation (g ha^{-1}) minus mean monthly total throughfall N (g ha^{-1}).

the Italian Alps and had mixed results. They found a net loss of both NO_3 and TON from forest canopies; N concentrations were greater in TF than bulk precipitation – however, most canopies took up NH_4 . This differed from our sites, which retained both NO_3 and NH_4 from bulk precipitation as is moved through the forest canopy, only TON was removed from the canopy.

Litter fall and forest floor N

Percent N in litter on northern hardwood was significantly greater (1.8% N) compared to all other sites, which ranged from 0.64% on oak-pine to 1.47% on cove site (table 4). The greatest total N in litterfall inputs was on northern hardwood, 47 kg ha⁻¹; the least litter N input was on oak-pine 22 kg N ha⁻¹. These deciduous forests lose most litterfall in the fall of the year (figure 3). The autumn litterfall contributes between 69% (oak-pine) and 85% (northern hardwood and cove) of the total N in litter on these sites.

Because forests are rarely fertilized, the internal cycling of nutrients via litterfall and subsequent decomposition is essential for adequate nutrient availability [25]. Litter inputs and chemistry represent a significant input of nutrients to soils in forest ecosystems. On our sites, N from litter inputs ranges from 22 to 47 kg ha⁻¹ yr⁻¹ deposited on the forest floor (table 4). This input is two to four times the amount of N added in bulk precipitation. Rueth and Baron [17] found increased foliar N concentration in Englemann spruce growing on sites with greater N deposition. Our data differ; mixed oak-high receives greater N deposition than the three low elevation sites (table 3). Yet, the N input as litterfall and the percent N of the litter was significantly less than northern hardwood (table 4), the other high elevation site that receives similar N deposition. Templer *et al.* [26] used ¹⁵N to trace the fate of N deposition in mixed stands dominated by sugar maple, American beech, red oak, and eastern hemlock. There was no difference among species in total ¹⁵N recovery; the short term fate of added ¹⁵N was in the forest floor and litter. In the longer term, sugar maple retained the least N in forest floor material compared to other species. When fertilization was increased, there was a decrease in total ¹⁵N retention, suggesting that increased N deposition may result in increasing N losses. Ollinger *et al.* [27] conducted a regional study of relationships between soil N

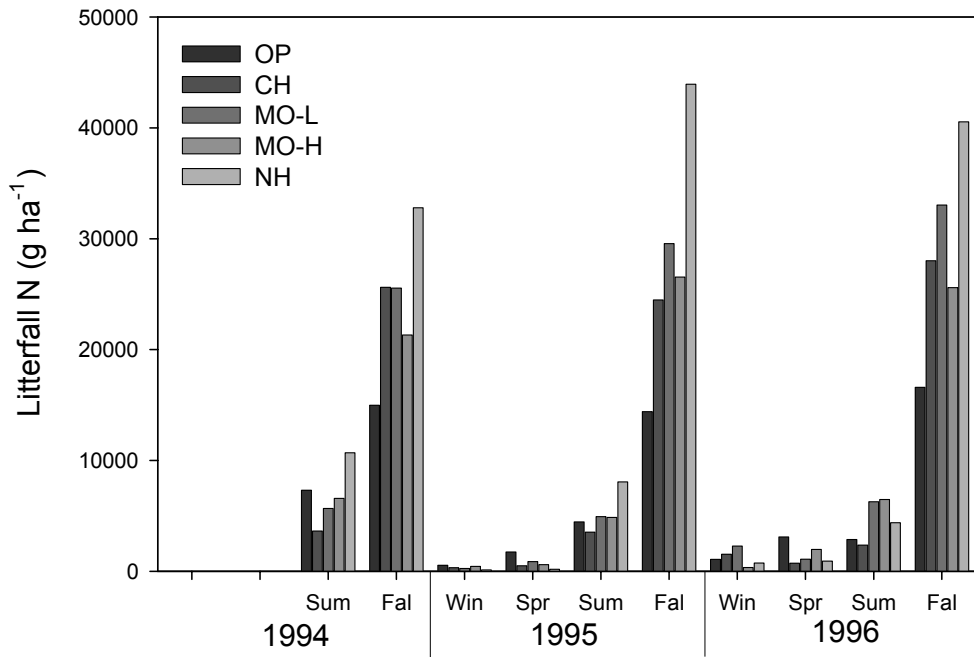


Figure 3. Total quarterly litterfall N for each study site, mixed oak pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH) during 1994 through 1996.

Table 4. Measurement of N availability on sites representing a gradient in N deposition, elevation, and vegetation types. Litterfall N and litter N concentrations were measured as part of the Coweeta LTER program. Site values with different letters within a variable are significantly different ($p < 0.10$).

	OP	CH	MO-L	MO-H	NH
Total soil N (mg kg ⁻¹)	800 d	3700 b	1700 c	1500 c	6700 a
Soil C:N	38.7 a	18.4 d	22.8 c	28.7 b	14.7 e
N mineralization (g ha ⁻¹ yr ⁻¹)	3118 c	14789 b	5421 c	3184 c	31231 a
Nitrification (g ha ⁻¹ yr ⁻¹)	285 b	2477 b	1447 b	422 b	13861 a
Solution NO ₃ (15 cm) (mg L ⁻¹)	0.004 b	0.014 b	0.007 b	0.005 b	0.147 a
Solution NO ₃ (>40 cm) (mg L ⁻¹)	0.003 b	0.002 b	0.004 b	0.007 b	0.074 a
Litterfall N (kg ha ⁻¹ yr ⁻¹)	22 c	30 bc	37 ab	32 bc	47 a
Litter N (%)	0.64 d	1.47 b	1.33 bc	1.17 c	1.77 a
Oa horizon N (kg ha ⁻¹)	207 abc	74 bc	215 ab	306 a	70 c

availability and N deposition across the White Mountains of New Hampshire; Nmin was positively related to canopy N concentrations.

Measures of N availability – soil N and lysimeters

Soil nitrogen transformations. Soil mineralization and nitrification rates differed significantly among sites, among months, and showed significant site by month interactions. Nitrogen mineralization was greatest in northern hardwood followed by cove; both were significantly greater than oak-pine, oak-low, and oak-high. Annual N mineralization rates ranged from 31,231 g N ha⁻¹ yr⁻¹ on northern hardwood to 3118 g N ha⁻¹ yr⁻¹ for oak-pine (table 4). Nitrification was significantly greater in northern hardwood compared to all other sites (table 4). Nitrification rates ranged from 13861 g N ha⁻¹ yr⁻¹ on northern hardwood to 285 g N ha⁻¹ yr⁻¹ on oak-pine. Both N mineralization and nitrification rates were greatest in the spring and summer and lowest in the winter (figure 4).

Garten [28] found differences in N availability along an elevation gradient; but, there was no direct relationship between N availability (measured from N mineralization rates) and elevation. The gradient effect resulted from changes in substrate C:N ratios, rather than potential N mineralization rates. The high N, high elevation forest systems had lower substrate C:N which resulted in greater N release per unit C respired. This corresponds well with findings of Knoepp *et al.* [29] on the same sites examined in this study. In an examination of all soil data collected on these sites they found that the northern hardwood site had the highest ranking for C availability; determined by measurement of microbial biomass and mg CO₂ respired for each g microbial C. This site also has the greatest rates of N mineralization and nitrification. Ross *et al.* [30] examined site differences in N mineralization and nitrification in the northeastern United States and found that gross N mineralization rates were related to soil C:N ratio. They also found that sites with some degree of soil disturbance had greater rates of nitrification.

The relationship between soil C:N ratios and N transformation rates have been examined in many studies [17, 27]. C:N ratios of 20 or less are a point at which N is not considered

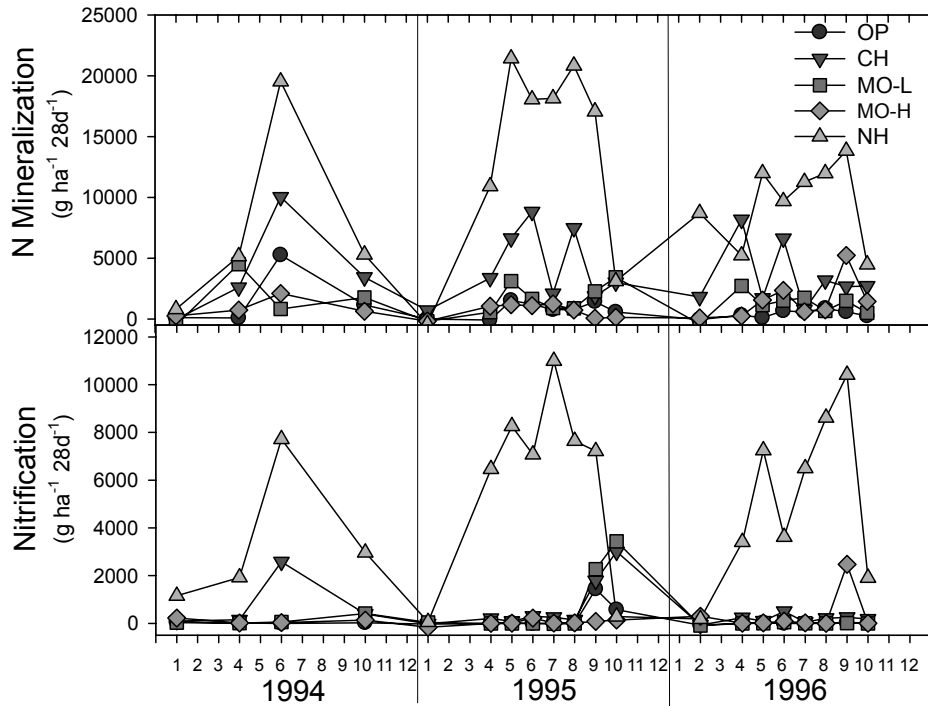


Figure 4. Mean N mineralization and nitrification rates ($\text{g ha}^{-1} 28\text{d}^{-1}$) determined *in situ* in the surface 10 cm of soil on mixed oak pine (OP), cove hardwood (CH), low elevation mixed oak (MO-L), high elevation mixed oak (MO-H), and northern hardwood (NH) during 1994 through 1996.

limiting and net N mineralization will occur; C:N above 30 normally result in net N immobilization [31]. Both northern hardwood and cove have C:N ratios less than 20 (cove = 18 and northern hardwood = 15) and these sites also have the greatest N transformation rates. Rueth and Baron [17] examined Englemann spruce sites with different amounts of N deposition. Although deposition was very low, $1\text{--}2 \text{ kg ha}^{-1} \text{ yr}^{-1}$ versus $3\text{--}5 \text{ kg ha}^{-1} \text{ yr}^{-1}$, the high deposition sites had lower C:N and greater rates of N mineralization and nitrification. Ollinger *et al.* [27] conducted a regional study of relationships between soil N availability and N deposition across the White Mountains of New Hampshire. They also found that N mineralization was related to soil C:N ratios. On the other hand, in a study of sites along a climatic gradient in temperature, precipitation, and N deposition Fernandez *et al.* [32] found very little variation in forest floor C:N ratios and N concentration was the best predictor of N mineralization.

Soil solution. Mean NO_3 soil solution concentrations were greatest on the northern hardwood site, 0.15 mg N L^{-1} , compared to all other sites (table 4). Other sites did not differ significantly; NO_3 concentrations in shallow lysimeters ranged from 0.003 to 0.01 mg N L^{-1} . There were few differences in lysimeter NH_4 concentrations (data not shown); oak-low and northern hardwood concentrations were significantly greater than oak-pine. TON concentrations were greatest in cove shallow soil solutions averaging 0.30 mg L^{-1} compared to all other sites which averaged between 0.10 and $0.18 \text{ mg TON L}^{-1}$ (data not shown). There were no significant differences among months for either NO_3 or NH_4 concentrations in shallow lysimeters. TON concentrations were greatest in September. There were no significant site by month interactions for lysimeter N concentrations.

Nutrient concentrations in soil solutions can indicate the spatial and temporal variability of site nutrients and also nutrient mobility and availability to plants [33, 34]. In a previous study at Coweeta, Montagnini *et al.* [35] also found significant differences in soil solution N concentrations among sites with differing vegetation communities. $\text{NO}_3\text{-N}$ concentrations were greatest in a site dominated by N-fixing black locust with high N availability.

McDowell *et al.* [36] studied the effects of chronic N additions for 10 years in hardwood and pine forests of the northeastern United States on soil solutions beneath the organic horizons and found very low concentrations in untreated plots; the addition of N increased the movement of NO_3 , NH_4 , and TON out of the forest floor into the mineral soil. Unlike our results, their data showed significant seasonal differences in solution N concentrations, with greatest concentrations during summer. In another N addition study, Edwards *et al.* [37] found increased NO_3 concentrations in A, B and C horizon lysimeter solutions. Unlike our study, the one by Edwards *et al.* showed surface soil solution concentrations to be lower than deeper soils. Edwards *et al.* attributed the increase to biological assimilation of N in surface soils or the downward transport of N in capillary water.

Watershed N losses. Stream N export from the high and low elevation watersheds differed significantly (figure 5). Stream exports averaged $101 \text{ g NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ from low elevation WS 18 and $340 \text{ g NO}_3\text{-N ha}^{-1} \text{ yr}^{-1}$ from high elevation WS 27. Ammonium export was much less, averaging $59 \text{ g N ha}^{-1} \text{ yr}^{-1}$ in WS18 and $82 \text{ g N ha}^{-1} \text{ yr}^{-1}$ for WS27. Total organic N export was not measured during the study period. We measured NO_3 , NH_4 , and total dissolved nitrogen ($\text{DON}=\text{TN}-\text{NO}_3\text{-NH}_4$) concentrations in streams from September 2005 through September 2006 (figure 6). Data show that stream N export as DON is similar to $\text{NO}_3\text{-N}$ export in both WS18 and WS27. The high elevation watershed had an average DON concentration of $0.093 \text{ mg N L}^{-1}$ while $\text{NO}_3\text{-N}$ is $0.085 \text{ mg N L}^{-1}$; low elevation WS 18 had NO_3 concentrations of $0.016 \text{ mg N L}^{-1}$ while DON in $0.022 \text{ mg N L}^{-1}$. Together NO_3 and DON made up 86 and 93% of the N exported from WS18 and WS27, respectively.

Nitrogen export via stream was greater from high elevation WS27, concentration of $\text{NO}_3\text{-N}$ in deep lysimeters, below the rooting zone suggesting leaching losses, was significantly greater in northern hardwood; this vegetation community type occupies all but a very small portion of WS 27. Shallow lysimeter N concentrations were also significantly greater on northern hardwood; while high elevation mixed oak site had deep lysimeter NO_3 concentrations averaging 0.007 mg L^{-1} , not significantly different from the low elevation, WS18, plots. There were no site differences in soil solution NH_4 or TON concentrations. The variable responses of leaching via soil solution and total losses from WS18 and WS27 could result from many factors.

Differences between the two watersheds include 29% greater precipitation on WS27, substantially greater storm runoff, and a shorter growing season resulting in reduced Et [8] which reduces N demand and increases leaching potential. In a review concerning within stream nutrient transformations Peterson *et al.* [38] found that total losses from a watershed depend on which pathways are present, and often the exported amount is much less than the amount produced in the soil. Campbell *et al.* [7] examined net retention of inorganic N in 24 watersheds in the NE. Differences among watersheds were not related to N deposition patterns but factors such as, watershed hydrology, vegetation, and land use history were important in controlling N export and retention.

Extensive research on the N cycling in mature and disturbed mixed hardwood watersheds at Coweeta have elucidated some of the controls on stream N exports. Small but measurable increases in stream NO_3 were observed following logging and was associated with small

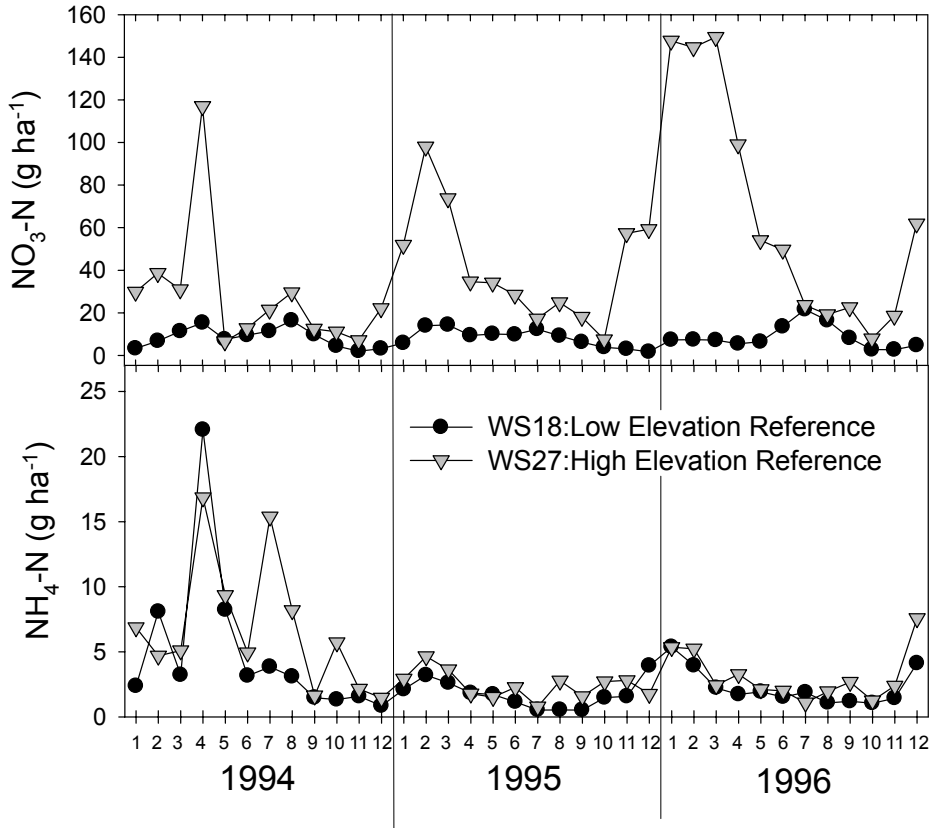


Figure 5. Total monthly stream export of N from high elevation (WS27) and low elevation (WS18) reference watersheds during 1994 through 1996.

increases in soil N mineralization and substantial increases in nitrification [39]. Most of the increased inorganic N was recycled through rapidly growing vegetation and only a small fraction was exported in the stream.

At Hubbard Brook, variations in stream NO_3 export were linked with temperature and moisture regulation of N mineralization which was the source of soil and subsequently stream N [5]. Our studies have shown that WS27, which is cooler and wetter than WS18, has the greatest rates of N mineralization [29, 40]. Christopher *et al.* [6] studied two catchments in upstate New York. They found significant differences in NO_3 and Ca export, although the watersheds were similar physiographically and had similar deposition patterns. They concluded that the slight differences in vegetation on the two watersheds interacted with the soils to increase soil Ca and N availability.

Zak *et al.* [41] conducted an experimental increase in NO_3 deposition for nine years in sugar maple dominated northern hardwood forests. They found no changes in either microbial activity or soil N transformation rates. There was no effect on net mineralization, but nitrification rates were significantly increased with NO_3 deposition [41]. The increased rates of nitrification did not explain the increased NO_3 in N exported from the sites. Zak *et al.* concluded that alterations in the C and N cycling processes were due to changes in the forest floor.

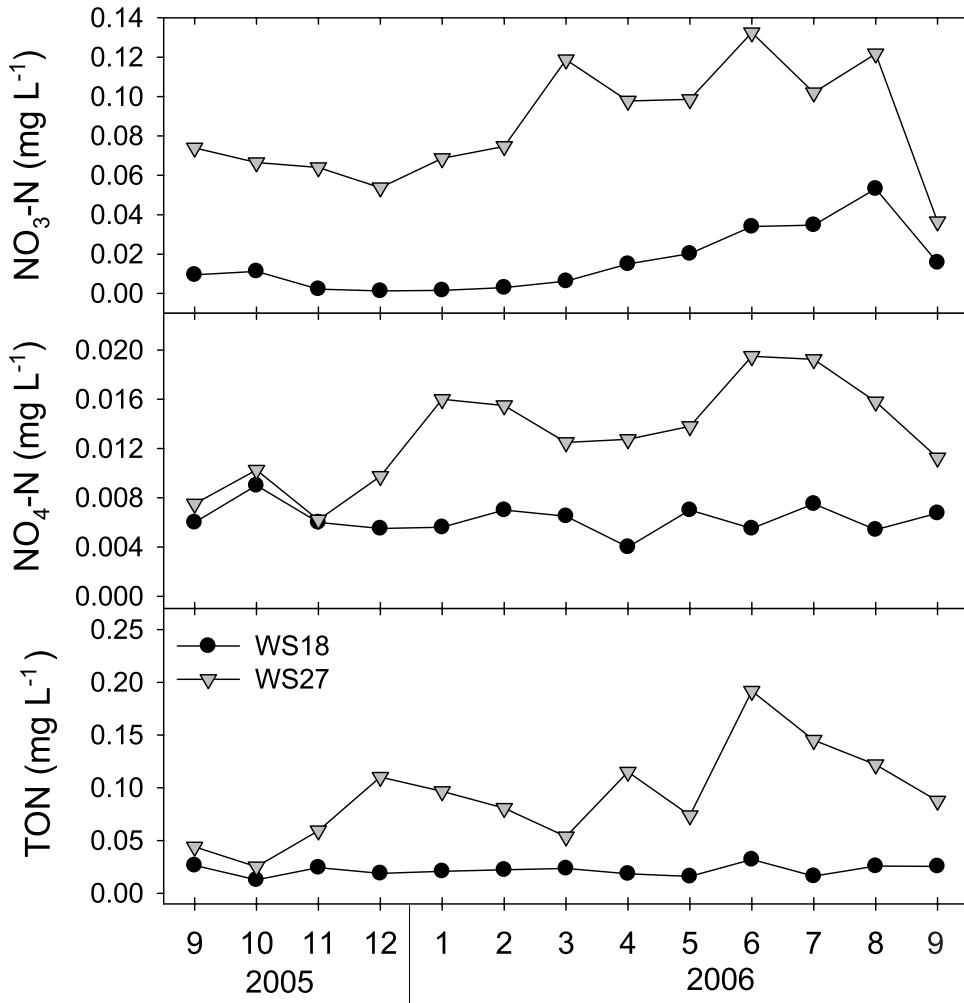


Figure 6. Mean monthly concentration of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and TON (mg L^{-1}) in streams for high elevation (WS27) and low elevation (WS18) reference watersheds determined from September 2005 through September 2006.

Relationships among N cycling variables; abiotic and biotic controls

We used multivariate analyses to explore the relationships among abiotic and biotic site parameters as well as relationships of abiotic and biotic variables with soil N availability (N transformations and lysimeter N concentrations) and canopy N cycling (net canopy N retention) measurements (table 5). We found that the biotic site parameters, total soil N and soil C:N were related to soil H_2O content. On the other hand, biotic parameters such as litterfall N, litter mass and N index ($\text{N}_{\text{min}}/\text{total \%N}$) were related to a combination of abiotic parameters, including precipitation N inputs, temperature (air and/or soil), and soil H_2O content.

Measurements of soil N availability and canopy N cycling differed in relationships to abiotic and biotic variables (table 5). N mineralization was the only soil measurement with a significant relationship to abiotic site variables; precipitation NH_4 concentration, soil

Table 5. Results of stepwise multivariate analysis showing significant interactions between site biotic characteristics, site abiotic factors, nitrogen availability, nutrient cycling processes and combinations of both. Abbreviations are as follows: PPT-precipitation; TON-total organic nitrogen; N index-N mineralization:total soil N. Monthly values for years 1994 through 1996 were used for the analysis. Presented are all variables significant at p -values < 0.10 , we present the model r^2 and the probability of a value greater than F (p -value) for each final model. Variables with a negative relationship are followed by (-).

Dependent variables	Independent variables	Model r^2	Data (n)	p -value
Biotic variables vs abiotic variables				
Total soil N	Soil H ₂ O content	0.45	68	<0.01
Total soil C:N	Soil H ₂ O content	0.48	68	<0.01
Litter %N	PPT-NO ₃ ; Soil H ₂ O; PPT-NH ₄ (-); PPT-TON (-)	0.63	67	<0.01
Total litter mass	PPT-NO ₃ (-); Air Temp (-); Soil Temp	0.41	67	<0.01
N index	PPT-NH ₄ ; Soil Temp; PPT-NO ₃ (-)	0.34	68	<0.01
Soil N availability and canopy N cycling vs abiotic variables				
Soil N mineralization	PPT-NH ₄ ; Soil temp; Soil H ₂ O	0.30	95	<0.01
Nitrification	n.s.			
Lysimeter NO ₃ -shallow	n.s.			
Lysimeter NO ₃ -deep	n.s.			
Lysimeter NH ₄ -shallow	n.s.			
Lysimeter NH ₄ -deep	n.s.			
Canopy NH ₄ uptake	Rainfall (-); PPT-NH ₄ ; air temp	0.90	84	<0.01
Canopy NO ₃ uptake	PPT-NH ₄ ; air temp; soil temp (-)	0.42	84	<0.01
Canopy TON uptake	Rainfall (-); air temp (-)	0.56	24	<0.01
Soil N availability and canopy N cycling vs biotic variables				
N mineralization	Total soil N	0.61	42	<0.01
Nitrification	Total soil N; N index; Soil C:N	0.75	42	<0.01
Lysimeter NO ₃ -shallow	Total soil N	0.40	42	<0.01
Lysimeter NO ₃ -deep	Total soil N	0.33	42	<0.01
Lysimeter NH ₄ -shallow	Litter %N; Litterfall mass	0.34	42	<0.01
Lysimeter NH ₄ -deep	n.s.			
Canopy NH ₄ uptake	Litter mass; N index	0.44	42	<0.01
Canopy NO ₃ uptake	Litter mass	0.29	42	<0.01
Canopy TON uptake	Litter mass; Litter %N	0.30	22	<0.01
Soil N availability and canopy N cycling vs abiotic and biotic variables				
N mineralization	Total soil N; PPT-NH ₄ ; Soil H ₂ O (-); soil temp.	0.78	42	<0.01
Nitrification	Total soil N; soil H ₂ O (-); N index	0.80	42	<0.01
Lysimeter NO ₃ -shallow	Total soil N; PPT-TON	0.51	42	<0.01
Lysimeter NO ₃ -deep	Total soil N; Soil C:N; Air temp.; Soil temp.	0.59	42	<0.01
Lysimeter NH ₄ -shallow	Litter %N; Litterfall mass	0.34	42	<0.01
Lysimeter NH ₄ -deep	n.s.		42	
Canopy NH ₄ uptake	PPT-NH ₄ ; Rainfall(-); Litterfall mass(-); Litter %N; Soil total N	0.94	42	<0.01
Canopy NO ₃ uptake	PPT-NH ₄ ; PPT-TON; Litterfall mass (-)	0.59	42	<0.01
Canopy TON uptake	Air temp.; Litterfall mass (-)	0.47	22	<0.01

temperature and moisture content ($r^2 = 0.30$). Several abiotic variables were correlated with canopy N cycling. The net retention of N compounds was related to rainfall amount (negative); NH_4 deposition and soil and air temperature (NH_4 uptake, $r^2 = 0.90$; NO_3 uptake, $r^2 = 0.42$; TON uptake, $r^2 = 0.56$). Soil N availability measurements were highly correlated to site biotic variables, while canopy N cycling showed weaker relationships (table 5). Total soil N was the main factor related to soil N availability; N index and soil C:N explained some variation in nitrification rates. Shallow lysimeter NH_4 concentrations were related to plant based biotic variables, litter N content and litterfall mass, while deep lysimeter NH_4 concentrations were not related to any biotic or abiotic variables measured. Variation in canopy N cycling was related to total litter mass; N index also played a role in NH_4 retention. Examining the regulation of N availability and canopy N cycling by both abiotic and biotic variables combined suggests that site biotic variables are more important in the soil processes while abiotic variables dominate in canopy N cycling processes. For all soil based measures of N availability (except lysimeter NH_4) total soil N was the dominant regulating factor, followed by the abiotic variables identified above (r^2 values range from 0.51 to 0.80) (table 5). The multivariate analysis suggests that canopy N cycling processes are largely correlated with abiotic variables; first parameters identified are precipitation NH_4 and air temperature, followed by a negative relationship with litterfall mass and other biotic variables.

Conclusions

Our study sites represented an environmental and topographic gradient and differed significantly in both abiotic and biotic characteristics. Variation in biotic site characteristics, such as total soil N and soil C:N, were related to soil H_2O content, while vegetation associated variables varied with N deposition and temperature. We hypothesized that variation in N availability and N cycling processes would be explained largely by abiotic variables, such as N deposition, rainfall, and temperature. N cycling processes measured in forest canopies supported our hypothesis; nitrogen retention or leaching was largely related to abiotic variables such as, rainfall amount and N deposition. Relationships between site characteristics and N availability on the other hand, did not support our hypothesis. Soil N transformations and soil solution N concentrations varied with total soil N, a biotic variable, abiotic variables (soil H_2O and temperature) played a minor role. These findings lead us to conclude that long-term biotic site characteristics (e.g. soil organic matter) regulate N availability, while abiotic variables regulate short-term N cycling processes.

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